G TREDOUX

A PRELIMINARY INVESTIGATION OF THE NITRATE CONTENT OF GROUNDWATER AND LIMITATION OF THE NITRATE INPUT

Report to the
WATER RESEARCH COMMISSION
by the
GROUNDWATER PROGRAMME
DIVISION OF WATER TECHNOLOGY
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EXECUTIVE SUMMARY

Groundwater plays a vital role as a water supply source in nearly two-thirds of South Africa, even though groundwater resources supply only fifteen per cent of the total water consumption of the country. In the semi-arid to arid regions of the country, groundwater is generally the sole source of water and more than 280 towns and settlements, are at least in part dependent on groundwater. Despite these facts, little is known about groundwater quality and time related trends in particular. This holds true for all aspects of groundwater quality and especially for nitrate. To date the occurrence of nitrate in groundwater in Southern Africa and its health related impacts have only been studied on an *ad hoc* basis by researchers.

Objectives

The worldwide concern over rising nitrate levels has been echoed in South Africa and, therefore, the Water Research Commission (WRC) decided to fund a limited one-year investigation in order to make a preliminary assessment of the extent and severity of the problem in this country. The main objectives of this preliminary study were to:

- carry out a preliminary situation assessment concerning groundwater contamination in South Africa with respect to both the extent and severity of nitrate pollution using existing information;
- identify the major contributors (polluters) qualitatively;
- make an initial assessment of the possibilities to manage nitrate pollution caused by the major contributors (as gleaned from the literature);
- evaluate the need for further research.

Modus operandi

As set out above, this study is a preliminary situation assessment making use of the available information and, therefore, no in-depth research was undertaken. It was attempted to identify the major problems related to nitrate in groundwater which means that this is not meant to be an exhaustive treatise on nitrate in groundwater. The project commenced with a literature search and study, interviews with experts, and an evaluation of the hydrochemical data in the national groundwater database of the Department of Water Affairs & Forestry (DWA&F). The data was evaluated statistically and mapped using ArcInfo.

It was considered expedient to bring the nitrate problem to the attention of the groundwater fraternity and, therefore, permission was obtained from the WRC to prepare a paper for a local groundwater conference in 1991. Furthermore, permission was also obtained from the

WRC to prepare a paper for the International Workshop on Inorganic Nitrogen Compounds and Water Supply, at Hamburg in 1991. Funding was made available by the CSIR for attending this workshop. It afforded the opportunity to consult with overseas experts on nitrate both at the workshop and during individual visits in order to gain first hand knowledge of the nitrate problem, its impacts and the remedial measures applied in Europe. Finally, an abstract was accepted by the South African Institute of Agricultural Engineers for presentation of a paper at the SAIAE conference in October 1993. The CSIR is funding the paper preparation.

Nitrate in groundwater

Concerns

Nitrogen is one of the main biogeochemical elements and together with carbon, oxygen, sulphur and phosphorous, these elements in their biogeochemical cycles constitute the main life-supporting system for our planet. The occurrence of these elements and their compounds in water (including groundwater) thus also forms part of these natural cycles. Nevertheless, the presence of the nutrients nitrogen and phosphorous in water is generally considered to be a manifestation of pollution. In the case of groundwater, pollution is difficult to trace and the effects are not obvious. However, the deterioration is long-lasting and in cases where excessive nitrates occur, ingestion of the water could be fatal for babies and livestock. The only possible beneficial aspect of the occurrence of nitrate in water is its immediate availability as a plant nutrient when the water is used for irrigation.

Exposure to high doses of nitrate is generally perceived to be associated with adverse health effects ranging from the 'hot dog headache' and methaemoglobinaemia to cancer and other effects. The occurrence of infant methaemoglobinaemia resulting from the consumption of water with high nitrate concentrations was first recognised clinically by Comly in 1945. Hungary has the best statistics on the occurrence of methaemoglobinaemia as it has been a notifiable disease in that country since 1968. In contrast to infants, adults show no apparent effects from nitrate ingestion, at least in the short term.

The World Health Organization found no firm epidemiological evidence linking gastric cancer and drinking-water containing more than 10 mg/L of nitrate but according to them a link cannot be ruled out due to "the inadequacy of the data available".

Stock-losses due to nitrate poisoning have occurred in Namibia and in Bophuthatswana. In these cases, the nitrate concentration was usually several hundred mg/L. It would seem, however, that detrimental effects particularly on dairy cows could occur at much lower concentrations.

Nitrogen chemistry, biochemistry and analytical techniques

Nitrogen can exist in a range of oxidation states at ambient conditions which gives rise to a series of stable nitrogen compounds occurring in the environment. These include nitrogen gas, ammonia and nitrate. Nitrate itself has a low primary toxicity but the partially reduced form nitrite which is produced by bacteria in the digestive tract that is hazardous to infants and livestock.

Nitrogen is one of the main biogeochemical elements supporting life on our planet. The occurrence of nitrogen and its compounds in water (including groundwater) forms part of these cycles. Virtually all natural conversions between the various nitrogen compounds are dependent either on bacterial action or biochemical reactions in plants or animals.

Inter laboratory studies have shown that even today many laboratories generate incorrect nitrate results. If not clearly specified, the way in which the concentration of nitrate is reported (e.g. nitrate as N, nitrate as NO_3^- etc.) may also lead to erroneous interpretation.

Nitrogen cycle in the soil

Nitrogen transfers between soil and vegetation constitute 95 per cent of the nitrogen flow and thus by far exceed other global nitrogen transfers. Only five per cent of the total flow is concerned with exchanges to and from the atmosphere and the hydrosphere.

Denitrification in the soil zone is crucial for maintaining a balance and to prevent nitrate accumulation in the subsurface. This is a natural process which depends on the action of denitrifying bacteria. It has been recorded in many instances in various types of aquifer and both under natural and polluted conditions. Confirmation of denitrification was obtained by means of gas analyses and isotopic ratios.

Nitrogen isotopes

Nitrogen has two naturally occurring isotopes, one with atomic mass of 14 (^{14}N) and the other with atomic mass of 15 (^{15}N). Once the constants of isotopic fractionation are known, the natural systems can be studied by the analysis of isotopes. Diagrams are included which indicate the extent to which nitrate sources, i.e. from fertilizers, natural soil nitrification or animal/sewage waste can be distinguished.

Conclusions

The objectives of this preliminary situation assessment as set out above have been reached. The conclusions of the study are presented in terms of the four objectives and these are discussed in the following paragraphs. Following the groundwater nitrate situation assessment the phenomenon of natural accumulation is discussed in view of its importance in understanding the processes leading to the occurrence of nitrate in groundwater. The nitrate contamination threat posed by anthropogenic activities is considered subsequently and, based on the limited information available, main contributors are identified. Reduction of groundwater nitrogen inputs essentially relate to anthropogenic activities and it needs a dual approach as both legislative and voluntary control is essential but where accumulation has occurred treatment by denitrification has to be considered. The results have indicated that further research is urgently required.

Groundwater nitrate situation assessment

The hydrochemical data contained in the national groundwater database of the DWA&F provided an overview of nitrate occurrences in groundwater. The median nitrate concentration for the 18 827 groundwater sampling points was 4,5 mg/L. However, 27 per cent of the sources exceeded 10 mg/L, 15 per cent 20 mg/L and 4,3 per cent 50 mg/L. The higher nitrate levels (> 20 mg/L, but mostly > 50 mg/L) occur largely in the following areas:

- in the Kalahari Beds in the Gordonia District adjacent to the Namibian border;
- in the Asbestos Hills Formation, Griquatown Group, in the vicinity of Prieska;
- on the Ghaap Plateau, south-west of Vryburg;
- in the Springbok Flats;
- along the Crocodile River.

The first two occurrences are considered to be due to natural nitrate accumulation, while the last two are related to anthropogenic activities. The extensive Ghaap Plateau nitrate occurrences could be due either to anthropogenic inputs or to natural phenomena or both.

Impacts

Groundwater nitrates have caused methaemoglobinaemia in infants in Southern Africa, sometimes with fatal consequences. Although individual cases are known, statistics are unavailable. The simultaneous occurrence of faecal pollution increases the risk for infants. An epidemiological study was carried out in an area with slightly elevated nitrate levels, but no studies have been undertaken in areas where the nitrate levels are high (i.e. approaching 50 mg/L).

No conclusive evidence has been found linking gastric cancer and drinking-water containing 10 mg/L or more nitrate. However, a link cannot be ruled out completely due to the inadequacy of the data available.

Livestock losses due to nitrate poisoning would appear to occur relatively frequently but only at relatively high (» 100 mg/L) nitrate concentrations. Sub-lethal concentrations, however, also affect animals detrimentally, particularly dairy cows.

The availability of nitrate in irrigation water, complying with salinity and other irrigation requirements, could be considered beneficial in certain instances.

Accumulation phenomena

Under natural conditions the "internal" nitrogen cycle is virtually closed within the topsoil. However, environmental conditions exist under which natural leaching of nitrate from the soil zone takes place and natural accumulation occurs in groundwater. Preconditions for accumulation relate to aspects of vegetation, rainfall, temperature, soil, geology and hydrology. This phenomenon has lead to extensive areas in South Africa and adjacent territories having elevated nitrate concentrations in groundwater. Natural nitrate accumulations are also known from Chile, Australia and the USA.

Anthropogenic inputs and activities (main contributors)

Surplus nitrogenous inputs to the soil, mostly derived from anthropogenic sources, result in increased transport of nitrate to groundwater. This is often manifested by isolated occurrences of elevated nitrate concentrations in boreholes near feedlots, kraals, pit latrines and other pollution sources.

Potential point sources of serious concern are sewage sludge (uncomposted) and effluent disposal to land, on-site sanitation and waste disposal by landfilling. Some of these activities, such as landfilling, is controlled by the Central Government by means of a permitting system. However, on-site sanitation is widely practised without proper regard to the pollution potential. The risk involved has been proven in neighbouring territories and elsewhere but local information is lacking.

Although conclusive scientific evidence is lacking for South Africa, it is considered highly probable that fertilizer and manure application to land constitutes the most widespread diffuse source of nitrate pollution as it was identified in other parts of the world. The highly variable rainfall worsen the situation in the case of fertilized dry land farming due to the associated unpredictable plant cover and fertilizer needs.

Nitrogen isotope studies have provided proof that the cultivation of the soil leads to mineralization of soil organic nitrogen followed by leaching and accumulation in the groundwater even without any artificial nitrogen inputs. The situation in the Springbok Flats is ascribed to this phenomenon.

Trends

Worldwide, groundwater nitrate concentrations brought about by anthropogenic activities are on the increase. This is in all probability also true for South Africa but longer term records are lacking. In the case of the Springbok Flats it was concluded that no general trend existed and that the high nitrate values are possibly largely due to a one-time nitrogen mobilisation. The modelling of nitrate transport to groundwater has been attempted in many countries (e.g. USA, Britain, Germany, Czechoslovakia, etc.) with a reasonable degree of success. These models provide valuable insights into expected future trends in groundwater nitrate levels. In addition to long term (upward) trends in nitrate concentrations short term drastic changes in groundwater nitrate levels have been recorded. In Namibia stock losses are largely due to such sudden changes.

Control measures for nitrogen management

Control measures for reducing nitrogenous inputs to the environment are essential for protecting groundwater resources. In view of the considerable delay (varying from years to decades) between the introduction of control measures and any decrease in groundwater nitrate levels it is a matter of extreme urgency to take action in this regard. Overseas experience provides valuable guidelines for developing workable local measures.

Information programme

Informing the public and particularly the farming community as well as farming related industries of the hazards of nitrate pollution is considered an important tool for voluntary reduction of nitrogenous inputs, both with respect to diffuse sources as well as the myriad of small point sources. The impacts of a variety of anthropogenic activities causing groundwater pollution is unknown and ignored by local authorities, planners, developers and others.

The compilation of guides, such as the one jointly published by the Water Research Commission and the Department of Agriculture for the handling of manure from animal feeding units, is considered to play a crucial role in environmental (and groundwater) protection.

Denitrification processes

In view of the fact that groundwater is already contaminated in many areas in South Africa denitrification for potable use and/or stockwatering will be needed in areas where no alternative supplies are available. A number of treatment processes are being used successfully for the removal of nitrate from drinking water, e.g. biological denitrification, ion exchange and partial desalination by ion exchange, electrodialysis or reverse osmosis. In virtually all cases the denitrification stage is followed by activated carbon adsorption to remove traces of organic compounds added to the water during treatment. This clearly has serious financial implications.

In the case of stockwatering the product water does not need to comply to the same high (aesthetical) standards and biological denitrification is economically feasible using molasses as organic substrate.

In situ denitrification (aquifer restoration) is being investigated abroad and some degree of success has been achieved. Only when the technique is fully developed should it be adapted for this country.

Need for further research

From the information gathered during this project it is evident that there is a need for further research. This is based on the fact that the problem is poorly quantified at present and conclusions are largely drawn from anecdotal information, while the processes are not fully understood and management and control measures are undefined. The areas of research are therefore:

- proper quantification of the problem
- nitrate pollution and subsurface accumulation studies
- development of management and control measures, including policies, strategies and information documents.

Recommendations

The following recommendations are listed in order of priority, based on the facts that emerged from the study.

Reduction of nitrogen inputs

Groundwater nitrate is derived either from natural accumulation or from pollution. Control measures cannot significantly affect natural accumulation. Anthropogenic activities on the other hand, can be controlled and the reduction of anthropogenic nitrogen inputs to groundwater should receive attention as a matter of urgency as any actions will take years and even decades to effect a reduction in groundwater nitrate levels.

A dual approach is recommended:

Regulatory control measures: These are required to address both point source pollution, such as that emanating from feedlots, sludge application to land, multiple septic tanks and french drains, etc. as well as diffuse pollution arising from fertilizer or manure application to land. For point sources control could for example be exercised by means of a permitting system, similar to that which was instituted for waste disposal sites. As in the case of waste disposal geohydrological and other studies should be required before a permit is issued. The effectiveness of the control measures should be confirmed by monitoring programmes and studies involving nitrogen isotope analysis. In the case of on-site sanitation a limit should be set for the density of sanitation units per unit area.

Information programme: A publicity programme should be aimed at the farming community, local and regional developers, local and regional authorities and industrial concerns active in farming related activities in order to create a public awareness of the nitrate problem, its causes, prevention and remediation. Farmers in particular should be made aware of the fact that many farming activities result in groundwater pollution and that it is in their own interest to protect their groundwater resources. Agricultural extension officers and others should be briefed on the groundwater nitrate hazards for them to further disseminate this information. At the same time guides, such as the one published by the Water Research Commission and the Department of Agriculture for the handling of manure from animal feeding units should be compiled for other polluting activities, as these guides can play a crucial role in protecting the environment, including groundwater.

Long-term trends

It is recommended that the long-term trends of the nitrate concentration in groundwater be determined in various situations both where accumulation pertaining to natural conditions and presumable pollution phenomena occur. The established trends will determine the extent and severity of control measures and enforcement actions required. There is no need for strict measures in areas where the environmental conditions do not favour accumulation of nitrate in the groundwater. Conversely, strict control measures with proper enforcement will be needed in areas where rising nitrate levels have been established or for protecting vulnerable sole source aquifers. Nitrate in groundwater presents a special problem, often unrelated to increases in salinity and other quality problems, but the determination of trends should in some way or another be linked to the national groundwater quality monitoring strategy.

Delineation of vulnerable areas

The identification and delineation of areas and aquifers at risk due to cultivation and release of natural soil nitrogen is recommended. Those areas where the accumulation of nitrate in groundwater is favoured need stricter control measures for all potentially polluting activities, including farming practices, in order to allow protection of groundwater quality. For delineating such areas the information derived from the vulnerability map being compiled for the Water Research Commission could be used as a first estimate. Subsequently mapping of each of the factors enhancing subsurface nitrate accumulation should be carried out and the maps be combined through GIS to provide a nitrate specific vulnerability map.

Delineation and study of groundwater nitrate pollution

It is recommended that areas affected by nitrate pollution be delineated. Detailed studies should be undertaken at selected points within such areas, in order to identify the processes involved. The investigation of epidemiological effects, particularly in areas where nitrate levels approach 50 mg/L or more, is essential for determining the real impact on the local population where alternative supplies are unavailable. The dolomitic area on the Ghaap Plateau south-west of Vryburg is considered a priority area for such a study. It could possibly provide an opportunity for studying nitrate accumulation due to both natural and anthropogenic factors.

Natural nitrate accumulation

Subsurface nitrate accumulation seems to occur widely in Southern Africa and its extent should be determined and the conditions enhancing this phenomenon defined. Evidently such accumulation occurs not only in the Kalahari but also in areas underlain by hard rock formations as for example at Prieska. Detailed studies similar to those for identifying the pollution processes should be carried out at selected sites.

In situ denitrification (aquifer restoration)

In due course when advances abroad justify its local application, *in situ* denitrification should be investigated as an alternative to treatment after abstraction as it could entail a number of advantages. In contrast to the general restoration of aquifers which has not been very successful *in situ* denitrification has at least shown some promise.

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Mr H M du Plessis, (Chairman)	Water Research Commission
Mr L Bredenhann	Department of Water Affairs & Forestry
Dr D B Bredenkamp	Department of Water Affairs & Forestry
Mr F P Marais (Secretary)	Water Research Commission
Mr G Offringa	Water Research Commission
Mr C Siebert	Development Bank of Southern Africa
Mr A S Talma	Ematek, CSIR
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1. INTRODUCTION

1.1 Background and justification of project

Groundwater plays a vital role as a water supply source in nearly two-thirds of South Africa, even though groundwater resources supply only fifteen per cent of the total water consumption of the country. In the semi-arid to arid regions of the country, groundwater is generally the sole source of water and more than 280 towns and small settlements, are largely dependent on groundwater (DWA&F, 1991). Despite these facts, little is known about the groundwater quality and time related trends in particular. This holds true for all aspects of groundwater quality and especially for nitrate concentrations. Furthermore, some of the earlier analyses need to be treated with caution, since the general accuracy and precision of the manual analyses for nitrate carried out two to three decades ago was often significantly lower than that of the present automated analytical methods, using the chemical reduction procedure. Even today, many laboratories generate incorrect results (Smith, 1989). Incorrect sample handling and storage aggravates the situation. All these factors contribute to the lack of information on nitrate in groundwater.

To date the occurrence of nitrate in groundwater in Southern Africa has only been studied on an *ad hoc* basis by a number of researchers. Frood & Hall (1919) carried out a study of nitrate deposits in the vicinity of Prieska in the northern Cape Province, but did not include groundwater as part of their study. Bond (1946) completed the first systematic interpretation of groundwater quality related to geology and compiled the first geohydrochemical map for South Africa. This map only depicted hardness, salinity and pH, but in the accompanying tables, nitrate analyses were included for most of the sources. Bond (1946) questioned the accuracy of the older analyses, but in turn, it would seem that some of the nitrate data included in his dissertation could also be of questionable accuracy. Thus resampling and analysis of the boreholes included in his study may not provide any conclusive results with respect to any trends in nitrate concentrations in groundwater.

The occurrence of high nitrate concentrations in groundwater in the Springbok Flats (Transvaal) has been the subject of many investigations over more than two decades. Some of the more important studies were carried out by Verhoef (1973), Grobler (1976) and Heaton (1985). Levin (1980) reported on high nitrate occurrences in the north-western Cape Province. Hesseling, Toens & Visser (1991) reported on an epidemiological survey to assess the effect of well-water nitrates on infant health at Rietfontein in the northern Cape Province close to the border with Namibia. This followed an earlier epidemiological study in Namibia (Super *et al.*, 1981). Detailed information is available on the distribution of nitrate in groundwater in Namibia (Tredoux & Kirchner, 1985). Studies in the Stampriet Artesian Basin (Namibia) have shown that the occurrence of nitrate is largely confined to the phreatic aquifer and that it can attain concentrations of several hundred mg/L (as N) in the Salt Block (Kirchner & Tredoux, 1975).

Henning & Stoffberg (1990) noted nitrates in the north-western Orange Free State, while Connelly & Taussig (1991) described nitrate occurrences in Venda (northern Transvaal).

Infant mortalities ascribed to methaemoglobinaemia are known to have occurred both in South Africa and in Namibia (Hamman, 1967) but statistics are unavailable. Stock losses due to nitrate poisoning have also occurred in Namibia (Anonymous, 1974) and in Bophuthatswana. In the latter case, the loss of 140 head of cattle was recorded in a dolomitic area (Marais, 1991).

A number of institutions have focused attention on the nitrate problem and especially the World Health Organization (WHO, 1985). The disconcerting fact is, however, that a marked *increase* in the levels of nitrate in groundwater was found in almost all countries studied, especially during the decade from 1970 to 1980 (WHO, 1985). Experience, notably in Great Britain has shown that it can take decades for the nitrates to move through the unsaturated zone (Young, Oakes & Wilkinson, 1976). In the Netherlands where the groundwater level is in general relatively close to the surface, Peters & Boukes (1987) used a computer simulation in order to estimate the future trend in nitrate concentrations. The considerable delay between the actual polluting activity and the appearance of nitrate in the abstracted water is named as a serious problem in the whole study. The WHO (1985) has concluded that a rising trend in groundwater nitrate levels is likely to continue for several decades, even if the input is reduced by changes in agricultural practices which constitute the most important anthropogenic nitrate source.

Despite the scant knowledge about nitrate occurrences in South Africa, the urgency when evaluating the groundwater nitrate problem, does not lie only in a better definition of the areas of high nitrate but rather in determining the extent and degree of unintentional but preventable nitrate pollution through activities such as sludge disposal, high densities of septic tank systems, agricultural fertilizer usage, and feedlot operations.

1.2 Objectives

The worldwide concern over rising nitrate levels has also been echoed in South Africa and, therefore, the Water Research Commission (WRC) decided to fund a one-year preliminary investigation in order to assess the extent and severity of the problem in this country. The main objectives of this preliminary study were to:

- carry out a preliminary situation assessment concerning groundwater contamination in South Africa with respect to both the extent and severity of nitrate pollution using existing information;
- identify the major contributors (polluters) qualitatively;
- make an initial assessment of the possibilities to manage nitrate pollution caused by the major contributors (as gleaned from the literature);
- evaluate the need for further research.

1.3 Modus operandi

As set out above, this study is a preliminary situation assessment making use of the available information and, therefore, no in-depth research was undertaken. It was attempted to identify the major problems related to nitrate in groundwater which means that this is not meant to be an exhaustive treatise on nitrate in groundwater. The project commenced with a literature search and study, interviews with experts, and an evaluation of the hydrochemical data in the national groundwater database of the Department of Water Affairs & Forestry (DWA&F). The data was evaluated statistically and mapped using ArcInfo.

It was considered expedient to bring the nitrate problem to the attention of the groundwater fraternity and, therefore, permission was obtained from the WRC to prepare a paper for a local conference (Tredoux & Du Plessis, 1991a). Furthermore, permission was also obtained from the WRC to prepare a paper for the International Workshop on Inorganic Nitrogen Compounds and Water Supply, Hamburg (Tredoux & Du Plessis, 1991b). Funding was made available by the CSIR for attending this workshop. It afforded the opportunity to consult with overseas experts on nitrate both at the workshop and during individual visits in order to gain first hand knowledge of the nitrate problem, its impacts and the remedial measures applied in Europe. As the workshop only took place at the end of November 1991 and the overseas information was considered to be of direct relevance the WRC agreed to the extension of the project until 31 May 1992.

1.4 Reporting of nitrate values

Throughout this report, nitrate concentrations are expressed in mg/L as nitrogen (NO_3-N) except in Table 2 where the limits are given in the units as specified. This is the preferred expression of results of the International Water Supply Association (IWSA) according to Packham (1991). There is, however, no final ruling in this regard and considerable confusion still exists in the literature as authors do not always clearly indicate which method is being followed. Where necessary, the following conversion factors should be used:

1 mg of compound expressed as nitrogen (N) is equivalent to:

4,43 mg when expressed as nitrate (NO_3^-)
3,29 mg when expressed as nitrite (NO_2^-)
1,29 mg when expressed as ammonium (NH_4^+)

1 milliequivalent of compound is equivalent to:

62 mg when expressed as nitrate (NO_3^-)
46 mg when expressed as nitrite (NO_2^-)
18 mg when expressed as ammonium (NH_4^+)
14 mg when expressed as nitrogen (N)

2. GROUNDWATER QUALITY CONCERNS RELATED TO NITRATE

Nitrogen is one of the main biogeochemical elements and together with carbon, oxygen, sulphur and phosphorous, these elements in their biogeochemical cycles constitute the main life-supporting system for our planet. The occurrence of these elements and their compounds in water (including groundwater) thus also forms part of these natural cycles. Nevertheless, the presence of the nutrients nitrogen and phosphorous in water is generally considered to be a manifestation of pollution. Particularly in the case of surface water, their elevated concentrations create an aesthetic problem due to their promotion of algal growth. In the case of groundwater, pollution is more difficult to trace and the effects are not as obvious. However, the deterioration is long-lasting and in cases where excessive nitrates occur, ingestion of the water could be fatal for babies and livestock. The only possible beneficial aspect of the occurrence of nitrate in water is its immediate availability as a plant nutrient when the water is used for irrigation. Even then problems with ripening or maturing can be created which affect the quality of the produce (Ayers & Westcot, 1985).

2.1 Health hazards

Exposure to high doses of nitrate is generally perceived to be associated with adverse health effects in humans and other species. These range from the 'hot dog headache' and methaemoglobinaemia to cancer and other effects. According to the WHO (1985, p 19) daily dietary intakes of nitrate and nitrite have been estimated in different countries. Certain vegetables (e.g. lettuce, spinach, beetroot and celery) contain relatively high levels of nitrate (>3000 mg/kg for lettuce (Parsons 1977)) but the nitrite levels are usually very low. Nitrates and nitrites are also added as preservatives in some foods, such as cured meats. In most European countries the mean nitrate intake is about 10 - 30 mg/day. Vegetarians usually have a two- to four-fold higher intake of nitrates than non-vegetarians. Usually drinking water contributes less than 30 per cent of the total dietary nitrate intake. When the drinking water nitrate level exceeds 10 mg/L, the contribution may be considerably higher. These effects are discussed briefly below to put them into proper perspective.

Methaemoglobinaemia

Nitrate itself has a low primary toxicity (Rohmann & Sontheimer, 1985, p. 253) but when reduced to nitrite (NO_2) it becomes an oxidising agent, capable of converting haemoglobin in the blood to methaemoglobin (WHO, 1985, p. 49). This methaemoglobin is considerably more stable than the oxygen haemoglobin complex that fulfils the oxygen transport function of the blood. Once the concentration of methaemoglobin in the blood exceeds 5 per cent the first symptoms of 'cyanosis' are generally noticeable while death results at levels of 50 per cent and higher (Terblanche, 1991). In most countries, methaemoglobinaemia is not a notifiable disease, making its true incidence unknown. Hungary is one of the exceptions when since 1968, methaemoglobinaemia has been a notifiable disease (WHO, 1985, p. 51).

The occurrence of infant methaemoglobinaemia resulting from the consumption of water with high nitrate concentrations was first recognised clinically by Comly (1945). The infants were both less than one month old and had received rural well-water containing 90 and 140 mg/L nitrate respectively. Comly (1945) already suggested a recommended limit of 10 mg/L and a maximum of 20 mg/L. Shuval & Gruener (1972) studied 1702 infants living in the Israel coastal plain in areas with medium to high nitrate (11,3 to 20,3 mg/L) and compared these with a control group of 759 infants in Jerusalem with only 1,1 mg/L of nitrate in the water supply. No significant difference was found between the methaemoglobin levels in the 1702 infants in the study area as compared to the 758 infants in the control area. They do, however, concede that only six per cent of the infants included in the study received appreciable amounts of tap water together with formula prepared from powdered milk. In addition, most of the infants were given substantial quantities of vitamin C containing juices. In a later paper (Shuval & Gruener, 1977) these authors confirm a direct relationship between the occurrence of methaemoglobinaemia in infants and the presence of high concentrations (> 10 mg/L) of nitrate in water. It is stated that although this is the principal determinant of the occurrence of methaemoglobinaemia in infants, it is not the only one. Other factors important in the pathogenesis of the disease are the following (Ross & Desforges, 1959):

- age: usually infants 0-3 months old, are affected;
- presence of bacteria: nitrate reducing bacteria should be present in sufficient numbers in the gastro-intestinal tract;
- gastric acidity: a pH higher than 4 (normal pH between 2 and 5);
- gastro-intestinal disturbances;
- type of powdered milk product;
- high fluid intake;
- effect of nutrition: food rich in nitrates can increase severity of illness while certain nutrients such as vitamin C can cure or prevent methaemoglobinaemia;
- foetal haemoglobin: haemoglobin-F is oxidized more readily to methaemoglobin (the blood of new born babies consists of more than 80 per cent haemoglobin-F);
- methaemoglobin reduction: the methaemoglobin reduction velocity is affected by a number of factors.

Terblanche (1991) reviewed the health hazards of nitrate in drinking water based on experience in other countries and observed that very few studies have been published on the health effects of nitrates in drinking water in South Africa.

Shortly afterwards the first epidemiological survey in South Africa to assess the effect of well-water nitrates on infant health was published. This was carried out at Rietfontein in the northern Cape Province (Hesseling, *et al.*, 1991). The survey was undertaken due to the concern about the risk of methaemoglobinaemia in infants in the Rietfontein area as a result of the large number of boreholes exceeding 10 mg/L of nitrate-nitrogen. The nitrate content of the groundwater varied from 4,8 mg/L to 22 mg/L with a median of 11,6 mg/L. All infants had a methaemoglobinaemia level in excess of the accepted upper limit of 0,5 g/100 mL ranging from 0,51 to 2,5 g/100 mL and a mean value of 1,2 g/100 mL. This was not associated with clinical symptoms. The conclusion was that under conditions such as those prevailing at Rietfontein, applying the maximum nitrate level of 20 mg/L will result in better utilization of the groundwater resource without appreciable risk to the community (Hesseling, *et al.*, 1991). No correlation was found between the nitrate content of the groundwater used and the methaemoglobin levels in the blood. On the contrary, in a similar epidemiological study on a comparable population group in neighbouring Namibia (Super *et al.*, 1981) a correlation was found between the nitrate level in the groundwater and blood methaemoglobin levels. The main difference between the two studies was that the levels of nitrate in groundwater in the case of the Namibian study was much higher and had a maximum of 56 mg/L of nitrate-nitrogen.

From 1945 until 1970, some 2000 cases of methaemoglobinaemia have been reported in the world literature (Shuval & Gruener, 1972) with a case fatality of about 8 per cent. The WHO (1985) cites literature indicating that ten cases of methaemoglobinaemia have been reported in the United Kingdom since 1950 when the first cases of methaemoglobinaemia were reported in East Anglia. Only one death was reported during this period. In 1986 a two-month old infant in South Dakota (USA) died of methaemoglobinaemia (GWN, 1986). The exact nitrate concentration is unknown. In another non-fatal case in Iowa the water apparently contained 285 mg/L nitrate (as N) but the five-week old infant survived (Rajagopal & Tobin, 1989).

Hungary is possibly the country with the best statistics on the occurrence of methaemoglobinaemia. Since 1968, methaemoglobinaemia has been a notifiable disease in the country (WHO, 1985). In the first five years after 1968, a total of 883 cases was reported. In 92 per cent of the recorded cases, the nitrate level in the drinking water exceeded 22,6 mg/L, while in the remaining 8 per cent it was between 9 and 22,6 mg/L. Detailed statistics for the period from 1976 to 1990 was provided by Csanady (1991) during the presentation of his paper at the Nitrogen Workshop in Hamburg (see Table 1 below). The highest number of cases was reported in 1977 and the measures taken to supply the population with drinking water of low nitrate have resulted in a definite decrease in the number of cases each year.

Ingestion of nitrate has no apparent short-term effects on adults. Adults on a farm near Otjiwarongo, Namibia, continued drinking water with 268 mg/L of nitrate, even after stock losses occurred on that farm (Tredoux, 1974) with no apparent ill-effects (Von Ascheraden, 1969).

Gastric cancer

Shuval & Gruener (1977) refer to the possible carcinogenic, teratogenic and mutagenic properties of nitrosamines which can theoretically develop in food or in the human digestive tract if nitrates and nitrites are exposed to secondary and tertiary amines under certain conditions. No conclusions are drawn as to the real nature of the potential risks involved. In an earlier paper, Wolff & Wasserman (1972) reviewed 60 publications on the potential hazard of nitrate, nitrite and nitrosamines in the environment. They came to the conclusion that 'the extent of real danger is not yet known, but deliberate consideration of the available information would suggest that the hazard is not sufficiently great to cause alarm'.

TABLE 1: Occurrence of methaemoglobinaemia in Hungary (Csanady, 1991)

YEAR	NUMBER OF CASES	NUMBER OF FATALITIES
1976	207	4
1977	293	7
1978	239	3
1979	180	2
1980	172	3
1981	166	1
1982	91	1
1983	67	-
1984	33	-
1985	46	1
1986	41	-
1987	30	-
1988	31	2
1989	35	2
1990	22	-
TOTAL	1653	26

Hartman (1983) published a graph showing the relationship between gastric cancer mortality rates and nitrate ingestion in twelve countries (see Fig. 1). The graph refers to total nitrate ingestion and does not specifically refer to the ingestion via drinking water. It is, however, questionable whether the seemingly good correlation is actually related to nitrate ingestion only or possibly also to other dietary factors relating to the various population groups.

After considering all available evidence, the WHO (1985, p. 61) came to the conclusion that 'no convincing evidence of a relationship between gastric cancer and consumption of drinking-water containing nitrate levels up to 10 mg/L has emerged. Furthermore, no firm epidemiological evidence has been found linking gastric cancer and drinking-water containing higher levels of nitrate but a link cannot be ruled out due to the inadequacy of the data available.'

Other health effects

Nitrate ingestion has been named as a possible cause for a number of other adverse effects such as birth defects (congenital malformations) which were studied in South Australia and also in eastern England. Detailed investigation has provided no evidence

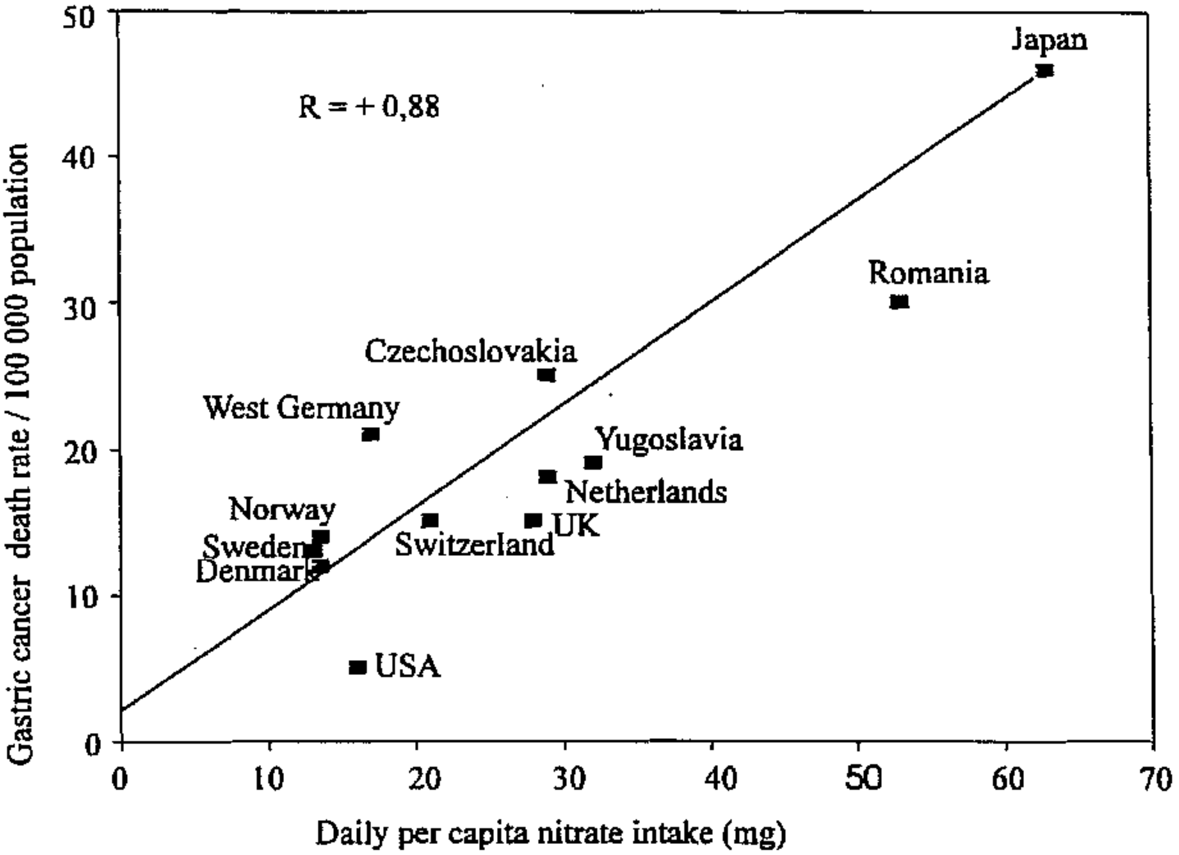


FIGURE 1: Relationship of age-adjusted gastric cancer mortality rates and nitrate ingestion in twelve countries. The line is drawn to a least-squares fit to the data points. Data on gastric cancer mortality are for the years 1974-1975 (Hartman, 1983).

that these were associated with nitrate levels in water supplies (WHO, 1985). It has also been suggested that chronic exposure to high levels of nitrate in drinking water may have adverse effects on the cardiovascular system. The WHO (1985), however, reported that an inverse relationship between cardiovascular mortality and nitrate concentration in water supplies had been demonstrated.

Other possible effects of nitrates relate to the thyroid function. Some animal studies indicate that chronic exposure to high levels of nitrates can reduce the intra-thyroid iodine pool and thus render the gland more sensitive to goitrogens (WHO, 1985). However, whether or not exposure to nitrate is an etiological factor in human goitre remains to be determined.

The 'hot-dog headache' has been described in the literature and has been related to nitrites used in the curing of meat to give it a uniform colour (Johnson & Goldfinger, 1982). The nitrites are also vaso-dilators, so that some people find that soon after eating these meat products, they develop flushing of the face and a headache. The hot-dog is the classical example, but other meat products including bacon, ham and salami can also cause these symptoms. A farmer in the Springbok Flats regularly complained about hot-dog headaches. The problem was solved when he started using nitrate-free water (Talma, 1991).

2.2 Drinking water standards

Various limits and guideline values for nitrate in drinking water is given in Table 2. It is evident that most of the authorities consider approximately 10 mg/L as an acceptable limit. Packham (1991) remarked as follows: 'The first limit for nitrate in drinking-water was set by the USA Public Health Service in 1962 and it was annotated as follows: - because of the uncertainty introduced by tardy analysis, the frequent lack of attention to possible interfering factors in the analysis, the health of the infant and the uncertain influence of associated bacterial pollution, 10 mg nitrate-nitrogen (NO_3-N) per litre of water is a limit which should not be exceeded' (quoted by Packham, 1991).

On the basis of their epidemiological studies, both Super *et al.* (1981) and Hesseling *et al.* (1991) argued that up to 20 mg/L of nitrate would still be acceptable as it presented a low risk to infants. Parsons (1977) studied all the available information and concluded that 'the drinking water limit for nitrates is inconsistent with the facts and should be raised to at least 22,6 mg/L'. However, the US EPA and the WHO retained the limit of 10 mg/L suggested by Comly (1945) while the EC even introduced a lower guide level equivalent to 5,6 mg/L in 1980 (see Table 2).

2.3 Stock-watering

Although infants are sensitive to the occurrence of nitrate in drinking-water, adults can ingest large quantities without any apparent ill-effects. In the case of livestock, fully grown animals are also at risk. However, it would seem that chronic toxicity only occurs at higher nitrate levels. Accordingly, nitrate limits for stock-watering are set considerably higher, for example in Namibia the limit for stock-watering is set at 110 mg/L (DWA Namibia, 1977). In South Africa 90,3 mg/L is used as a guideline value for the watering of dairy cows (Baard, 1992).

According to Davison *et al.* (1964) cattle ingesting nitrates have a reduced life-span, inhibition of growth and increased incidence of abortion and related infertility. In their experiments milk production was similar for the control groups and the heifers fed various levels of nitrate. Stock-losses due to nitrate poisoning have occurred in neighbouring Namibia (Anonymous, 1974; Tredoux, 1974). In these cases, the nitrate concentration was usually several hundred mg/L. In a dolomitic area in Bophuthatswana a loss of some 140 head of cattle was recorded in 1989 (Marais, 1991). The nitrate concentration was 691 mg/L (as N). It would seem, however, that detrimental effects particularly on dairy cows could occur at much lower concentrations and for this reason a farmer in the Springbok Flats installed his own microbiological denitrification unit for stock-watering to protect his dairy cows (Anonymous, 1985). He is reportedly reducing the nitrate concentration from 34,3 mg/L to 0,2 mg/L using molasses as a carbon substrate.

TABLE 2: Limits and guideline values for nitrate in drinking water (Aucamp & Viviers, 1987; DWA-Namibia, 1977; Packham, 1991; SABS, 1984)

ORGANIZATION		YEAR	CONCENTRATION (mg/L)	
			as NO_3	as N
WHO (European)	Max. Desirable[1]	1970	100	(22,6)
	Max. Acceptable	1970	50	(11,3)
WHO (International)		1971	45	(10,2)
US EPA		1977	(44,3)	10
Health and Welfare, Canada		1978	(44,3)	10
EC	Maximum admissible	1980	50	(11,3)
	Guide level	1980	25	(5,6)
WHO Guideline value		1984	(44,3)	10
SA DNHPD[2]	No risk	1987	(26,6)	6
	Insignificant risk	1987	(44,3)	10
	Low risk	1987	(88,5)	20
SABS-241	Recommended[3]	1984	(26,6)	6
	Max. allowable[3]	1984	(44,3)	10
Namibia[4]		1962	(88,5)	20

Notes

1. Brackets indicate derived units
2. Department of National Health and Population Development, suggested new guideline criteria
3. Nitrate plus nitrite
4. Indicated as unsuitable for infants under one year

Enquiries regarding the incidence of stock losses due to nitrate poisoning were made at the Office of the State Veterinarian, the Directorate of Animal Health, Onderstepoort and other Government offices. It was established that this was not a controlled disease and no records were kept of such occurrences. The general perception amongst veterinarians was that nitrate poisoning due to the ingestion of high nitrate water occurred seldom. One veterinarian mentioned that he has witnessed nitrate poisoning of cattle after ingestion of turnips and that he saw this as a problem.

2.4 Economic concerns

The economic implications of the occurrence of methaemoglobinaemia is difficult to estimate, particularly in the case of fatalities. In other cases, the direct medical expenses could be calculated. On the other hand, the cost of providing alternate supplies (or even bottled water) can be determined accurately. In the case of denitrification, the addition of this process could add up to 50 per cent to the water treatment cost depending on the size of the plant and the method used.

Stock losses due to nitrate poisoning often involve a large number of cattle (Anonymous, 1974; Marais, 1991). Thus the financial implications can be considerable. Also at sub-lethal dosages, cattle could have a reduced life-span, inhibition of growth and increased incidence of abortion and related infertility (Davison *et al.*, 1964) with all related financial implications.

Kumm (1976) studied the profitability of nitrogen fertilization for certain crops in Sweden. In most cases the nitrogen application rate per unit area was well in excess of the optimum for maximum profitability. In addition, the excess nitrogen is leached into the groundwater or into surface water bodies. It is argued that according to the law of diminishing returns, world production of food stuffs would rise more rapidly if the surplus nitrogen fertilizer is routed to the developing countries instead of the developed countries such as Sweden, Germany and the Netherlands.

Power & Schepers (1989) categorically state that the primary factor of concern for the farmer is his net income. Individual farmers may drastically alter management systems by producing specialty crops, utilizing organic wastes, or other such practices. However, by far the largest majority must operate profitably within conventional boundaries of inputs and outputs. They conclude that there are no simple solutions and that the farmer cannot bear environmental protection costs from which he gains no direct benefit.

Possibly one of the only advantages of nitrogenous groundwater is that it can be applied fruitfully for the irrigation of certain crops during part of the growth cycle. In their discussion of nitrate in underground waters of Central Australia, Murray & Siebert (1962) suggested that fixation of atmospheric nitrogen by legumes could account for the areas giving rise to moderately and highly nitrated waters. They continued: 'should it be proved, the possibility arises of producing such waters for irrigation purposes by the planting of selected *Acacia* species on catchment areas which provide sufficient waters of suitable quality'.

3. NITROGEN PROPERTIES

3.1 Nitrogen chemistry and analytical techniques

Nitrogen can exist in a range of oxidation states at ambient conditions which gives rise to a series of stable nitrogen compounds occurring in the environment. The diatomic gas, N_2, represents the zero oxidation state while ammonia, NH_3, at -3 represents the lowest and nitrate, NO_3^-, at +5 the highest oxidation states (see Table 3). These are stable at ambient conditions, so much so that ammonia and nitrate can, within limits, coexist in the compound ammonium nitrate, NH_4NO_3. Due to its special characteristics it can serve both as an explosive and as a fertilizer. The latter is mostly stabilized with limestone and sold as LAN. A series of oxides of nitrogen exists including nitrous oxide (N_2O) and nitric oxide (NO). With the exception of nitrate all the others are metastable (Barnett & Wilson, 1959) and mainly occur during the transition processes of nitrification and denitrification. A further important characteristic of ammonium and nitrate salts is their high solubility in water. This also holds for the simple organic compound urea, $CO(NH_2)_2$, widely used as fertilizer.

The fact that all nitrates are soluble excludes any possibility of nitrate removal by conventional water treatment process such as chemical precipitation. Reduction to a harmless and relatively insoluble product such as nitrogen gas, therefore, presents one of the few biochemical treatment possibilities.

TABLE 3: Examples of nitrogen compounds in various oxidation states

COMPOUND	FORMULA	OXIDATION STATE
Ammonia	NH_3	-3
Hydrazine	NH_2NH_2	-2
Hydroxylamine	NH_2OH	-1
Nitrogen	N_2	0
Nitrogen (I) Oxide	N_2O	+1
Nitrogen (II) Oxide	NO	+2
Nitrous Acid	HNO_2	+3
Nitrogen Dioxide	NO_2	+4
Nitric Acid	HNO_3	+5

The most important reactions involving nitrogen are of a biochemical nature and are either driven by microorganisms or enzymes. For this reason the impact of nitrates on groundwater needs to be considered in terms of the nitrogen biogeochemical cycle.

Due to its chemical characteristics, nitrate in water is mostly determined indirectly, i.e. nitrate is reduced to nitrite which is then measured after reaction with reagents producing intensely coloured compounds. Ten to fifteen years ago nitrite was determined separately in parallel (without reduction of the nitrate) but today it is often reported as NO_x^- (i.e. $NO_2^- + NO_3^-$) as the nitrite concentration is usually negligible and often only arises due to nitrate reduction during sample storage.

Nitrate may be determined directly either by ion chromatography (APHA, 1989) or by means of UV spectrometry but the latter is subject to interference from organic matter and this method is recommended as a general sorting/screening test only (WHO, 1985). Another direct measurement technique uses ion-selective electrodes but precision is relatively poor and again it is recommended for use as a sorting/screening test or for rapid monitoring in an environment where the other constituents remain relatively constant (WHO, 1985).

Since automated analytical methods (using the chemical reduction procedure) have become available, the general accuracy and precision of nitrate determinations has improved significantly compared to manual analysis. However, such analyses need to be carried out with extreme care regularly interspersed with standards of known composition. Inter laboratory studies have shown that even today many laboratories generate incorrect results (Smith, 1989). If not clearly specified, the way in which the concentration of nitrate is reported (e.g. nitrate as N, nitrate as NO_3^- etc.) may also lead to erroneous interpretation.

For a detailed description of the analytical methods and the inaccuracies involved, the reader is referred to "Standard Methods" (APHA, 1989). When interpreting analytical data, the above aspects should be taken into account as well as correct sampling methods, sample preservation and storage (Weaver, 1992).

3.2 Nitrogen biogeochemistry

Nitrogen is one of the main biogeochemical elements and along with carbon, oxygen, sulphur and phosphorus these elements in their biogeochemical cycles constitute the main life-supporting system for our planet. The occurrence of these elements and their compounds in water (including groundwater) forms part of these cycles (Svensson & Söderlund, 1976). Nitrogen is an integral part of all living organisms occurring in the form of amino acids in proteins. The primary source of nitrogen is the atmosphere where the strongly bonded gaseous molecule N_2 is the predominant gas. Only a few species of bacteria and algae have the ability to utilize molecular nitrogen. All other living organisms on the earth require combined nitrogen for carrying out their life activities (Stevenson, 1965).

The geochemical distribution of nitrogen in the various global shells are given in Table 4 (Stevenson, 1965). The large quantity of nitrogen in the lithoshell is based on the value of 0,04 mL/g for the nitrogen in igneous rocks and this value has been used to calculate the total mass of nitrogen in the fundamental rocks. Stevenson (1965) remarks that the nature of the nitrogen in fundamental rocks is not known with certainty but that the general view was that it existed as nitrides of iron, titanium, and other metals, or as ammonium salts. The nitrogen is only released during weathering. However, in the lithoshell soil organic matter is also included and amounts to $0{,}3 \times 10^{15}$ tons (Söderlund & Svensson, 1976).

TABLE 4 Geochemical distribution of nitrogen (Stevenson, 1965)

Shell distribution	Nitrogen contained in each geoshell	
	Mass 10^{15} tons	Percentage (%)
Atmoshell	3,9	1,96
Lithoshell	193,4	98,04
Bioshell	0,000014*	0,000001

*As recalculated by Söderlund & Svensson (1976)

Rohmann & Sontheimer (1985) provided a practical description of the main elements of the global nitrogen cycle (see Fig. 2).

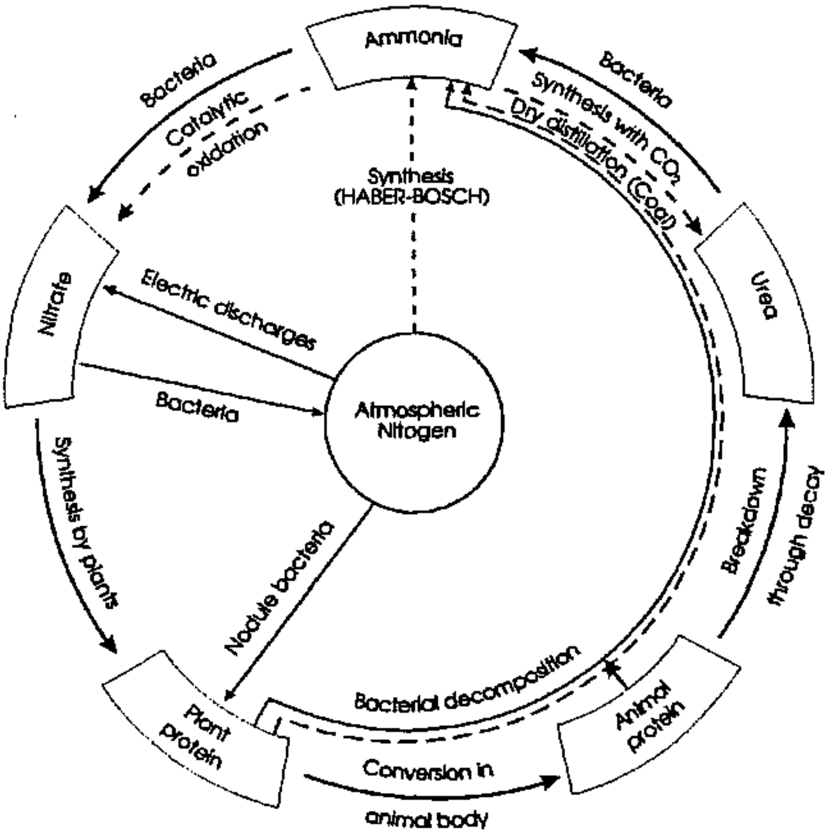


Figure 2. Main transformations in the global biogeochemical nitrogen cycle. Natural processes are indicated with solid lines; synthetic processes are indicated with dotted lines. (Rohmann & Sontheimer, 1985)

From Figure 2 it is evident that virtually all natural conversions between the various nitrogen compounds are dependent either on bacterial action or biochemical reactions in plants or animals. The only exception is the transformation of nitrogen to nitrate by electrical discharges. However, the fraction of nitrate produced in this way is relatively small (Hem, 1970, p. 181). Rohmann & Sontheimer (1985, p 35) also state that "small amounts" of NO_x are formed by electrical discharges in the atmosphere but give no indication of quantities. Jenkinson (1990) estimated this quantity at 8 million metric tons per annum which is equivalent to nearly six per cent of the estimated input derived from biological fixation worldwide.

Rohmann & Sontheimer (1985) compiled all the available information on nitrate in rainwater and came to the conclusion that the total annual input from this source averages 11 kg N/ha for Germany. Most of this nitrate is ascribed to emissions from power stations, vehicles and industry. For the United States Schepers & Fox (1989) made a compilation of the available data and found that the nitrate input from rain varied between 1,7 and 7,5 kg N/ha. Heaton (1984) gives the mean nitrate value for rain water in Pretoria as approximately 0,4 mg/L and assumed that the value in the western Kalahari would be similar. This yields approximately 1 kg N/ha at a rainfall of 250 mm/a.

3.3 Nitrogen cycle in the soil

Nitrogen transfers between soil and vegetation constitute 95 per cent of the nitrogen flow and thus by far exceed other global nitrogen transfers (Rosswall, 1976). Only five per cent of the total flow is concerned with exchanges to and from the atmosphere and the hydrosphere. The vegetational cover of the earth is dependent on inorganic nitrogen for growth, and the amounts of plant-available ammonium- or nitrate-nitrogen at any one time are usually limiting under natural conditions. The major part (95, often 98 per cent, Juergens-Gschwind, 1989) of soil nitrogen occurs, however, in organic form and must be mineralised to inorganic nitrogen before it can be taken up by plants. A flow chart describing the nitrogen inputs, storages, soil processes or transformations and losses is given in Fig. 3.

In this flow chart natural biological nitrogen fixation constitutes the largest input of 139 million metric tons per year (Söderlund & Svensson, 1976) which is four times as much as the input from industrial sources (fertilizers). Later estimates (Jenkinson, 1990) set the input from industrial sources at 74 million tons which is approximately half that of natural fixation. These inputs are balanced by gaseous losses almost exclusively as a result of denitrification. The role of denitrification in maintaining the balance in the 'internal' cycle should, therefore, be recognised. Based on estimated transfer rates, Rosswall (1976) calculated the turnover time of nitrogen in various parts of the global terrestrial system. For soil organic matter the nitrogen turnover time in various terrestrial ecosystems varies from 100 to approximately 400 years compared to an approximate turnover time of 4 to 5 years for plants. Due to the slow mineralisation of soil organic matter, nitrogen is released at a slow rate for a century or more, even if no further inputs are made.

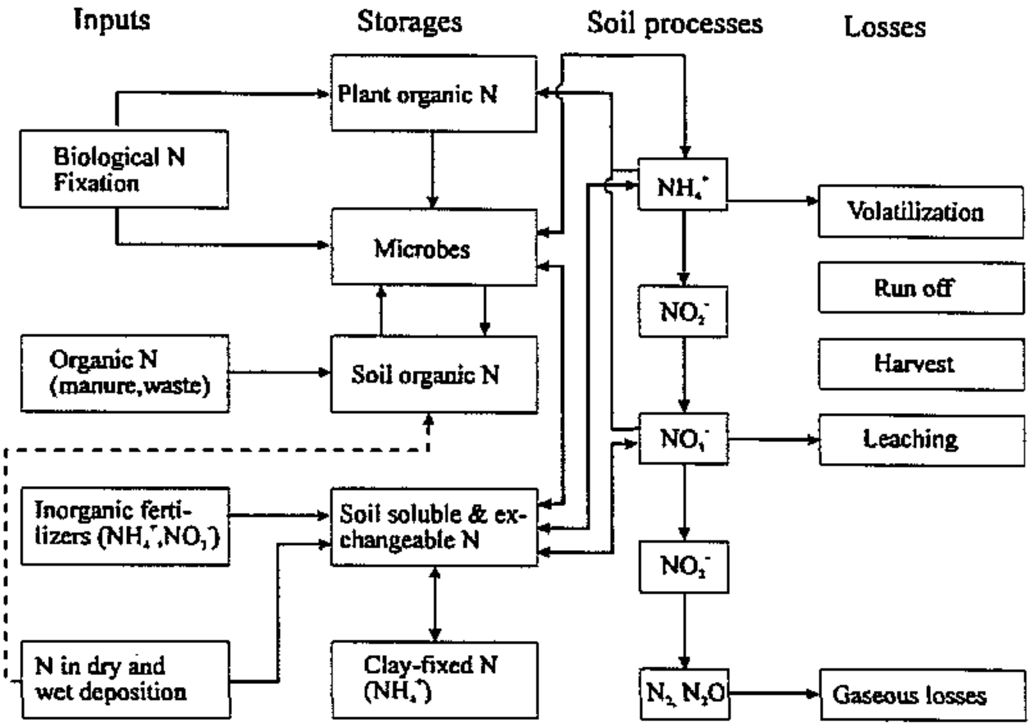


FIGURE 3: A flow chart for nitrogen in soil (Rosswall, 1976).

Jenny (1941) studied the trends of soil fertility over long periods and stated that the formation of a fertile soil rich in nitrogen and organic matter, requires periods of hundreds and thousands of years. Under exploitive systems of farming soil fertility deteriorates rapidly. Data from Midwestern (USA) experimental stations is given in Fig. 4 (from Jenny, 1941, p. 252). The nitrogen content of virgin prairie soil is taken as 100 per cent. The reductions for three consecutive periods of 20 years are approximately 25, 10 and 7 per cent respectively (Jenny, 1941). It is anticipated that in the course of time a 'steady state' of the nitrogen content of the soil is reached, when the removal of soil nitrogen by crops is balanced by the natural rejuvenation by nitrogen fixation.

As 95 per cent of soil nitrogen occurs in the organic form mineralisation is essential for nitrogen uptake by plants. Juergens-Gschwind (1989) stated that nitrate has been an end product in the natural degeneration (ammonification, followed by nitrification) of soil organic nitrogen since millions of years. Mineralisation thus also leads to water soluble end products causing nitrogen losses through leaching. Loss in soil productivity through mineralisation of organic reserves is a problem which is closely linked to the type of plant cover or the lack thereof. Barnard & Fölscher (1973) carried out lysimeter investigations over four seasons at the University Experimental Farm, Pretoria, where several annual crops conventionally used in rotation with maize, together with perennial grass were tested for the conservation of plant nutrients. It was found that under annual babala nitrification of organic soil nitrogen and other reduced nitrogen is apparently reduced to much the same extent as under perennial grass. This is in contrast to considerable nitrification and leaching from soils planted with crops such as maize, sunflowers and soya beans.

Russell (1973) investigated the recovery of fertility when laying arable land down to grass. Usually the organic matter and humus content increases considerably. The

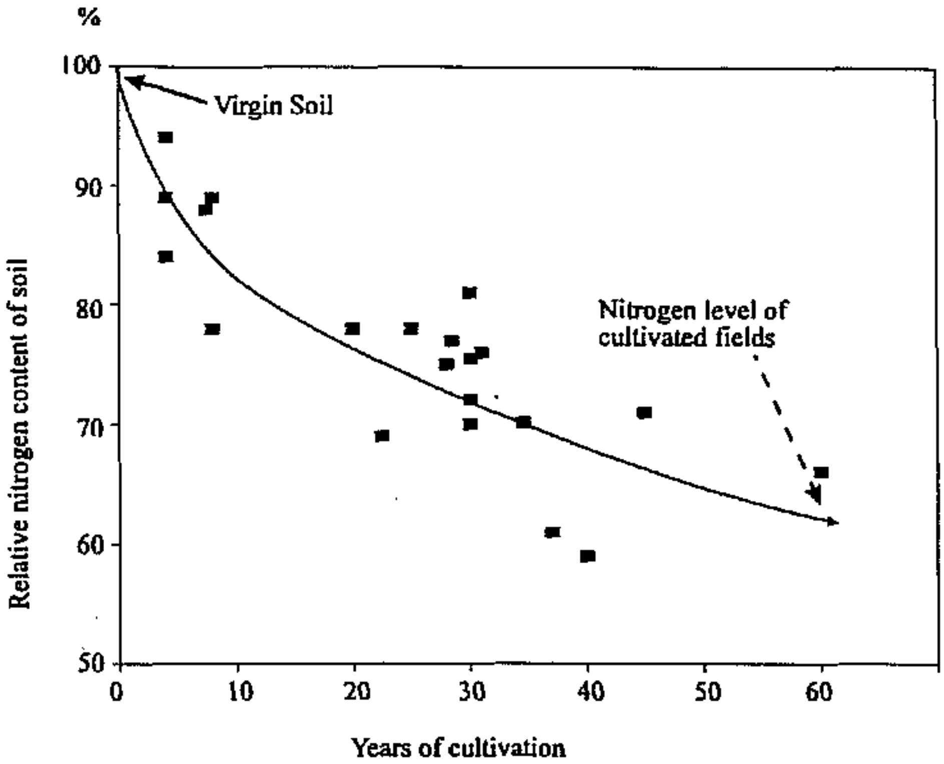


FIGURE 4: Decline of soil nitrogen under average farming conditions in the north central USA (Jenny, 1941, p. 252)

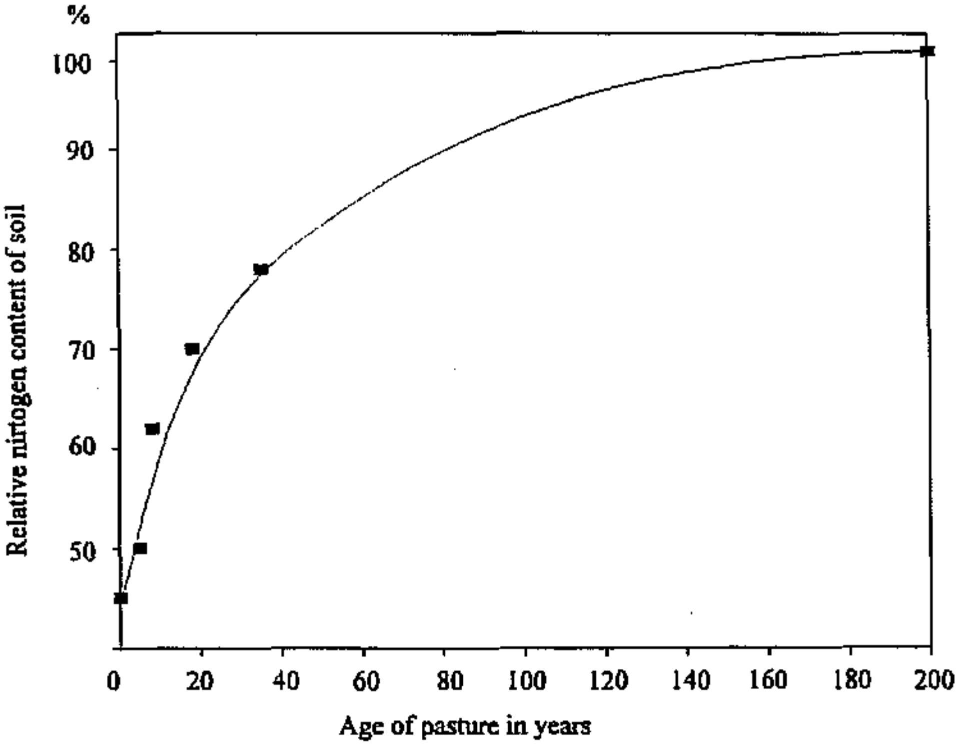


FIGURE 5: The rate of accumulation of nitrogen in the top 22 cm of soil at Rothamsted (UK) when old arable land is laid down to grass (Russell, 1973, p. 324)

Rothamsted (UK) soil nitrogen content illustrated in Fig. 5 (from Russell, 1973, p. 324) took approximately 25 years under grass to increase half way from the old arable land to the old pasture level.

As explained above, denitrification in the soil zone is crucial for maintaining a balance and to prevent nitrate accumulation in the subsurface. This is a natural process which depends on the action of denitrifying bacteria. Denitrification only commences once all free oxygen has been consumed as it largely depends on facultative anaerobic bacteria. The reduction of nitrates to nitrous oxide (N_2O) and free nitrogen gas (N_2) occurs in soils that are weakly acidic, usually above pH 5,0, under conditions of poor aeration in the presence of an active microbial population, and can therefore be important during wet periods in warm soils well supplied with decomposable organic matter (Russell, 1973). In studies quoted by Russell (1973) it has been shown that denitrification can be a very active process as in a laboratory experiment soils containing 300 mg/kg of NO_3-N could lose almost the whole amount by denitrification in between 28 and 96 hours if there was also a source of decomposable organic matter present.

Hiscock *et al.* (1991) reviewed biological denitrification and stated that the reduction of nitrate to nitrogen involves several steps, with many bacteria only able to perform one or two of these steps. Thus, the denitrifying microflora must be considered as a group of complementary microorganisms able to carry out the conversion of nitrate to nitrogen in its entirety. Most denitrifying bacteria are heterotrophic and hence are able to utilise a wide range of carbon compounds (e.g. sugars, organic acids, amino acids) as sources of electrons. Rödelsperger *et al.* (1992) stated that the importance of natural denitrification in the saturated zone was only recognised recently when the nitrate loading increased, particularly due to fertilizer applications not properly related to vegetation requirements. Their research was justified by the perceived lack of information regarding the factors controlling natural denitrification in the aquifer. They also attempted to quantify the longer term denitrification capacity of the subsurface. Although this did not fully succeed they confirmed the requirement of sufficient organic material to be present in the aquifer for denitrification to proceed.

Denitrification has been recorded in many instances in various types of aquifer and both under natural and polluted conditions (e.g. Ineson & Downing, 1963; Tredoux & Kirchner, 1981; Vogel *et al.*, 1981; Howard, 1985; Trudell *et al.*, 1986; Wilson *et al.*, 1990). Confirmation of denitrification was obtained by means of gas analyses and isotopic ratios. Gurevich (1961) recorded natural, bacterial denitrification in an aquifer at a depth of 1800 m and more. It is therefore evident that denitrification takes place widely and serves a very important purpose. However, Howard (1985) concluded that natural denitrification cannot be relied upon to reduce elevated concentrations of nitrate in modern recharge waters.

Mills (1985) pointed out the inhibiting effect certain agricultural chemicals have on denitrification. It was stated that the impact of these chemicals (pesticides) on nitrogen transformations had been evaluated as to their effects on nitrification to a greater extent than denitrification. In general, fungicides inhibit nitrification more than insecticides or herbicides. Direct suppression of the denitrification process as measured by reduced N_2 and N_2O evolution and increased NO_3 retention in the medium was obtained with chemicals such as nitrapyrin and terrazole. It was concluded that certain pesticides have the potential to affect soil nitrogen transformations. The influence of these chemicals on soil nitrogen transformations have both positive and negative effects. The positive effects are increased nitrogen utilization and plant growth, while the negative aspect is the potential for increased nitrate and/or nitrite retention in the soil with the subsequent risk of leaching of these ions into groundwater (Mills, 1985). Juergens-Gschwind (1989) and Peterson & Frye (1989) both refer to the use of nitrification inhibitors to control the rate of nitrification in the soil and the controlled availability of nitrogen fertilizers.

3.4 Nitrogen isotopes

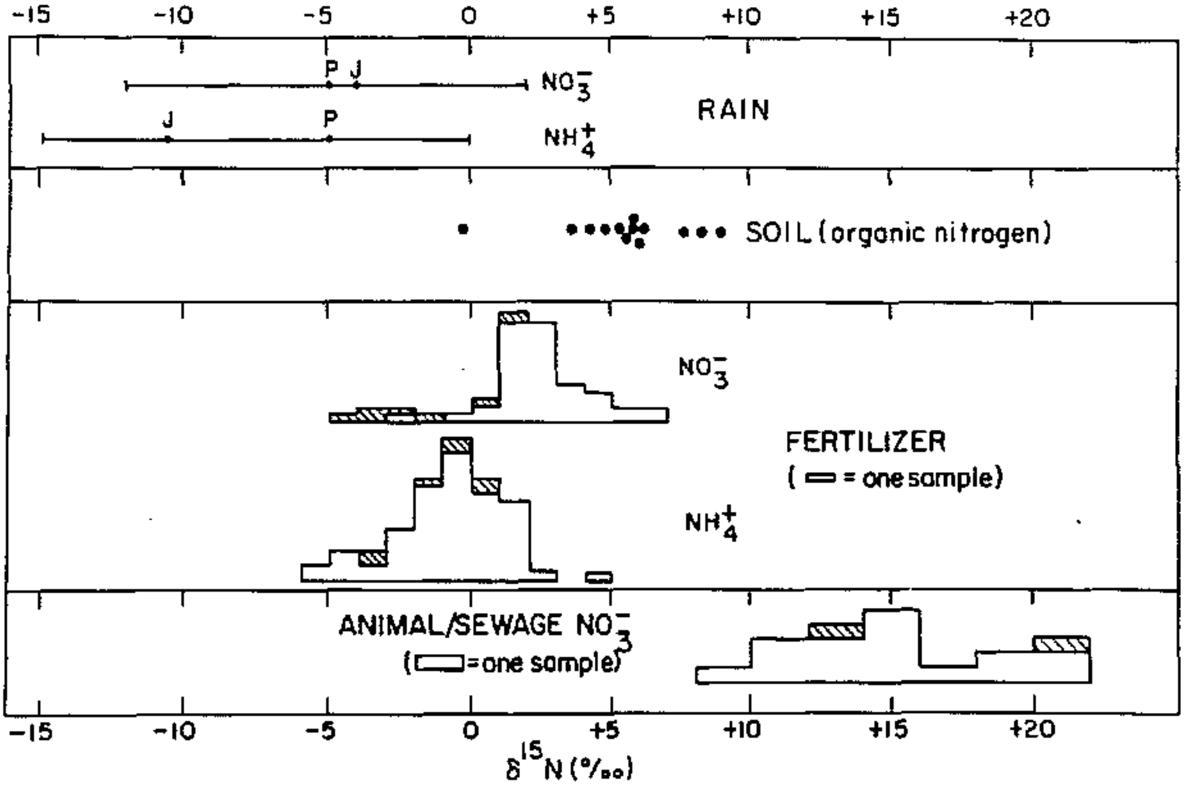
Nitrogen has two naturally occurring isotopes, one with atomic mass of 14 (^{14}N) and the other with atomic mass of 15 (^{15}N). Most of the nitrogen occurs as ^{14}N and only 0,38 per cent of the nitrogen consists of ^{15}N (Moeller, 1961). The seven per cent difference in the atomic masses of the two isotopes leads to isotopic fractionation in natural systems. Thus, the isotopic ratio of a nitrogen compound is the result of (Kreitler, 1975):

- physical fractionation;
- chemical equilibrium fractionation;
- chemical kinetic fractionation, and
- the isotopic ratio of the source material.

Once the constants of isotopic fractionation are known, the natural systems can be studied by the analysis of isotopes. Kreitler (1975) in his study to identify the source of nitrate in southern Runnels county, Texas, was startled to conclude that in that particular case, the estimated contribution of nitrate from soil nitrogen is 1000 times greater than the nitrate contribution of animal wastes. It is concluded that the oxidation of soil humus by cultivation can be a major source of nitrate in groundwater.

In Southern Africa, Heaton (1984; 1985; 1986), Vogel *et al.* (1981) and Heaton *et al.* (1983) made a considerable contribution to the understanding of nitrate accumulation in the environment. Heaton's results are summarised in the two figures below where it is also compared with overseas data (see Fig. 6 and Fig. 7). A set of similar results was provided by Philipot *et al.* (1983). From these figures, the extent to which nitrate sources, i.e. from fertilizers, natural soil nitrification or animal/sewage waste can be distinguished, can clearly be seen.

The application of these principles for identifying sources for each of the study areas provide excellent examples of the success of this isotopic technique. Finally, it is noteworthy that these techniques are applicable under various climatic conditions even though the general level of nitrate concentrations in the hot arid zones are considerably higher than in the more humid, cooler zones such as France (see Fig. 7).



NOTES:

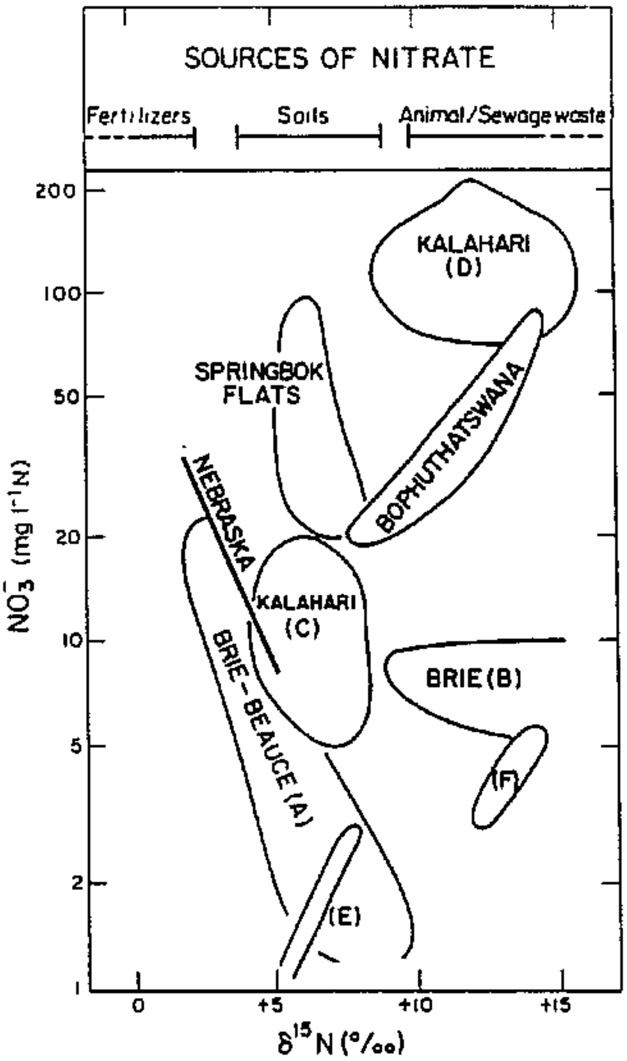
Rain: Bars show the range for 90 per cent of the samples, and points *J* and *P* the modal values, of rain collected at Jülich (F.R.G.) and Pretoria (S.A.), respectively (Freyer, 1978; Heaton & Collett, 1985; Fig. 6).

Soil: Points show means for $\delta^{15}N$ of total N in soils reported in 13 studies (Cheng *et al.*, 1964; Bremner *et al.*, 1966; Delwiche & Steyn, 1970; Bremner & Tabatabai, 1973; Wada *et al.*, 1975; Black & Waring, 1977; Riga *et al.*, 1977; Freyer, 1978; Shearer *et al.*, 1978; Gormly & Spalding, 1979; Karamanos *et al.*, 1981; Mariotti, 1984; Heaton, 1985). The data cover seven countries and are based on ~350 separate soils or soil profiles, but exclude soils from forests and the uppermost organic-rich horizons of profiles.

Fertilizer: Histogram summaries for samples from the U.S.A. (Edwards, 1973; Shearer *et al.*, 1974; Kreitler, 1979); F.R.G. (Freyer & Aly, 1974); Australia (Black & Waring, 1977); France (Mariotti & Létolle, 1977); and South Africa (*hatched* samples, Table I).

Animal waste: Histogram summary for nitrate extracted from manure, barnyard soils and soils contaminated by sewage (Shearer *et al.*, 1974; Kreitler, 1975, 1979; Gormly & Spalding, 1979; Lindau & Spalding, 1984), with *hatched* samples for Pretoria barnyards.

FIGURE 6: Summary of the range of $\delta^{15}N$-values for the major potential sources of nitrogen in ground- and surface water (Reprinted from Heaton, 1986, Fig. 2, p. 91; references are from Heaton, 1986)



NOTES:
France: A = main section of Brie-Beauce aquifer, B = portion of Brie aquifer recharged by polluted Yerres river (Mariotti, 1984)
USA: Linear regression through data from Nebraska (Gormly & Spalding, 1979)
Southern Africa: C = artesian palaeowater from western Kalahari (prior to denitrification; Heaton *et al.*, 1983), D = 'high-nitrate' phreatic water from western Kalahari (Heaton, 1984), the Springbok Flats (Heaton, 1985), Bophuthatswana (four rural boreholes, own unpublished data, 1982), and Pretoria (E = uncontaminated, F = faecally contaminated boreholes, Table II). The sources of nitrate are indicated at the top of the figure

FIGURE 7: General distribution of isotopic composition and concentration (logarithmic scale) of nitrate in groundwater from a number of studies (reprinted from Heaton, 1986, Fig. 5, p. 94; references are from Heaton, 1986)

4. NITRATE IN GROUNDWATER : SITUATION ASSESSMENT

4.1 Information from abroad on nitrate in groundwater

In most European countries, at least 98 to 99 per cent of the water supplies comply with the 1970 World Health Organization European recommended limit of 11,3 mg/L of NO_3-N (WHO, 1985). Hungary is the only exception where about 7 per cent of the total publicly supplied water contains nitrate around or above the Hungarian guideline level of 9,0 mg/L. In 1980 the EEC Directive on quality of water for human consumption, however, set a stricter 'guide level' of 5,6 mg/L and a 'maximum admissible concentration' of 11,3 mg/L. In 1984 the WHO 'guideline value' for drinking water quality was set to 10 mg/L (WHO, 1985).

The WHO studied the occurrence of nitrate in water and came to the conclusion that nitrate concentrations in surface waters have increased 'substantially' over the last 30 to 40 years (WHO, 1985). Almost all countries studied (largely Western Europe and United Kingdom) showed a more marked increase in the levels of nitrates in groundwater, especially during the decade from 1970 to 1980. Furthermore, it is expected that the rising trend in groundwater nitrate is likely to continue for several decades, even if nitrate leaching from soils is reduced by changes in agricultural practices.

Despite these 'general' observations by the WHO, Young (1985) points out that few reliable long-term records of nitrate concentrations from groundwater supply sources are available in Britain. Medium term (15 years plus) time series from 75 sites revealed that 65 per cent of these had an increasing trend, while a further 30 per cent showed apparently stable levels, but subject to significant fluctuations (Young, 1985).

Well-documented information on the increase in nitrate in groundwater comes from Denmark (see Fig. 8). Although the 'average concentration' amounted only to 3 mg/L (as N) in 1980 it represented a three-fold increase on the 1950 value (Schroder, *et al.*, 1985). The reason for these increases in groundwater nitrate is explained by the vast increases in fertilizer and other inputs as shown in Table 5.

As shown in the table, the nitrogen inputs more than doubled while the outputs in terms of products increased by only 60 per cent leaving a considerably larger surplus. This is seen as a typical example of the situation in most developed countries. Approximately half this surplus is lost to the atmosphere, either by ammonia volatilisation, denitrification or the burning of straw. Most of the other half is lost by leaching while only a small portion is lost as surface runoff.

In the Netherlands, 70 per cent of the water supply is derived from groundwater. First Van Duyvenboden and Loch (1983) and then Van Beek (1985) expressed concern about rising nitrate levels in the country and the ability of waterworks to comply with the drinking water limit of 11,3 mg/L for nitrate adopted in 1984. Peters & Boukes (1987) constructed a mathematical model to predict future nitrate trends. According to their model nitrate concentrations in the study area will only level off 25 years after the introduction of control measures.

TABLE 5: Nitrogen mass-balances for Danish agriculture in 1950 and 1980 (from: Schroder, *et al.*, 1985)

YEAR	1950	1980
	kg N per ha	
INPUT		
Fertilizers	20	130
Imported animal feedstuffs	17	62
Biological N_2-fixation	60	10
Precipitation	5	15
Total input	102	217
OUTPUT (Products)		
Vegetable products	12	10
Animal products	7	20
Total output (products)	19	30
Nitrogen lost to the environment	83	187

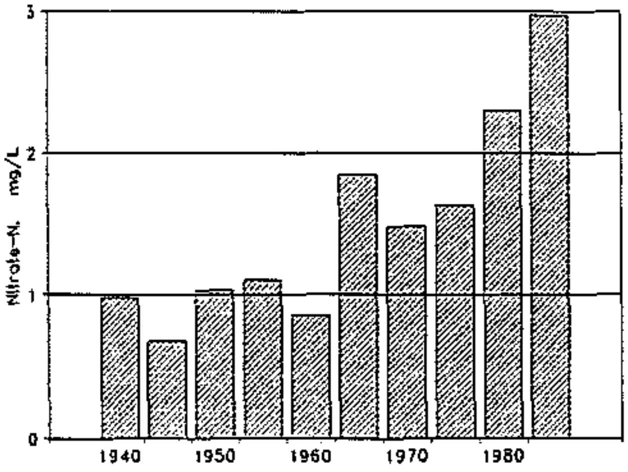


Figure 8 The average concentration of nitrate in Danish groundwater versus time, based on 11 000 samples from depths of more than 10 m (Schroder, *et al.*, 1985)

Jacks & Sharma (1983) found nitrate concentrations in excess of 300 mg/L (as N) in village wells in Southern India. In the irrigation area, the levels were lower but the median nitrate content in groundwater still approached 11 mg/L (as N).

In Australia, the occurrence of nitrate-rich groundwater is widespread in a variety of geological situations, but usually have characteristics of an unsaturated zone of high hydraulic conductivity and heterogeneity. The waters are invariably shallow, and may be stratified with respect to the nitrate component. Biological fixation in the soil is considered to be the principal origin, but point sources such as sewage effluent, animal and industrial waste are locally important (Lawrence, 1983).

In the United States of America significant deposits of nitrate ("nitre spots") are found in the soils or geological formations in many of the western states. These natural accumulations of nitrate salts result from nitrification in these soils and represent another possible increase in stored soil nitrogen (NAS, 1972).

4.2 Nitrate in groundwater in South Africa

The hydrochemical data contained in the national groundwater database maintained by the Department of Water Affairs & Forestry (DWA&F) was made available for this investigation. This data was obtained from all the groundwater investigations the DWA&F had carried out over the past 20 years. The data largely refers to boreholes drilled by the DWA&F and private borehole data is only included where this formed part of an investigation. At this stage the database, therefore, provides only partial coverage of the existing boreholes in the country. Nevertheless, a total of 18 827 complete analyses comprising all the major cations and anions were available. The median nitrate concentration for these analyses was found to be 4,5 mg/L. Forty five per cent of the sources exceeded 5 mg/L, 27 per cent 10 mg/L and 15 per cent 20 mg/L. Due to the investigations in the Springbok Flats and the northern Cape Province, where extensive occurrences of elevated nitrate concentrations are found, a slight bias could have been introduced because of the inclusion of virtually all boreholes in those areas. The large number of sources (814, that is 4,3 per cent of the total) having nitrate concentrations in excess of 50 mg/L is thus not necessarily representative of the country as a whole.

The geographical distribution of the 18 827 sampling points is shown on the map in Figure 9. The sampling points provided reasonable coverage of most of the country except for the eastern and south-eastern areas where sample numbers were very low (less than 10 samples per square degree) (see Fig. 9). On average there were 150 data points in each square degree.

In Figure 10 the areal nitrate distribution is summarised for each square degree. In each square degree the number of sampling points, the median nitrate concentration and the 90th percentile nitrate values are shown. The inner and outer rectangles in certain square degrees highlight those in which the median value exceeds 10 mg/L and the ninetieth percentile exceeds 50 mg/L respectively. This clearly depicts the areas in the northern Cape Province (Kalahari, Prieska and Vryburg) and the northern Transvaal (Springbok Flats) where elevated nitrate concentrations occur. These occurrences are discussed in more detail below. The population affected by these high nitrate occurrences is essentially the farming community and people living in rural settlements and towns supplied by groundwater in the indicated areas.

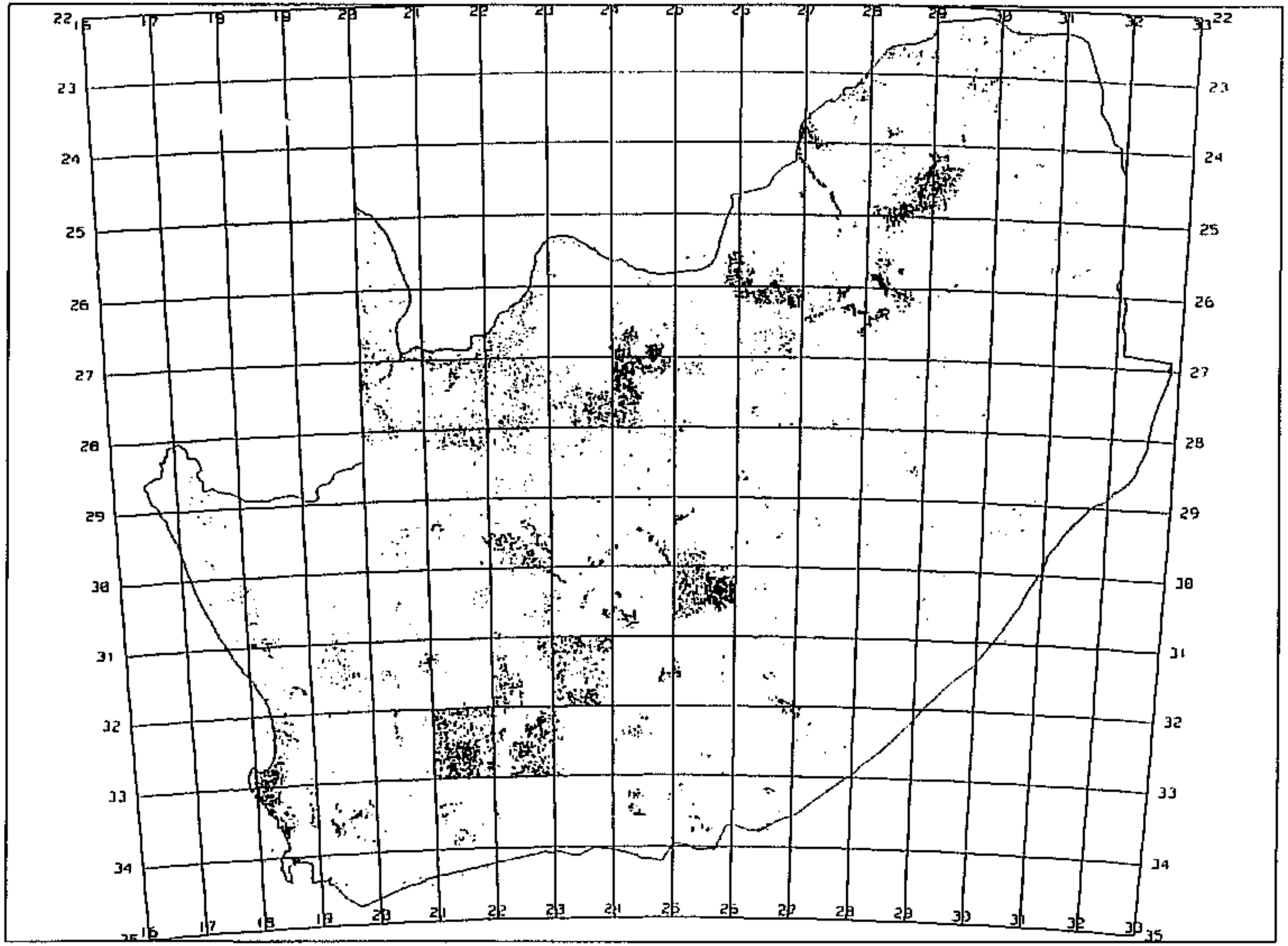


FIGURE 9: Geographical distribution of sampling points included in the hydrochemical database

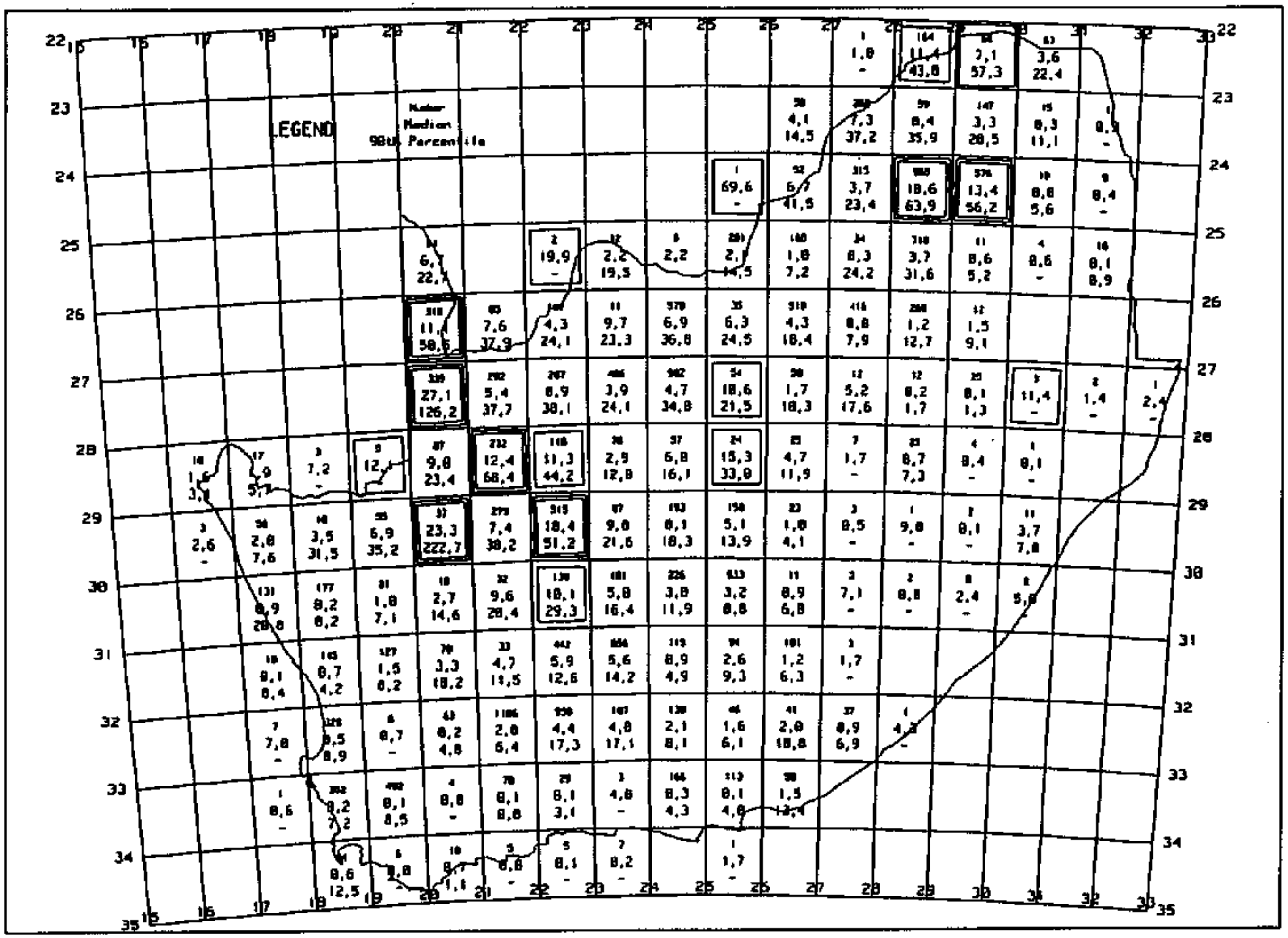


FIGURE 10: Statistical summary of nitrate occurrences in groundwater for each square degree, showing: number of data points, median and 90th percentile concentration value in mg/L (as N). The inner and outer rectangles in certain square degrees highlight those in which the median value exceeds 10 mg/L and the ninetieth percentile exceeds 50 mg/L respectively

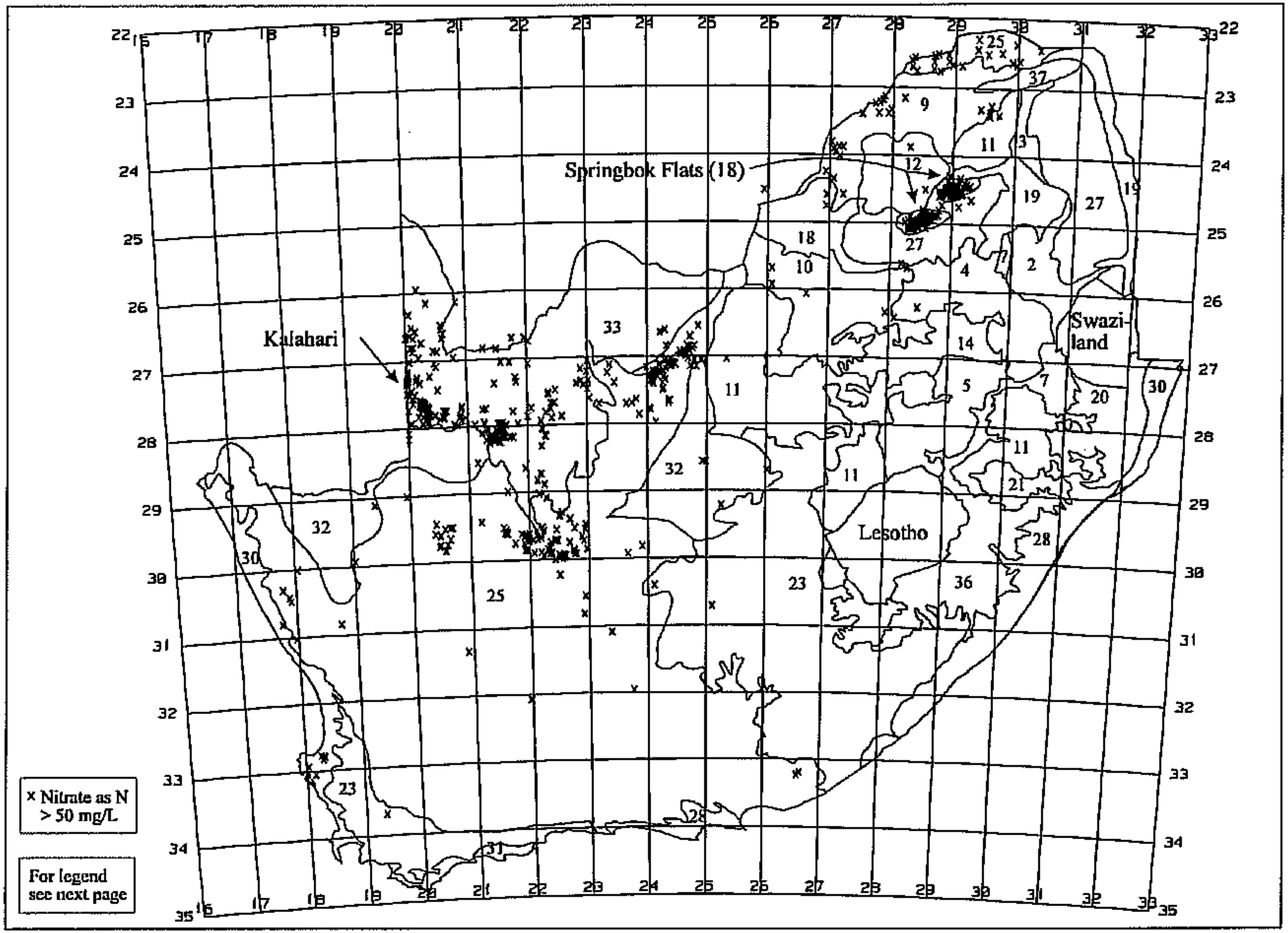


FIGURE 11: Nitrate concentrations in groundwater exceeding 50 mg/L (as N) plotted on a simplified soil type map of South Africa

Legend of soil types as illustrated in Figure 11

LATOSOLS (Freely drained)

2	Non-humic red and yellow with varying amounts of rock and lithosols
3	Non-humic red with varying amounts of rock and lithosols

RED-YELLOW-GREY LATOSOL PLINTIC CATENA

4	Acid, sands/loams, red dominant
5	Acid, sands/loams, yellow-grey dominant
7	Acid, clays, red dominant
9	Neutral, sands/loams, red dominant
10	Neutral, sands/loams, red dominant with much rocky land
11	Neutral, sands/loams, yellow-grey dominant
12	Neutral, sands/loams, yellow-grey dominant with much rocky land

BLACK MONTMORILLONITIC CLAYS, RED CLAYS, SOLONETZIC SOILS

14	Black clays
15	Black clays with much rocky land
18	Black and red clays
19	Black and red clays with much rocky land
20	Black and red clays and solonetzic soils
21	Black clays and solonetzic soils
23	Solonetzic soils

WEAKLY DEVELOPED SOILS ON ROCK

25	With lime in upland and bottomland sites with much rocky land
27	Lime common in bottomland sites, but absent in upland sites
28	Lime rare or absent

SANDS

30	Littoral and near-littoral (most commonly grey)
31	Littoral and near-littoral (most commonly grey) with lithosols
32	Continental red or brown non-shifting with varying amounts of rock and lithosols
33	Continental red or brown shifting sands

SWAMPS AND ALLUVIAL PLAINS

36	Undifferentiated

ROCK AND LITHOSOLS

37	Undifferentiated

Kalahari

In the northern Cape Province (Kalahari) elevated nitrate concentrations exceeding 50 mg/L occur over a wide area extending over more than three hundred kilometres (see Fig. 11). In fact, this area with high nitrate in groundwater also extends several hundred kilometres into Namibia where the nitrate concentration even exceeds 200 mg/L (Tredoux & Kirchner, 1985). The area is covered by Cenozoic sediments of the Kalahari Group and is characterised by red or brown sand dunes with occasional flood basins (pans) consisting of clayey deposits. The soil type in this area is described as continental red or brown shifting sand (soil classification no. 33, see Fig. 11). The vegetation in this area is described as the typical Kalahari Thornveld (Acocks, 1988, p 45). It is described as an extremely open savanna of *Acacia erioloba* and *A. haematoxylon*, except along rivers and near ranges of hills and mountains, where besides greater quantities of these two species, other species also are important. The grasses are tufted and entirely of the 'white' type, mostly *Aristida* spp. and *Eragrostis* spp. with the silvery *Stipagrostis uniplumus* conspicuous (Acocks, 1988, p. 46). The area is utilised as uncultivated natural pasture devoted to small stock farming (mostly Karakul sheep). The water table is well below surface (often 50 m or more) and due to the variability of rainfall stock carrying capacities are low.

Based on the minimal anthropogenic activity in this area the occurrence of nitrate is considered to be a natural phenomenon and pollution could at most be of significance at isolated boreholes near settlements or livestock enclosures.

As mentioned above, the Kalahari is characterised by pans. Verhagen (1990) studied the nature and genesis of pans and presented an ecological mechanism related to the presence of large herds of hoofed animals. This apparently also links with the presence of high nitrate concentrations in the subsurface (both in the sediments and in the pore fluids) which tend to increase towards the surface. Verhagen (1990) also refers to the Mogatse pan in Botswana where a high nitrate content is found in its subsurface. Although the game population in this area is low at present these nitrates are linked historically to the gathering of herds of animals.

During the late fifties and early sixties the Geological Survey of South Africa collected brines from 102 salt pans in the country (GSO, 1976, p. 395). The partial analyses of these brines are summarised by Hugo (1974). Unfortunately, nitrate results are not reported consistently and in most cases it is impossible to establish whether nitrate was not found or whether the brines were not analysed for nitrate. Nevertheless, the available information on the distribution of nitrate in brines from salt pans is shown in Figure 12. In general the nitrate concentration is relatively low and only in exceptional cases does the nitrate in the brines exceed 100 parts per million. Pans in the Kalahari and in the vicinity of Prieska (also see next section) exceed this value.

Heaton (1984) in his study of the phreatic groundwater in the western Kalahari, came to the conclusion that approximately 4 milliequivalents of nitrate per litre (~ 56 mg/L) could be due to natural accumulation derived from soil nitrogen. Based on Verhagen's proposed ecological mechanism linking the genesis of pans to large

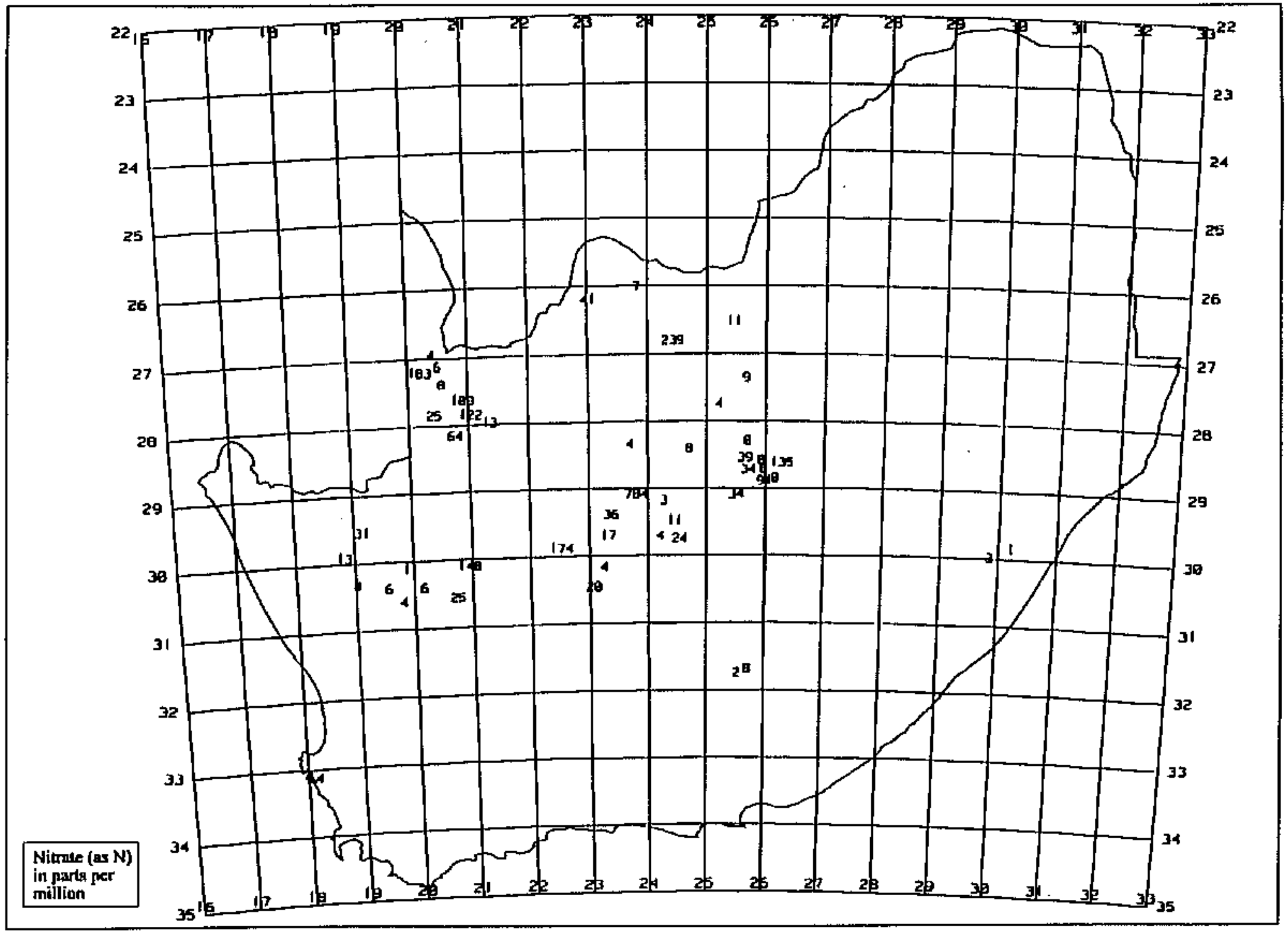


FIGURE 12: Occurrence of nitrate in brines from salt pans in South Africa (Data from Hugo, 1974)

herds it is conceivable that even nitrate levels higher than 56 mg/L could be due to 'natural' accumulation from herds of game and not to domestic livestock.

Prieska

In the vicinity of Prieska, an area between latitudes 29° and 30° S and longitudes 22° and 23° E display elevated nitrate concentrations in groundwater (see Fig. 11). This coincides with the area where investigations were carried out towards the end of the nineteenth century with a view to commercially exploit certain nitrate deposits (Frood & Hall, 1919). These nitrate occurrences extend from the farm Doornbergfontein, some 32 km south-east of Prieska, along the Doorn Mountains, in a general northerly to north-easterly direction through Prieska, across the Orange River and along the Asbestos Mountains towards Griqua Town. They occur in the banded ferruginous slates and jaspers belonging to the Asbestos Hills Formation of the Griquatown Group, Transvaal System. This formation is weathered in such a way that the countryside is characterized by many valleys, kloofs and gulleys. Cliffs and stony ledges is a characteristic feature of the Banded Ironstone Stage. Mostly, the nitrate deposits occur along the lower two to four metres of the base of the cliffs (Hall in: Frood & Hall, 1919).

Despite the detailed description of the nitrate occurrences themselves, no mention is made of nitrate occurrences in groundwater. It seems highly plausible that the abundance of nitrate would also lead to significant amounts of nitrate leaching into the groundwater in this area.

Vryburg (Ghaap Plateau)

In the area between latitude 26°45' and 28° S and between longitude 23°30' and 25° E elevated nitrate concentrations occur in groundwater. Mostly these exceed 20 mg/L but some exceed 50 mg/L. Most of these are situated on the dolomites of the Ghaap Plateau (Campbell Group, Transvaal System). It is considered possible that in part these occurrences could be due to natural accumulation, but anthropogenic activities is expected to contribute due to the nature of the terrain.

Springbok Flats

In the case of the Springbok Flats, northern Transvaal, the two areas with high nitrate concentrations are clearly delineated (see Fig. 11). This coincides with the distribution of Jurassic basalt rocks of the Letaba Formation which forms part of the Karoo Sequence in the area. A vertisol, locally known as the 'black turfs of the Springbok Flats' was formed on top of the basalt (no. 18 on soil classification, see Fig. 11). Verhoef (1973) completed the first extensive investigation of water quality in this area and found that the higher nitrate values were largely confined to the areas with black turf soil. Grobler (1976) determined the nitrogen content of the soil and came to the conclusion that the C:N ratio of the soil was low enough to ensure that nitrogen was freely available for autotrophic nitrifying bacteria. Ploughing of the soil caused mobilisation and leaching of nitrate followed by accumulation in the subsurface beyond the root zone. Heaton (1985) confirmed by means of a combined isotopic ($^{15}N/^{14}N$) and chemical study that increased cultivation was the only important process leading to the accumulation of nitrate. Kinzelbach *et al.* (1992) came to a similar conclusion when modelling the regional nitrate transport at Bruchsal-Karlsdorf in the upper Rhine valley. They concluded that present day inputs of nitrogen from agriculture were insufficient to interpret the nitrate concentration increases observed. The transformation of pasture to arable land during the preceding two decades was identified as another cause of these groundwater nitrate increases.

Acocks (1988) describes the 'Black Turfveld' as an open thornveld which in low-lying zones becomes practically grassveld. The principal trees are *Acacia karoo*, *A. nilotica* subsp. *kraussiana* and *Ziziphus mucronata*, scattered in a dense, tall, coarsely-tufted grassveld. Thus, as in the case of the Kalahari, nitrogen fixing *Acacia* species are freely available (Heaton, 1984).

North-western Orange Free State

Agricultural research carried out in the dry-land maize growing areas of the north-western Orange Free State lead to the discovery of nitrate in groundwater at a concentration near to or even exceeding the drinking water limit of 10 mg/L (Henning & Stoffberg, 1990). This area has relatively permeable sandy soils and the water level is generally less than 10 m below surface. Nitrate occurrence was considered to be a direct result of fertilizer application. Further confirmation of the agricultural nitrate contamination was provided during a study of pollution in the Orange Free State gold fields (Cogho, 1991).

Although it has been mentioned by several researchers that nitrate levels in groundwater was increasing due to agricultural activities, particularly fertilizer usage, published data is largely lacking. Considering the twenty-fold increase in fertilizer usage in South Africa from 1955 to 1981 (see Fig. 14) a severe impact on groundwater is to be expected. The decrease in fertilizer usage since 1981 is solely the result of cost increases leading to more effective fertilizer application.

Crocodile River

In the evaluation of the information contained in the national groundwater data base, it was noted that nitrate concentrations exceeding 20 mg/L were quite common in boreholes within the irrigated areas extending over 80 km along the Crocodile River in north-western Transvaal. Inspection showed the electrical conductivities of water from these boreholes also to be high (> 100 mS/m and in places even > 250 mS/m) which implies irrigation percolate as the source.

Point sources

Isolated occurrences of high nitrate concentrations (30 to 50 mg/L and higher) are observed in rural areas. These are considered to be due mainly to the effect of point sources such as livestock enclosures near unprotected boreholes, septic tank soakaways and feedlots. Heaton (1984) quoting a study conducted by Adam (1982) stated that it was found that when a borehole contained water with a very high level of nitrate (e.g. > 56 mg/L) it was generally sited close to a livestock enclosure. It was concluded that this suggested that these high levels of nitrate may represent pollution from animal waste. Heaton (1984) then proved by means of a nitrogen isotope study that in the western Kalahari the sporadic occurrence of very high levels of groundwater nitrate (> 56 mg/L) which had $\delta^{15}N$ values in the range 9,3 to 18,7 ‰, reflected pollution derived from animal waste.

Trends

Two attempts were made to identify trends in nitrate concentrations in the Springbok Flats. Van der Merwe & Levin (1990) compared the nitrate values of a set of boreholes sampled during the period 1968 to 1976 and again in 1985. No significant difference was found.

Orpen & Fayazi (1991) resampled 17 boreholes in 1991 which were originally sampled in 1982/83. No trends could be identified as some boreholes had increased and other decreased nitrate concentrations. Some of these boreholes had already been sampled in 1972 for the first time but also in these cases no definite trends could be identified over the period of nearly 20 years.

5. SUBSURFACE NITRATE ACCUMULATION

In discussing the mineral deposits in South Africa, Coetzee (1976) stated that climatic conditions in the country are not conducive to the formation of nitrate deposits and none had been discovered which was economically workable. It was stated that such deposits are only found in very arid localities because nitrates are very soluble in water. This identifies two of the factors of importance in the subsurface accumulation of nitrate, the climate and the easy leachability of nitrates. Coetzee (1976) also discussed the nitrate deposits between Prieska and Griquatown (see also par. 4.2) but gave no indication of a possible origin. In the case of the potassium nitrate which had been extracted from a cave on the farm Abjaterskop (107 KP), Marico District, and which formed a fairly high-grade crust on the floor of the cave, it was speculated that it originated through the oxidation of ammonia derived from bat guano.

In the subsequent paragraphs the natural factors responsible for the generation and accumulation of nitrate are discussed, also considering the role of geological formations in these processes. Anthropogenic activities and practises play a definite role in causing and aggravating subsurface nitrate accumulation and these are dealt with in Chapter 6.

5.1 Geological controls

South African geology extends over the whole of the geological time scale from the Archaean Complex (para- and granitic gneisses, granites) through to the Quaternary. Karoo sediments occur extensively and occupy approximately 40 per cent of the country. In total hard-rock formations ranging from the earliest Pre-Cambrian to Jurassic in age are present at or close to the surface over 90 per cent of the country's area.

Geological formations as such are not considered as the primary origin of nitrates. This has been confirmed in the South African context. In the case of the Springbok Flats, Verhoef (1973) discounted a basaltic origin for the nitrate on the basis that basalts usually contain very little nitrogen. Heaton (1985) agreed with this viewpoint but added that a 'geologic' origin of any type can be excluded in view of the groundwater chemistry. He argued that nitrate-rich horizons may occur in rock formations, but in all such cases the nitrate is accompanied by higher concentrations of other soluble anions (e.g. SO_4^{2-} and Cl^-). The chemistry of the groundwater in the Springbok Flats showed that an increase in nitrate is accompanied by very little increase in the other anions. A geological origin has, therefore, to be discounted in this case.

In a study in neighbouring Namibia it was attempted to identify the influence of the geological formations on the chemical quality of the groundwater (Tredoux & Kirchner, 1985). Several areas underlain by different rock types were studied.

Table 6 shows the nitrate distribution for 927 water samples derived from nine different formations north-west of the village of Outjo in northern Namibia. Here the nitrate distributions in the groundwater from the various rocks differ significantly. It is noteworthy that some of the older (even igneous) units showed higher nitrate concentrations. Similarly, Marrett *et al.* (1990) have found up to 73 mg/kg of water-extractable nitrate in volcanic rocks in the eastern Mojave Desert (USA). As the rocks themselves do not contain nitrate, the observed phenomena must be ascribed to secondary factors. These include the nature of the weathering products, or the presence, type and density of vegetation. It is, therefore, recognised that the characteristics of geological formations could favour the accumulation of nitrates and in this way exercise a 'secondary' control on the nitrate concentration in groundwater.

From a geohydrological perspective and particularly with respect to the accumulation of nitrate in groundwater, permeable formations such as dolomites (northern Cape Province and Transvaal), coarse sandstones and unconsolidated deposits (e.g. Kalahari sands) are important. Areally, much of the Tertiary and Quaternary successions in the Kalahari and along the west coast lie above the water-table. Such formations, however, provide the opportunity for rapid infiltration of rainfall and, therefore, the accumulation of nitrate in groundwater, provided the conditions for the formation and leaching of nitrate (as discussed below) are also met.

5.2 Natural accumulation

A number of site-related factors control nitrate generation in the soil, leaching to the subsurface and accumulation in groundwater. Under natural conditions nitrate generation is primarily dependent on the availability of organic nitrogen in the soil. This nitrogen pool is maintained through nitrogen fixation by specific plant species (e.g. the *Acacia* spp.) and the accompanying microflora in the soil. At the same time uptake of nutrients by plants as well as natural denitrification serves to balance nitrate generation. Vegetation is, therefore, a prerequisite in the whole sequence.

Plant growth is dependent on a number of factors of which climatic conditions and particularly rainfall (quantity and distribution) is of overriding importance. In a high rainfall area, the natural vegetation cover is dense and interception by the root systems of the plants of nitrate generated in the soil is virtually complete. Under similar conditions in more arid regions, the interception of soil nitrate is not necessarily complete, mainly because the plant cover is more sparse. Furthermore, the high variability of rainfall leads to a periodic die-off of plants and thus a varying the summer rainfall areas leaching of nitrate can, therefore, be expected to be at its highest at the start of the rainy season.

In studying the Chilean nitrate deposits, Mueller (1960) came to the conclusion that the primary nitrate generating mechanisms are present in all arid areas and that the average availability of nitrate in the area as a whole is no higher than in other areas. Secondary factors are responsible for the concentration of nitrates. In this case, salts are leached from the soil and collect as evaporites in salt pans. As the pans dry out, the remaining solution (consisting mainly of nitrates due to their solubility) migrates by 'capillary migration' to adjacent areas where the nitrates finally crystallize out.

TABLE 6

Nitrate distribution in the groundwater from various geological formations in the Outjo District (Tredoux & Kirchner, 1985)

ERA	LITHOSTRATIGRAPHIC UNITS*		LITHOLOGY	NO_3-N (mg/L) for the cumulative frequencies			NO. OF SOURCES
				25 %	50 %	75 %	
Tertiary to quaternary			Alluvium, sand, gravel, calcrete	0,7	2,3	7,1	73
Namibian 650 - 920 Ma	Damara Sequence	Mulden Group	Conglomerate, quartzite, schist	2,1	3,6	5,8	21
		Kuiseb Formation	Metagreywacke, metapellite, quartzite	0,6	1,5	5,2	54
		Karibib Formation	Dolomite, limestone	0,7	3,3	6,8	46
		Tsumeb Subgroup	Dolomite, limestone, shale, chert	0,8	4,3	6,9	44
		Ugab Subgroup	Schist, pellite, greywacke, dolomite, quartzite	2,8	7,2	16,7	43
Mokolian 1160 - 1960 Ma		Fransfontein Suite	Granite, granodiorite	1,6	9,2	13,6	61
		Khoabendus Group	Rocks of magmatic, volcanic and sedimentary origin	0,8	5,5	13,3	16
		Huab Formation	Paragneiss	4,6	13,0	24,8	569

*NOTE: Only relevant units of stratigraphic sequences indicated

In the Chilean example, the drainage systems end in salt pans. In the Kalahari and the Springbok Flats, similar situations occur. Both these cases are associated with areas with poor surface drainage systems. However, there is an important difference. Whereas the generation of nitrate both in Chile and the Kalahari takes place in an area with a rainfall of some 200 to 250 mm/a the Chilean nitrates are subsequently washed down into salt pans situated in the coastal plain in the desert where the rainfall is 10 mm/a or less. There secondary concentration processes lead to the nitrate enriched surface deposits (Mueller, 1968). In the Kalahari occasional flood plains (pans) exist between the sand dunes but these are not linked to any active river drainage system. Rainwater enriched in nitrate thus seeps into the underground leading to the observed subsurface nitrate accumulation. Similarly, the Nyl River in the Springbok Flats ends without reaching any major river. It is therefore postulated that the absence of active drainage systems favours accumulation of nitrate in the area as it limits the export of solutes. Conversely, active drainage systems allowing efficient transport of run-off and interflow, should promote the export of nitrate and other salts, thus preventing accumulation.

Tredoux & Kirchner (1985) postulated the need for a soil cover of sufficient thickness and permeability to allow rapid percolation and adequate storage of rainfall. This is considered to be part of the hydrodynamic requirements for nitrate accumulation discussed above.

As explained in section 5.1 it would seem that in general nitrate occurrences cannot be related to a geological formation as being the primary origin. However, occurrences of elevated nitrate concentrations over vast areas sometimes closely follow the areal distribution of a geological formation and/or the resultant soil overburden. It follows that although the geological formation itself does not serve as the primary source of nitrate, certain of its characteristics and/or those of the soil overburden enhances the generation and accumulation of nitrate.

The environmental conditions under which natural leaching of nitrate from the soil zone and accumulation in groundwater have been observed are summarised below:

- *Vegetation:* Maintenance of the nitrogen pool in the soil through nitrogen fixation by specific plant species and the accompanying microflora in the soil. Without the proper nitrogen fixing vegetation soil organic nitrogen will be insufficient to allow any substantial nitrate accumulation.

- *Rainfall:* The climate and particularly the quantity and distribution of rainfall is a critical factor both from the vegetation as the recharge and leaching perspective. It must be:
    - adequate to support the required vegetation type(s);
    - relatively low (possibly ~200 - 250 mm/a) to cause semi-arid conditions limiting total plant cover;
    - highly variable causing periodic die-off of plants and thus a varying plant cover;

  - consisting, at least at times, of storm events large enough to ensure relatively rapid natural recharge and leaching of nitrate.

- *Temperature:* sufficiently high to ensure microbiological nitrification (oxidation).

- *Soil:*
  - low C:N ratio for mineralisation;
  - low clay content;
  - soil cover of sufficient thickness and permeability to allow rapid percolation and adequate storage of rainfall; alternatively a geological formation with such characteristics is needed;

- *Hydrology:* absence of active open drainage systems (i.e. rivers ending in pans). Otherwise export of solutes such as nitrate (which is highly soluble) will take place as in Chile.

Wherever accumulation occurs a combination of most of these factors have been identified. This phenomenon has lead to extensive areas in South Africa and adjacent territories naturally having elevated nitrate concentrations in groundwater. Natural nitrate accumulations are also known from Chile, Australia and the USA. Obviously these factors would also enhance accumulation of anthropogenically induced nitrate generation.

6. MAJOR CONTRIBUTORS TO ANTHROPOGENICALLY INDUCED NITRATE ACCUMULATION

The assessment of groundwater quality in South Africa indicates a variety of reasons for the occurrence of high nitrate concentrations in groundwater. This covers the whole spectrum from natural nitrate accumulation to agricultural activities, feedlots, sludge application to land and industrial pollution. In this chapter nitrate accumulation due to anthropogenic activities will be discussed based on the available information.

Accumulation of nitrate in the subsoil takes place when the rate of leaching exceeds the rate of denitrification. In agricultural areas leaching generally increases with increased fertilizer application (Vrba *et al.*, 1985). Leaching is, however, affected by the hydrodynamic and hydrochemical characteristics of the aquifer, the landscape ecology, the manner of fertilizing (amount and type, dosage and pattern/timing of application) and other factors. Vrba *et al.* (1985) consider the following to be of special importance: aquifer transmissivity, redox conditions, thickness of the unsaturated zone and the cyclic character of natural processes.

Juergens-Gschwind (1989) studied the effect of land use patterns on the occurrence of nitrate in groundwater. He concluded that leaching of nitrate is a basic phenomenon. Nitrate is the end product of the natural mineralisation of the soil's vast organic N-pool. Natural or anthropogenic factors, especially land-use patterns, affect this process. He concluded that the presence and type of crop determine the duration and density of soil cover and thus have a dominant influence on the N-cycle. Leaching of nitrate increases from woodland to grassland to arable land to horticultural land. This is largely a function of the presence and type of root systems capable of intercepting the leaching nitrate. Whereas woodland has an extensive root system extending from shallow to deeper zones, grassland has an active shallow root system. Bare land, having no root system, causes the highest losses by percolation, releasing up to two times more nitrate than cropland and up to nine times more than grassland. Deforestation thus also causes nitrate leaching to groundwater. Faillat and Rambaud (1991) linked the occurrence of nitrate in deep fractured rock aquifers in rural parts of the Ivory Coast to the effect of deforestation. These conclusions are confirmed by the local observations. The studies in the Springbok Flats proved that ploughing of the land caused mineralisation of the organic nitrogen and leaching of nitrate to the groundwater (Heaton, 1985) (see also the section on the Springbok Flats in par. 4.2). Nitrification is enhanced due to the low organic carbon to nitrogen ratio of South African soils. Fertilizer application to land aggravates nitrate generation and leaching to the groundwater. This is indicated by the observations in the northern and north-western Orange Free State (Henning & Stoffberg, 1990; Cogho, 1991).

In the following paragraphs the known nitrogen sources are discussed and the available information is briefly considered in an attempt to identify the major contributors.

6.1 Agriculture

Agricultural farming consists of a variety of activities ranging from extensive dry land grazing to intensive animal feeding units, and from dry land cultivation to large irrigation schemes. The nitrate pollution potential of these activities vary widely. Vast areas of the country are used for dry land grazing and this in itself is expected to have little or no influence on the nitrate accumulation process. Gathering of the livestock in kraals or around feeding or watering points, however, significantly increases the risk of groundwater pollution due to the increased nitrogen loading per unit area and the increased availability of moisture.

Cultivation

The most important arable crops grown in South Africa are listed in Table 7. The area covered by these crops constitute approximately 9 per cent of the total farming area of 82,9 x 10^6 ha. The larger part of the remaining farming area is used for grazing. The area of arable crops grown and the production is directly dependent on the climatic conditions and therefore these numbers vary from year to year. Nevertheless, certain trends can be seen in the figures given in Table 7, considering the production in 1981/82 and that in 1990/91, nine years later. In the case of maize, the area grown has shrunk by approximately one-quarter, while the production remained virtually the same. This indicates a higher production per unit area. In the case of wheat, the area grown shrunk slightly while the production decreased considerably (although the estimated 1991/92 crop is virtually the same as for 1981/82). The area on which oats was grown more than doubled while the production halved. The reason for this change is unknown. Barley, sunflower seeds and soya beans production increased considerably but most of the other crops remained practically the same over the nine year period.

Considering the above information, it is evident that the largest individual impact is due to the growing of maize. Most of the maize is grown under dry land cultivation and to maintain and even increase the production per unit area, fertilization is essential. Tilling of the soil causes oxidation of organic soil nitrogen followed by leaching (Kreitler, 1975). This was also confirmed in the case of the Springbok Flats (Heaton, 1985). In addition, nitrification is enhanced due to the low organic carbon to nitrogen ratio of South African soils, high ambient temperatures and other factors. Vrba *et al.* (1985) concluded that in agricultural areas, leaching generally increases with increased fertilizer application. This is possibly also the reason for the observation of nitrate occurrences in the maize growing areas of the northern and north-western Orange Free State (Henning & Stoffberg, 1990; Cogho, 1991).

In a study of the relative nitrate leaching potential related to land-use Juergens-Gschwind (1989) found a largely consistent pattern based on information from a number of countries (e.g. Germany, France and the USA). The generalised sequence is shown in Table 8. Other factors such as soil types can, however, affect the leaching potential but in general woodland has the lowest potential while maize in has a higher potential than other cereals. The highest leaching potential occurs when a

TABLE 7: Most important arable crops in South Africa: area grown and annual production (data from Fiske, 1992)

Year	1981/82		1990/91	
Arable crop	Area grown 10^3 ha	Production 10^3 tons	Area grown 10^3 ha	Production 10^3 tons
Maize	4 198	8 504	3 026	8 047
Wheat	1 787	2 341	1 701	1 704
Oats	389	82	828	42
Barley	69	106	113	262
Grain sorghum	170	276	115	300
Dry beans	64	73	78	113
Sugar cane	393	19 532	373	18 083
Tobacco	30	34	25	34
Cotton	107	90	127	87
Groundnuts	238	83	86	98
Sunflower seed	307	257	575	585
Soya beans	22	21	87	124
Potatoes	60	996	63	1 383
Pineapples	10	249	13*	161

* Information for 1987/88

change in cultivation occurs, ploughing up of pasture land and when the land is laid bare.

The periodic droughts in South Africa further complicate the situation because during such periods, the soil remains bare and the nitrate (from natural nitrification or applied fertilizer) is not intercepted by plant roots at all. Juergens-Gschwind (1989) concluded that bare land causes the highest losses by percolation with the soil releasing up to two times more nitrate than crop land. Thus, if crops are lost due to drought, the potential leaching of nitrate into the underground after the first significant rainfall event could be considerable.

As direct information on groundwater quality deterioration and nitrate accumulation for South Africa was unavailable, data was obtained on the fertilizer consumption in South Africa in order to evaluate the potential threat to groundwater quality. This data is presented in Figure 13. From the graph it can be seen that fertilizer consumption was very low in 1955 and it only increased at a low rate until 1966. During the fifteen years from 1966 until 1981, when the highest consumption was recorded, fertilizer consumption increased at a high rate but crop production did not increase at the same rate (Van der Merwe, 1991). This would mean that an increased surplus quantity of nitrogen was available in the soil for oxidation to nitrate and

TABLE 8: Land use and leaching of nitrogen from the rhizosphere (Juergens-Gschwind, 1989)

Type of land use	Nitrate leaching
Woodland (except alder) Cut grassland Permanent pasture	Low potential
Cereals with intermediate crop without intermediate crop silage grasses, industrial crops	
Maize, root crops, field vegetables legumes, vines	
Horticultural and smallholdings (allotments)	
Change in cultivation such as ploughing up pasture, deforestation, afforestation	High potential

subsequent leaching. Considering the experience in countries abroad, a considerable quantity of this nitrate could still be present in the unsaturated zone in areas where the groundwater level is deeper below surface. In areas where the water table is shallow (< 10 m below surface) it is expected that the nitrate derived from the nitrogen applied during the previous two decades has already reached the groundwater.

A further important aspect with respect to soil nitrogen inputs is highlighted by Power & Schepers (1989). Fertilizer nitrogen has largely replaced legume nitrogen as the primary source of nitrogen for American agriculture (see Figure 14). According to Power & Schepers (1989) there was a steady increase in fertilizer nitrogen usage from about 1950 to 1980 while there was a corresponding decrease in legume production. The nitrogen provided by the legumes, is in an organic form and has to be mineralized and oxidised before leaching into the subsurface can occur. In South Africa nitrogen fixed by legumes (including grain legumes, lucerne and legume-based pastures) amounted to 95 000 ton in 1981 (Strijdom & Wassermann, 1984). Should all agronomic soil and natural pasture suited for legume pastures be exploited for this purpose the total contribution by nitrogen fixation could rise to over 400 000 ton.

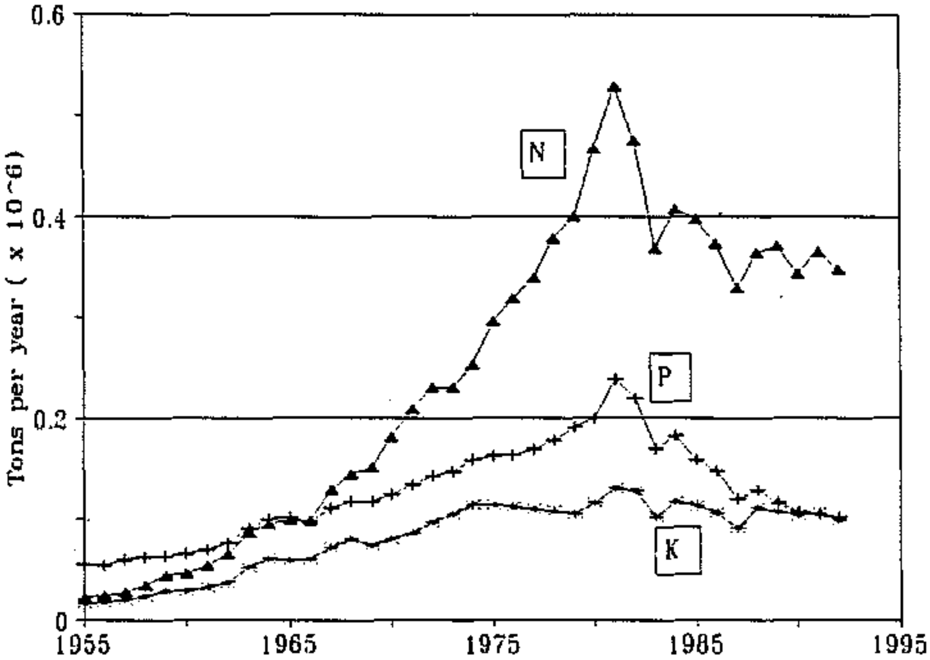


FIGURE 13: Fertilizer consumption in South Africa (data from Van Niekerk, 1989)

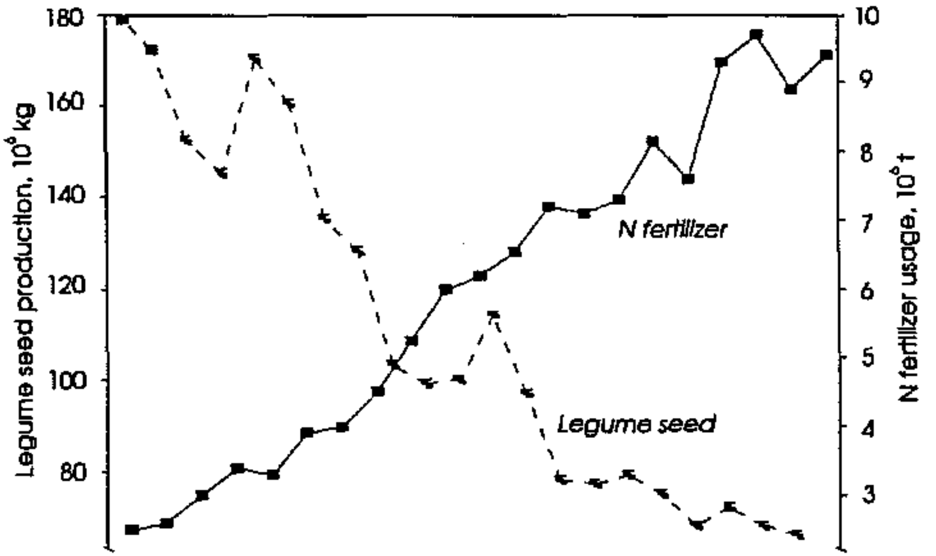


FIGURE 14: Legume seed production and fertilizer nitrogen use in the USA (Power & Schepers, 1989)

A nitrogen balance sheet was compiled for the agricultural soils in South Africa (Biesenbach, 1984). This balance sheet considered additions such as fertilizers, atmospheric contributions, nitrogen from irrigation water and natural nitrogen fixation. Nitrogen derived from manure and compost was excluded in the compilation as no statistics were available. It was also stated that the quantities were relatively small and would not play a significant role in the balance sheet. The nitrogen removals included in the balance sheet were the following: crops and plant residues, soil erosion by wind and water, as well as losses through leaching, denitrification and volatilisation. The data was compiled for a number of years over the period from 1960/61 to 1980/81. For the purpose of this report only the years 1960/61 and 1980/81 are of importance as it shows the relative weights of the various components as well as the changes over the 20 year period. The balance sheets calculated (Biesenbach, 1984) for these years are given in Table 9.

TABLE 9: An agricultural nitrogen balance sheet (after Biesenbach, 1984)

YEAR	1960/61		1980/81	
Fertilized area (10^6 ha)	12,3		14,4	
Irrigated area (10^6 ha)	0,7		1,1	
	kg/ha	total (t)	kg/ha	total (t)
Additions				
fertilizers	3,8	46 046	32,3	466 385
irrigation	2,4	1 680	2,4	2 678
atmosphere	(10)	(122 660)	(10)	(144 250)
N-fixation	?	unknown	?	unknown
Total		47 726		469 063
Removals				
crops & plant materials	14	181 715	26,7	414 397
erosion	3	36 798	3	43 274
losses (leaching, denitrification, volatilisation)	?	(122 660 + unknown)	?	(144 250 + unknown)
Total		218 513		457 672
Net gain (+) / loss (-)		-170 787		+11 391

It is noteworthy that in 1960/61 there was a considerable net loss of nitrogen from the soil while in 1980/81 there was a slight gain according to these balance sheets. The loss in 1960/61 was due to the small fertilizer input which could not cover the nitrogen losses due to removal of crops and plant materials. Two decades later the total fertilizer application had increased ten fold (8,5 fold for the application rate per hectare) while the removal by crops and plant materials had only doubled.

Biesenbach (1984) had no estimate for nitrogen fixation in the soil and assumed that together with the nitrogen derived from the atmosphere it balanced the losses due to leaching, denitrification and volatilisation. Strictly speaking this might not be true. In the case of Danish agriculture (Schroder *et al.*, 1985) it was found that biological nitrogen fixation decreased as other nitrogen inputs increased (see Table 5). Thus, even though the nitrogen balance sheet for agricultural soils in South Africa has certain shortcomings, trends are evident which point toward a nitrogen surplus developing in the soil zone, possibly creating a greater potential for leaching of nitrates to the subsurface.

When comparing the fertilizer application rate per unit area in Denmark in 1980 (see Table 5) with that in South Africa (see Table 9) it is clearly evident that the nitrogen application rates in Denmark are some ten times higher. That explains at least part of the very high losses calculated for Denmark. The calculations of Biesenbach (1984) although incomplete could, therefore, give an acceptable approximation of the situation in South Africa. This would mean that by 1960/61 there was a considerable over exploitation of the soil, while in 1980/81 fertilizer application rates were slightly too high.

There are clear indications that nitrogen recovery by crops vary considerably under South African conditions (Dijkhuis *et al.*, 1984). Nitrogen recovery was found to range from 31 to 122 per cent with exceptional cases as high as 258 per cent. They came to the conclusion that nitrogen recovery by crops may be governed by weather conditions, soil form and management. It was also concluded that more mineralisable nitrogen, than is normally accepted, may be stored in the soil and it was recommended that more local research is needed on the nitrogen delivery potential of soils.

Irrigation

Irrigation is generally practised in areas where the rainfall is relatively low and has to be supplemented with irrigation water. In most cases, over-application of water for the purpose of leaching forms part of the management of the irrigation system. It is therefore, to be expected that nitrate occurrences ascribed to percolate from irrigated lands will occur. In the case of the Hex River Valley, Weaver (1991) found nitrate levels of up to 33 mg/L in some of the wells monitoring shallow groundwater (< 3 m below surface). The higher nitrate values were accompanied by potassium values which were also considerably above the natural background levels.

As reported in Chapter 4, it was noted that nitrate concentrations exceeding 20 mg/L were quite common in boreholes within the irrigated areas extending over 80 km along the Crocodile River in north-western Transvaal. The fact that the electrical conductivities of the water from these boreholes was also high, implied irrigation percolate as the source.

Animal husbandry/intensive animal feeding units

Dry land grazing of stock in itself is expected to have little influence on nitrate accumulation. The gathering of livestock in kraals or around feeding/watering points, significantly increases the risk of groundwater pollution. Dairy farming presents a special problem as additional feeds are provided and the concentration of animals around the milking facilities are usually higher.

In their discussion of pollution sources in Bophuthatswana, Xu *et al.* (1991) refer to agricultural practices including stock-farming which tends to increase the nitrate load in the underlying aquifer. They state that farmers often build their kraals close to the water sources. This is also the situation in the western Kalahari (Heaton, 1984). At such sites, manure is concentrated and its leachate contains coliform organisms as well as inorganic substances. Xu *et al.* (1991) link the death of cattle of very high nitrate groundwater in the District of Kudumane to such conditions.

Intensive animal feeding units (feedlots) represent the most significant threat to groundwater quality. Information from the United States (Mielke & Ellis, 1976). indicate that the risk of groundwater pollution is relatively low, while the feedlot is in full operation. Under such conditions, nitrogen remains in reduced form and is largely lost as ammonia. However, when feedlots are only used partially or intermittently, or eventually abandoned, nitrification and transport of nitrates to the groundwater take place.

Botha (1984) estimated the total quantity of nitrogen contained in manure produced annually in intensive feeding units at 69 313 t/a. This was based on data for 1981. The breakdown for the various manure types is given in Table 10.

No statistics could be found with regard to the present number and distribution of feedlots in South Africa. Furthermore, it is expected that pollution could be a problem at feedlots but at this stage no studies have been published in this regard (Steyn, 1992). From an analysis of the numbers of livestock it would seem that the total number has remained relatively constant over the last two to three decades. However, meat production has increased by approximately 50 per cent over the past thirty years (see Fig. 15). Based on these numbers, the pollution potential is expected to have increased considerably.

Cogho (1991) found nitrate concentrations exceeding 30 mg/L near feedlots in the northern Orange Free State.

TABLE 10: Estimated total nitrogen content of manure produced annually in intensive feeding units (Botha, 1984) (Data given for 1981)

Type of manure	Total nitrogen content (t/a)
dairy cattle	17 460
beef cattle	12 420
pigs	18 200
poultry	20 848
sheep	385
Total	69 313

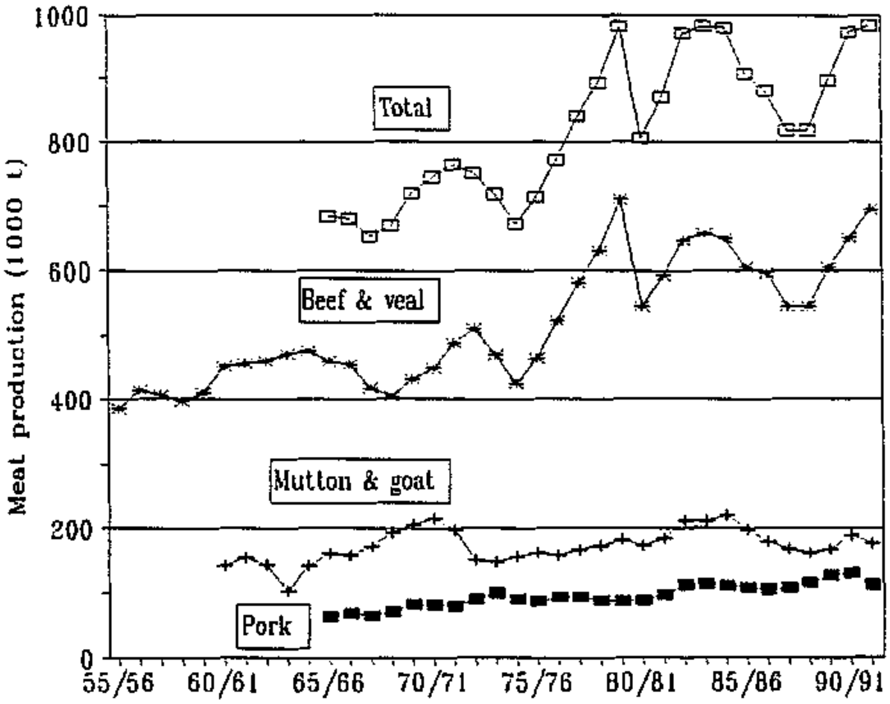


FIGURE 15: Annual meat production in South Africa for the indicated years (DAD, 1992)

6.2 Cities, towns and settlements

Sewage sludge and effluent disposal to land

Sewage sludge disposal to land is widely practised in and around most cities and towns (Engelbrecht *et al.*, 1981). Sludge drying beds and sludge disposal to land, as well as sanitary landfills, constitute important sources of groundwater pollution. Very few local studies have been published but data from the Cape Flats (Tredoux, 1984) suggests that groundwater pollution could be severe in such permeable soils. Xu *et al.* (1991) discusses aquifer protection strategies in Bophuthatswana and briefly mentions that there is much evidence to show sewage effluent and sewage sludge are disposed to land overlying aquifers as in the case of Mothibistad.

Effluent disposal by irrigation is legally practised in at least 240 instances. In Table 11 (Fuls & Du Plessis, 1977 *in:* Du Plessis, 1985) the number and type of permits are summarised as well as the effluent volumes and land areas involved. The maximum effluent volume irrigated is at least 127 x 10^6 m^3/a of which some 85 per cent involve municipal sewage effluents of various qualities. Although the actual quality is unknown it could be assumed that it will contain nutrients and for this reason these irrigated areas are often planted with grass, e.g.kikuyu. It is highly likely that at least in some areas leaching of nitrates could occur also in areas underlain by usable aquifers. Considering the estimated area of 25 471 ha involved the impact could be significant.

Du Plessis (1985) indicates that some reservations exist with respect to the use of lower quality effluents for irrigation but states that it is mostly applied according to scientific principles based on water quality and soil type.

TABLE 11: Maximum effluent volumes permit holders may use for irrigation and areas under effluent irrigation (Du Plessis, 1985)

Permit holder category	Number of permits	Max. effluent volume (10^3 m^3/a)	Estimated area irrigated (ha)	Mean area per permit holder (ha)
Municipalities (sewage effluent)	134	127 356	25 471	190
Agricultural product processors	60	8 777	1 755	29
Mines	29	8 323	1 666	88
Industries	17	5 593	2 404	141
Totals	240	150 055	31 296	136

Unsewered settlements

On-site sanitation is economically attractive but it presents a groundwater pollution risk. In most cases this risk can only be evaluated by carrying out a detailed hydrogeological field study before implementation of any such scheme. Up to now, no such studies have been carried out and therefore pollution could be expected from many of these settlements which may be located in vulnerable areas.

In the vicinity of rural settlements in Venda (northern Transvaal) Connelly & Taussig (1991) found that nitrate concentrations in many boreholes exceeded 20 mg/L and in one case it even reached 54 mg/L. The nitrate was ascribed to two possible sources: mobilization of natural nitrate by cultivation of the soil or on-site sanitation. Undoubtedly both factors can contribute to elevated nitrate levels. Rawhani (1986) reported on the incidence of microbial, fluoride and nitrate pollution in groundwater in Bophuthatswana. It was established that 17 per cent of the boreholes sampled between 1981 and 1986 exceeded the 10 mg/L limit for nitrates. Agricultural developments, inadequate waste disposal and sanitation practices, are considered to be the main contributors to high nitrate concentrations. Xu *et al.* (1991) ascribed the high nitrate concentrations to the situation of kraals close to water sources as well as the effect of sewage effluent and sewage sludge disposal to land overlying aquifers.

Hesseling *et al.* (1991) studied the occurrence of nitrates at Rietfontein in the north-western Cape Province. They found unacceptably high levels of nitrate in the centre of the village, considered to be likely due to human and animal pollution, while water of better quality was present on the periphery of the village.

Despite the widespread occurrence of on-site sanitation in South Africa the information is largely anecdotal as quoted above. Even in relatively densely populated areas pit latrines are used. Depending on local geohydrological conditions such sanitation can cause serious pollution if no precautionary measures are taken (Lewis *et al.*, 1980). This problem has been studied in some detail at places in neighbouring Botswana (Lewis *et al.*, 1978; Palmer, 1981) and in Moçambique (Muller, 1989). Some details are provided below.

Lewis *et al.* (1978) refer to extremely high nitrate concentrations in water supply boreholes in many villages in eastern Botswana causing serious concern about groundwater pollution. As a result a detailed investigation was carried out at Mochudi village. It was shown by means of tracers that the transit time between the pit latrines and the neighbouring water supply borehole some 25 m distant was less than 4 hours. This should be viewed against the background of the geohydrological conditions. The village is situated at the foot of an escarpment compound of Waterberg sandstones and shales resting on granites of the Basement Complex. The area is underlain by Waterberg talus and weathered Basement Complex rocks. The dark, clayey soils are thin and grade downwards within 2 to 3 m into the weathered rock material. The waterlevel is mostly less than 10 m below surface.

A study of the soil indicated that generally the highest nitrate concentration was found in the layer directly above the consolidated rock (Lewis *et al.*, 1978). From the soil analyses it was estimated that the total mass of nitrate in each square metre of soil column within a radius of 15 m around the pit latrine varied from 0,4 to 2,4 kg/m^2, representing a massive quantity of potentially leachable nitrate.

What is even more disconcerting is the bacterial contamination risk which is aggravated by the short travel times of liquid from the pit latrines to the borehole.

Palmer (1981) stressed the risks involved in introducing water-based on-site sanitation systems such as the septic tank. For a low nitrate impact dry system a modified pit latrine is recommended. Muller (1989) proposed a kind of flow chart approach consisting of sets of questions relating to nine parameters for assessing the on-site sanitation risk to any local groundwater supply.

Even in an urban development with water-borne sewage and stormwater run-off systems, groundwater pollution is possible (Wright, 1991). This was found to be the case in the township of Khayelitsha in the Cape Flats, which is situated on the Cape Flats aquifer. Nitrate was one of the pollutants observed in the groundwater.

Ward (1984) described a methodology for investigating sources of groundwater pollution giving details of the placement and construction of sampling holes. It also clearly stated that this kind of study has its limitations and negative results do not justify unmonitored sanitation and water supply programmes.

Waste disposal sites

As in the case of sewage sludge disposal to land, very few of the local studies on waste disposal sites and their impact on groundwater have been published. From the literature it is known that such sites can have a serious impact on groundwater quality. This was confirmed by the study in the Cape Flats at two waste disposal sites (Tredoux, 1984). In the one case, the sand was removed up to the water table which means that the body of the waste was in direct contact with the groundwater. Leachates entered the groundwater and pollution was severe. Immediately below the waste site, nitrogen was largely present as ammonia but approximately 100 m from the site, oxidation had already taken place and the nitrate concentration increased. In the other case, an unsaturated zone of at least 8 m existed and no pollution took place until the disposal of sludge at this site commenced. This increased the moisture content at the waste site to such an extent that leachates were detected in the groundwater at the monitoring holes within months.

Ball & Blight (1986) studied a closed landfill site in Johannesburg which had been in use for 50 years. When operated incorrectly in its initial stages significant groundwater pollution occurred down gradient of the site. Towards the end the site was well managed and produced no, or at worst, negligible groundwater pollution. No nitrate data is provided, only very low ammonia levels are shown in the paper.

Verhagen *et al.* (1991) studied a waste disposal site in a former clay quarry in a Karoo outlier in the karstic dolomite terrain in the Midrand area. From the results it was evident that general urban pollution related to the residential and industrial regions had taken place but that localised sources of pollution were superimposed on these. They concluded that the pollutants chloride and sulphate are associated with active, local recharge, including sources other than direct rain infiltration. On the other hand, nitrate which is also strongly associated with active recharge, correlates mainly with rainwater and, therefore, with ongoing natural and agricultural, rather than urban and industrial sources.

6.3 Industry

Due to mining activities in the northern Orange Free State nitrate pollution was recorded which was ascribed to the use of lead and zinc nitrate in the ore treatment processes (Cogho, 1991). As shown in Table 11 some 29 mines were permitted to irrigate some 1 666 ha of land with up to 8,3 x 10^6 m^3/a. High salinity is, however, the main problem (Cogho, 1991).

Irrigation of industrial effluents is practised at a number of locations in South Africa. Studies in such areas usually concentrate on the prevention of surface water pollution. Groundwater pollution is seldom taken into account. By 1977 a total of 17 industries were legally irrigating 5,6 x 10^6 m^3/a (see Table 11).

In south-eastern Australia, cheese factories have in some cases disposed of whey underground, often using sink holes in limestone for this purpose (Lawrence, 1983). This has given rise to plumes of nitrate-rich groundwater migrating and dispersing underground. Lawrence (1983) cites a study which modelled the nitrate transport, predicting that even when the underground disposal of dairy waste ceases, there would still be substantial and widespread distribution of nitrate in forty years' time. No detailed information is available on any such enterprises in South Africa except that some 60 permits have been issued to firms processing agricultural products. They could legally dispose of some 8,8 x 10^6 m^3 of effluent by irrigation per annum (see Table 11). Although the quantity is similar to that of the mines, the nutrient content is expected to be higher, particularly in the case of food processing effluents.

6.4 Polluted river systems and dams

Seepage from polluted dams and river systems has the potential to contaminate groundwater. At this stage, published information in this regard is unavailable for South Africa.

7. NITROGEN MANAGEMENT MEASURES

From the foregoing it can be concluded that there are large areas where nitrate levels in groundwater are high, either naturally or through anthropogenic activity. However, the potential exists for extensive further impacts due to anthropogenic activities such as fertilizer and manure application to land, ploughing, on-site sanitation in informal and other settlements, intensive stock breeding, waste water treatment and disposal, solid waste disposal and other activities. Addiscott *et al.* (1991) refer to the problem that water presently being abstracted from the chalk aquifer (England) was recharged some 50 years ago and therefore reflects agricultural practices of five centuries ago. In view of the delayed impact of nitrate pollution, management measures are urgently required for safeguarding groundwater supplies against nitrates, and other pollutants, which may only reach the groundwater after a number of decades. Groundwater remediation has met with little success so far and drinking water treatment is an expensive option, particularly in the rural setting.

7.1 Limitation of nitrogen input

Concern with regard to increasing groundwater nitrate concentrations worldwide has led to a number of countries proposing control measures for reducing the nitrogen input to groundwater. As agricultural practices are widely considered to be the most important contributor, most control measures relate to agricultural activities.

In South Africa the DWA&F has recently published a document on water quality management policies and strategies (DWA&F, 1991). This document also addresses groundwater quality listing known examples of pollution as well as problem areas to be addressed. With respect to agricultural (largely fertilizer-derived) pollution it states that diffuse as opposed to point source pollution is particularly problematic as it can affect an entire aquifer and can go unnoticed for decades. Once the effects appear, it may be necessary to abandon the aquifer (DWA&F, 1991).

Publication of this document demonstrates the commitment of the DWA&F to protect the country's water resources (including groundwater). As groundwater is private water in South Africa, except in limited areas where government groundwater control areas have been declared, it is virtually impossible to introduce the extensive control measures needed for groundwater protection in rural areas except in water control areas and in areas where groundwater is already utilised for town supply. In view of the water pollution threat posed by waste disposal sites a system of licensing of waste disposal sites has been introduced. This requires inter alia a full geohydrological investigation.

The measures referred to above largely address pollution point sources. Pollution from diffuse sources is, therefore, practically uncontrolled. Such sources largely refer to agricultural activities. An information campaign bringing the detrimental effect and the hazards of nitrate pollution to the attention of farmers, owners of smallholdings and others is, therefore, considered an essential additional measure for safeguarding groundwater supplies.

7.2 Agriculture

Power & Schepers (1989) came to the conclusion that there are several courses of action for short-term solutions to problems of groundwater nitrates. As agriculture is widely recognised as one of the largest contributors, their short-term measures all include improved soil and crop management practices. However, they add that there are often additional costs from adoption of some of these practices. For this reason, financial incentives need to be provided to achieve the short-term goals. Best management practices listed by Power & Schepers (1989) include:

- irrigation scheduling
- fertilization based on calibrated soil tests
- conservation tillage
- acceptable cropping practices
- recommended manuring rates.

All the above have been demonstrated to be highly effective in controlling leaching of nitrates.

Strebel *et al.* (1989) state that the nitrate leaching from agricultural land can be considerable. They recommend that all measures to reduce the nitrate leaching should be based on an analysis of the local situation (e.g. soil, crop rotation, groundwater depth, climate, etc.) to determine the main leaching period or whether nitrate leaching might occur during the growing period. Three sequential measures are listed:

The first is a crop type and crop development stage-specific nitrogen fertilization, taking into account the potential yield level and its dependence on site and climatic conditions. As part of the first step, the following three aspects have been taken into account:

- The nitrate content in the root zone measured at the beginning of growth in spring;
- The nitrogen mineralization during the growing period (by estimation or test measurement);
- Split the nitrogen fertilizer application according to the crop demand.

A fertilizing system based upon the nitrate content in the rootable soil layer in spring is the N_{min}-method which is used mainly in Belgium, Denmark, the Netherlands and Germany. Several examples are listed (Strebel *et al.*, 1989) where savings of fertilizers were achieved, often with increased yields and better qualities. Consequently, the nitrate content of soil at the end of the growing period could be reduced from more than 200 to about 40 kg N/ha. It is stressed that this result was obtained without any losses of yield. The cost of the N_{min}-method analysis was covered by the saving in nitrogen fertilizer.

The purpose of the second step is to minimize the amount of nitrate in the soil that could be leached out during the main leaching period in autumn. The site- and time-specific nitrate leaching risk can be quantified using a simulation model which describes the nitrate transport by convection, diffusion and dispersion. Under fallow conditions, the leaching risk on sandy soil is very high until the end of December (in Europe) with values exceeding 50 per cent. On loess soil, the situation is more favourable. A very effective measure in this regard is the cropping of deep-rooting catch-crops after harvesting of the main crop. Any application of nitrogen fertilizers, in particular of liquid manure, during the period of high nitrate leaching risk, should be avoided.

Other measures related to steps one and two include
- proper water management;
- removing nitrogen-rich crop residues (sugar beets, vegetables) from the field after harvest;
- reduced soil tillage (decreased nitrogen mineralization in autumn);
- straw application after harvest (nitrogen immobilization), and
- the use of nitrification inhibitors.

The third step involves an overall reduction of the total nitrate input in the groundwater recharge. In a recharge area with different land use intensities, the areas with low nitrate inputs into the groundwater should be enlarged at the expense of areas with high nitrate inputs.

In the state, Baden-Württemberg new legislation came into effect on 1 January 1988 providing clear instructions on groundwater protection (Traub, 1991). Baden-Württemberg was the first state of the German Federation attaching such a high priority to groundwater protection. This act declared the intake areas (natural recharge areas) of aquifers as protection areas. In such areas, the nitrogen content of the soil may not exceed 45 kg/ha at the end of the growing season (i.e. after harvesting). If the farmer succeeds, he is paid DM 310/ha. Compliance is checked by the agricultural extension officers and for this purpose, some $0{,}5 \times 10^6$ soil samples are taken and are analysed at a cost of between DM 200 and DM 300×10^6. The system of payments to the farmer is possibly the type of financial incentive scheme Power & Schepers had in mind.

Pekny *et al.* (1989) noted that in several highly agriculturally developed countries, the trend in nitrate concentrations in groundwater is closely related to farming activities. This applies particularly to fertilizer application to land. Management of the agro-water system should be based on sound scientific information. This requires a specific approach and solution in each region, comprehensive analysis of the physical and socio-economic aspects between the relevant soil and water users, and establishment and implementation of strategies and policies for soil and water resources utilization in a given region. Pekny *et al.* (1989) provided the following extensive list of activities and control measures for determining a policy and the management of agro-groundwater systems:

" - determination of the geometry, hydraulic and physical properties of the hydrogeological and soil system;
- evaluation of biochemical processes in the soil environment with a special regard to maintaining the stability of the soil organic matter;
- evaluation of climatic influences, precipitation and temperature on the above processes;
- selection of suitable crops and designation of the sowing rotation system;
- selection of suitable kinds of solid or liquid fertilizers, chemical inhibitors and pesticides with regard to climatic and hydrogeological conditions and soil types;
- determination of doses, times and manner of fertilizer application, including organic fertilizer with regard to kind of plant, soil composition and climatic conditions;
- determination of irrigation schemes and methods in irrigated and drainage regions;
- selection of suitable cultivation techniques, especially tillage, in respect to the slope of the land, type of soil and climatic conditions;
- maintenance of a suitable regional structure of the agrosystem, particularly elimination of monocultures and/or fast crop rotation, regulation of extent of arable land and grass land, regulation of animal production in relation to extension of the farm land, etc.;
- determination of the recharge, contribution and vulnerable areas of the hydrogeological system;
- design of soil and groundwater quality monitoring network and programme, including vertical profiling of the unsaturated zone and aquifer in highly vulnerable areas;
- study and modelling of the physical and biochemical processes and solute transport in the soil-plant-water system in representative areas;
- evaluation and analysis of laboratory, field and model studies as a base for decision-making;
- recommendations for changes in extent and intensity in agricultural activities in a given region, with special regard to the drinking water protection areas and overall protection of all utilizable groundwater resources;
- evaluation of economic and social consequences of changes recommended for the given agro-water system;
- determination of control system, policy instruments and institutional and legislative implementation of designed changes in the given agro-water system;
- optimal integration of the competing soil and water users' interests, i.e. the water supply and agricultural sectors."

Protection zones for safeguarding groundwater supplies have been introduced in a number of countries. In Czechoslovakia legislation was introduced defining two zones with three levels of protection (Vrba *et al.*, 1985). These consist of a first zone comprising an area of at least 10 m by 10 m around a production well, and a second zone consisting of an internal and an external area. The internal part is defined by a groundwater residence time of 50 days and is intended for protection from bacteriological contamination. The external part is the recharge area for that source. The first zone is covered with grass, enclosed and excluded from agricultural use. The internal part of the second zone may be used for plant cultivation. In the external part fertilizers may be used but even though no statutory regulations limiting the dosages of inorganic fertilizers individual application based on the particular natural and ecological conditions is recommended. The use of municipal and agricultural effluents on agricultural land in protection zones is prohibited unless they are composted beforehand. Thus composting of wastes is seen as an important control measure.

In the Netherlands similar control measures have been proposed. They proposed a 60 day, 10 year and 25 year groundwater residence time zoning (Van Beek, 1985).

Based on the control measures applied abroad, workable local measures could be developed.

7.3 Waste disposal

Whereas agricultural nitrate pollution consists largely of diffuse sources, waste disposal leads to relatively well-defined point sources in the form of waste disposal sites. Provided the location of these sites are well known, pollution can be detected and monitored. Furthermore, strict guidelines as to the licensing, construction, operation, monitoring and closure of waste disposal sites have been issued in terms of Section 20(1) of the Environment Conservation Act, 1989 (Act 73 of 1989). Compliance is controlled by the issuing of permits. In this way, pollution from such sites can be minimized.

Bredenhann (1991, 1992) stated that: "In South Africa there are existing control measures in terms of Sections 21, 22, 23 and 23A of the Water Act, 1956 (Act 54 of 1956). Section 21 of the said Act states that a person using water for industrial purposes must purify or treat the water so used, or any effluent produced by or resulting from such use, according to the standards set out in Government Notice No. 991 of 18 May 1984. A contravention of this section is an offence and a person so convicted, can be fined an amount not exceeding R50 000 in the case of a first conviction, or sentenced to imprisonment not exceeding two years or to both such fine and such imprisonment. In the case of a subsequent conviction a person can be fined an amount not exceeding R100 000 or sentenced to imprisonment for a period not exceeding four years or to both such fine and such imprisonment.

"Section 23 of the said Act states that any person who wilfully or negligently commits any act which could pollute public or private water, including underground or sea water in such a way as to render it less fit for the purposes for which it is or could be ordinarily used by other persons, for the propagation of fish or other aquatic life, for recreational or other legitimate purposes, shall be guilty of an offence. The fines and sentences mentioned under the discussion of Section 21 above are also applicable in this case.

"In terms of Section 23A of the said Act the Minister can if he is of the opinion that the concentration of livestock or any farming operations is causing or is likely to cause the pollution of public or private water, including underground water require the owner of the land or the person carrying out such operations to take at his own expense such steps as the Minister may deem necessary. A person who wilfully fails to comply with the requirements of the Minister, is guilty of an offence.

"Section 22 of the said Act places the responsibility to prevent water pollution or any person who has control over land on which anything is or was done which involved or involves a substance capable of causing water pollution.

"Section 22(3) authorises the Minister of Water Affairs and Forestry to take such steps as he may consider necessary to be taken on aforementioned land to prevent water from being polluted or being further polluted."

Bredenhann (1992) discussed waste management legislation and provided a list of accomplishments and future plans for accomplishing the above which is reproduced in Table 12. Should all the controls be put into place, this pollution source can be controlled, including the emanation of nitrates from such sites.

7.4 Location of polluting activities

Generally all polluting activities should be sited, taking the vulnerability of the particular aquifer into account. This also holds for nitrate producing activities, such as on-site sanitation. Ward & Schertenleib (1982) gave an overview with regard to groundwater pollution from unsewered sanitation systems. Emphasis was placed on microbiological contaminants and nitrates. Apart from the characteristics of the soil and the underlying formations, the hydraulic loading rate was considered the most important criterion. Further study, development of guidelines and controls adapted to local conditions could be necessary.

Irrigation of industrial wastes is widely practised as a disposal method. Control with regard to groundwater pollution is required and disposal should not be allowed without a thorough geohydrological study and a proper disposal management plan followed by monitoring.

7.5 Aquifer restoration

Groundwater polluted with nitrate can be treated after abstraction as is the case with any other pollutant. Treatment of the water could include artificial recharge of a suitable aquifer (slow sand filtration) with an organic substrate which will promote denitrification. Alternatively, depending on the characteristics of the polluted aquifer, *in situ* treatment involving the transformation of nitrate into gaseous nitrogen could be carried out. In 1985, WHO (1985) indicated that the technique was still being studied and was not yet operational. Papers (Chalupa, 1985; Conesson *et al.*, 1985; Kruithof *et al.*, 1985) published at that stage indicated various degrees of success in preliminary studies in Czechoslovakia, France and the Netherlands. Subsequently Janda *et al.* (1988) and Mercado *et al.* (1988) reported on further *in situ*

TABLE 12 Waste management legislatory control perspectives (Bredenhann, 1992)

Year	Legislation/ Administration	Method of control
<1982	No waste control legislation	Voluntary cooperation
1982	Promulgation of Environment Conservation Act (Act 100 of 1982)	Issue concept permits
1989	Promulgation of Environment Conservation Act (Act 73 of 1989)	Publication of regulations for waste disposal sites
1990	Identification of matter as waste	Issue permits for sites where wastes are accumulated, stored and disposed
1990	Implement section 20(1) of Environment Conservation Act	Issue permits for the establishment and operation of waste management facilities
1991	Computerised waste management information system	Register of waste management facilities; types and volumes of waste disposed; results of water quality monitoring
1992	Minimum requirements for waste management facilities	Permit conditions for siting, design, construction, management, closure and rehabilitation of waste management facilities
1992	Criteria for hazardous waste management	Specifications for pretreatment and disposal
1993	Control over generators and transporters of hazardous waste	Duty of care and waste manifest system
1995	Liability for damage	Polluter pays; environmental insurances
1996	Waste minimization	Re-use and recycling technologies
1997	Waste prevention	Prevention by technologies and products
1999	Chemical control	Inventory of chemicals imported, used and manufactured
>2000	One waste act	Integrated waste management

denitrification studies with promising yet unsatisfactory results.

Strebel *et al.* (1989) reported that denitrification processes with organic carbon had an efficiency between 25 and 70 per cent. They also report on a study in an unconfined sandy aquifer in north-western Germany where denitrification was carried out with reduced sulphur compounds. In that case, the denitrification efficiency was nearly 100 per cent. Strebel *et al.* (1989) emphasised the importance of side-effects of such denitrification reactions. These include a gradual consumption of the stock of microbiologically oxidizable compounds, increased sulphate and an increased risk of clogging of the production well. Hamon & Fustec (1991) reported on laboratory and field denitrification studies. Whereas the laboratory nitrate removal efficiency reached 100 per cent in a week, the *in situ* field study only had a removal efficiency of approximately 70 per cent.

In general, polluted aquifer restoration has been decidedly unsuccessful despite investment of milliards of dollars in terms of the U S Superfund aquifer restoration programme. With *in situ* denitrification of aquifers polluted with nitrate considerable progress has, however, been made and in due course local investigations in this regard may be warranted, depending on the characteristics of the polluted aquifer.

7.6 Denitrification of water supplies

Adam (1980) reviewed the water treatment methods for removal of nitrate. Ion exchange, reverse osmosis, electrodialysis, chemical reduction, distillation and freezing are mentioned as well as biological methods involving algal ponds and bacterial denitrification. Adam favoured ion exchange as it involved a technically simple process and because it yields a high-quality drinking water. Solar distillation is also seen as a viable option for household and small communities in remote areas. Bacterial denitrification is also considered a suitable process with high degrees of denitrification (over 90 per cent) but the presence of biological sludge residues, colour and micro-organisms necessitates further treatment to render the water suitable for human consumption. The water can, however, be used for stockwatering. Rohman & Sontheimer (1985, p. 280) list five methods for which the technical aspects have been worked out and which provide feasible means of nitrate removal. These are:

- partial desalination by reverse osmosis
- partial desalination by electrodialysis
- partial desalination by ion exchange
- anion exchange
- biological denitrification.

All these techniques provide viable options under various circumstances for the removal of nitrate from drinking water. However, in virtually all cases, the treatment is followed by activated carbon adsorption to remove any organic substances added to the water during treatment. This aspect increases the cost considerably.

When it is taken into consideration that countries are now aiming to reach the EC guideline of 5,6 mg/L which means that water with a nitrate content < 10 mg/L is now being denitrified at great cost, the rationale of lowering the guideline to 5,6 mg/L is questioned. Parsons (1977) suggested 22,6 mg/L as a more realistic limit and little or no evidence has been provided to disprove the validity of this value.

7.7 Information programme

Nitrate pollution is largely due to diffuse sources in agriculture. In general, should such sources be controlled only the farmer himself or his neighbours or at most the local town will benefit from any reduction in the nitrate in the groundwater. Furthermore, enforcement of control measures is difficult if not impossible. Voluntary reduction of nitrogenous inputs could, therefore, be a viable means of controlling a large part of the pollution. An information programme informing the farmers, industrialists active in the farming sphere, as well as the public at large of the problems related to nitrate accumulation is considered a useful but essential tool for achieving voluntary reduction.

In addition to the diffuse agricultural sources, the effects of on-site sanitation, sewage sludge and effluent disposal and other practices which are mostly regarded as point sources have been pointed out in the preceding paragraphs. Therefore planners, developers as well as local and regional authorities need to informed of the risks involved in these practices and of the correct preventative measures.

The compilation of guides such as the one on the handling of manure from intensive animal feeding units by Funke *et al.* (1984) fulfil a crucial role in this regard. The publication by the Borehole Water Association of Southern Africa and others (BWA, 1990) similarly fulfils a crucial role in educating the farmers and the public at large on the nature, value, and vulnerability of groundwater. It may even be advisable to compile a publication specifically devoted to nitrate in groundwater for this purpose.

8. CONCLUSIONS

The objectives of this preliminary situation assessment as set out in paragraph 1.2 have been reached. The conclusions of the study are presented in terms of the four objectives and these are discussed in paragraphs 8.1, 8.3, 8.4 and 8.5 respectively. Following the groundwater nitrate situation assessment (par. 8.1) the phenomenon of natural accumulation is discussed in a separate section (see 8.2) in view of its importance in understanding the processes leading to the occurrence of nitrate in groundwater. The nitrate contamination threat posed by anthropogenic activities is considered in paragraph 8.3 and, based on the limited information available, main contributors are identified. Reduction of groundwater nitrogen inputs needs a dual approach as both legislative and voluntary control is essential (par. 8.4) but where accumulation has occurred treatment by denitrification has to be considered. The results have indicated that further research, as detailed in paragraph 8.5, is urgently required.

8.1 Groundwater nitrate situation assessment

Nitrate occurrence

The hydrochemical data contained in the national groundwater database of the DWA&F was the only data set available covering the country as a whole. The distribution of sampling points is very uneven and possibly introduces a bias towards higher values as areas with water quality problems may have received more attention and may be better represented than other areas.

The median nitrate concentration for the 18 827 groundwater sampling points was 4,5 mg/L. However, 27 per cent of the sources exceeded 10 mg/L, 15 per cent 20 mg/L and 4,3 per cent 50 mg/L. The higher nitrate levels (> 20 mg/L, but mostly > 50 mg/L) occur largely in the following areas:

- in the Kalahari Beds in the Gordonia District adjacent to the Namibian border;
- in the Asbestos Hills Formation, Griquatown Group, in the vicinity of Prieska;
- on the Ghaap Plateau, south-west of Vryburg;
- in the Springbok Flats;
- along the Crocodile River.

The first two occurrences listed are considered to be due to natural nitrate accumulation, while the last two are related to anthropogenic activities. The extensive Ghaap Plateau nitrate occurrences could be due either to anthropogenic inputs or to natural phenomena or possibly both.

Impacts

Groundwater nitrates have caused methaemoglobinaemia in infants in Southern Africa, sometimes with fatal consequences. Although individual cases are known, statistics are unavailable. The simultaneous occurrence of faecal pollution increases the risk for infants.

An epidemiological study was carried out in an area with slightly elevated nitrate levels, but no studies have been undertaken in areas where the nitrate levels are high (i.e. approaching 50 mg/L).

No conclusive evidence has been found linking gastric cancer and drinking-water containing 10 mg/L or more nitrate. However, a link cannot be ruled out completely due to the inadequacy of the data available.

Livestock losses due to nitrate poisoning would appear to occur relatively frequently but only at relatively high (>>100 mg/L) nitrate concentrations. Statistics are not kept either by the authorities or by veterinary institutions. Sub-lethal concentrations, however, also affect animals detrimentally, particularly dairy cows.

The availability of nitrate in irrigation water, complying with salinity and other irrigation requirements, could be considered beneficial in certain instances.

8.2 Accumulation phenomena

Under natural conditions the "internal" nitrogen cycle is virtually closed within the soil horizon. However, environmental conditions exist under which natural leaching of nitrate from the soil zone and accumulation in groundwater occurs. These conditions include

- *vegetation:* maintenance of the nitrogen pool in the soil through nitrogen fixation by specific plant species and the accompanying microflora in the soil;

- *rainfall:*
  - adequate to support the required vegetation type(s);
  - semi-arid conditions (possibly ~200 - 250 mm/a) to limit total plant cover;
  - highly variable causing periodic die-off of plants and thus a varying plant cover;
  - rainfall consisting, at least at times, of storm events large enough to ensure relatively rapid natural recharge and leaching of nitrate;

- *temperature:* sufficiently high to ensure microbiological nitrification (oxidation);

- *soil:*
  - low C:N ratio for mineralisation;

  - low clay content;
  - soil cover of sufficient thickness and permeability to allow rapid percolation and adequate storage of rainfall; alternatively a geological formation with such characteristics is needed;

- *hydrology:* absence of active open drainage systems (i.e. rivers ending in pans).

Wherever accumulation occurs a combination of most of these factors have been identified. This phenomenon has lead to extensive areas in South Africa and adjacent territories naturally having elevated nitrate concentrations in groundwater. Natural nitrate accumulations are also known from Chile, Australia and the USA. Obviously these factors would also enhance accumulation of anthropogenically induced nitrate generation.

8.3 Anthropogenic inputs and activities

Sources

Surplus nitrogenous inputs to the soil, mostly derived from anthropogenic sources, result in increased transport of nitrate to groundwater. This is often manifested by isolated occurrences of elevated nitrate concentrations in boreholes near feedlots, kraals, pit latrines and other pollution sources. Each of these anthropogenic activities can lead to serious groundwater pollution and thus they need to be managed.

Potential point sources of serious concern are sewage sludge (uncomposted) and effluent disposal to land, on-site sanitation and waste disposal by landfilling. Some of these activities, such as landfilling, is controlled by the Central Government by means of a permitting system. However, on-site sanitation is widely practised without proper regard to the pollution potential. The risk involved has been proven in neighbouring territories and elsewhere but local information is lacking.

Although conclusive scientific evidence is lacking for South Africa, it is considered highly probable that fertilizer and manure application to land constitutes the most widespread diffuse source of nitrate pollution as it was identified in other parts of the world. The highly variable rainfall worsen the situation in the case of fertilized dry land farming due to the associated unpredictable plant cover and fertilizer needs.

Nitrogen isotope studies have provided proof that cultivation of the soil leads to mineralization of soil organic nitrogen followed by leaching and accumulation in the groundwater even without any artificial nitrogen inputs. The situation in the Springbok Flats is ascribed to this phenomenon.

Trends

Worldwide, groundwater nitrate concentrations brought about by anthropogenic activities are on the increase. In view of the increased fertilizer, manure and sludge application to land, this is in all probability also true for South Africa. However, longer term records quantifying such increases are lacking as the earlier data is unreliable due to possible analytical inaccuracies. In the case of the Springbok Flats it was concluded that no general trend existed and that the high nitrate values are possibly largely due to a one-time nitrogen mobilisation.

The modelling of nitrate transport to groundwater has been attempted in many countries (e.g. USA, Britain, Germany, Czechoslovakia, etc.) with a reasonable degree of success. These models provide valuable insights into expected future trends in groundwater nitrate levels.

In addition to long term (upward) trends in nitrate concentrations short term drastic changes in groundwater nitrate levels have been recorded. In Namibia stock losses are largely due to such sudden changes.

8.4 Nitrate management

Control measures

Control measures for reducing nitrogenous inputs to the environment are essential for protecting the groundwater resources. In view of the considerable delay (varying from years to decades) between the introduction of control measures and any decrease in groundwater nitrate levels it is a matter of extreme urgency to take action in this regard. Overseas experience provides valuable guidelines for developing workable local measures. This relates largely to fertilizer usage, manure and sludge application to land, feedlot operations, septic tank and pit latrine density, as well as control of other pollution sources. It has been proven that stable nitrogen isotope analysis can be used successfully to identify pollution sources. This technique can be used to confirm the effectiveness of any control measures adopted.

In view of the fact that the groundwater in many countries are already contaminated and that control measures will take many years (if not decades) to reduce these nitrate levels denitrification of drinking water is widely practised. In South Africa denitrification for potable use and/or stockwatering will be needed in areas where no alternative supplies are available.

Information programme

Informing the public and particularly the farming community as well as farming related industries of the hazards of nitrate pollution is considered an important tool for voluntary reduction of nitrogenous inputs, both with respect to diffuse sources as well as the myriad of small point sources. The impacts of a variety of anthropogenic activities causing groundwater pollution is unknown and ignored by local authorities, planners, developers and others.

The compilation of guides, such as the one jointly published by the Water Research Commission and the Department of Agriculture for the handling of manure from animal feeding units, is considered to play a crucial role in environmental (and groundwater) protection.

Denitrification processes

Wherever legislative and voluntary control of nitrogen inputs have failed or where natural accumulation has lead to high nitrate levels, treatment by denitrification is indicated. A number of treatment processes are being used successfully for the removal of nitrate from drinking water, e.g. biological denitrification, ion exchange and partial desalination by ion exchange, electrodialysis or reverse osmosis. In virtually all cases the denitrification stage is followed by activated carbon to remove traces of organic compounds added to the water during treatment. This clearly has serious financial implications.

In the case of stockwatering the product water does not need to comply to the same high (aesthetical) standards and biological denitrification is economically feasible using molasses as organic substrate.

In situ denitrification (aquifer restoration) is being investigated abroad and some degree of success has been achieved. Only when the technique is fully developed should it be adapted for this country.

8.5 Need for further research

From the information gathered during this project it is evident that there is a need for further research. This is based on the fact that the problem is poorly quantified at present and conclusions are largely drawn from anecdotal information, while the processes are not fully understood and management and control measures are undefined. These needs are explained below.

Proper quantification of the problem

The preliminary delineation of affected areas was based on the arbitrary collection of data in the National Groundwater Database of the DWA&F. A systematic coverage for the country as a whole is essential and this the Database cannot provide. Furthermore reliable information covering a decade or more is required for determining trends. Such data is presently unavailable. Computer simulation of the accumulation processes could provide further insight into likely future trends.

Proper epidemiological study is required in affected areas (preferably where nitrate-nitrogen exceeds 20 mg/L) for establishing the actual impact. The possible contribution by microbiological pollution to the hazard of nitrate ingestion by infants should be considered. These studies should be complemented with a thorough risk assessment.

Process studies

The accumulation phenomena are presently only partially understood. The compounding effect of anthropogenic nitrate pollution enhanced by natural factors favouring accumulation needs to be thoroughly investigated, possibly in a few problem situations. The extent of aquifer vulnerability for nitrate accumulation should be determined and could possibly be linked to the aquifer vulnerability map which is currently being compiled.

Process studies are also required for practices such as on-site sanitation as the impacts for the various methods vary widely. Local case studies are urgently needed for complementing investigations abroad.

Management and control measures

Research into management and control measures for the following activities and enterprises is urgently needed:

- on-site sanitation
- sanitary landfilling
- sludge disposal to land
- effluent disposal by irrigation
- agriculture, essentially with regard to fertilizer and manure application
- stockbreeding, as well as dairy farming.

9. RECOMMENDATIONS

The results of this preliminary assessment prompted the following recommendations. These are listed in order of priority, based on the facts that emerged from the study. This does not mean that two or more items could not be addressed simultaneously.

9.1 Reduction of nitrogen inputs

Groundwater nitrate is derived either from natural accumulation or from pollution. Control measures cannot significantly affect natural accumulation. Anthropogenic activities on the other hand, can be controlled and the reduction of anthropogenic nitrogen inputs to groundwater should receive attention as a matter of urgency as any actions will take years and even decades to effect a reduction in groundwater nitrate levels.

A dual approach is recommended:

Regulatory control measures: These are required to address both point source pollution, such as that emanating from feedlots, sludge application to land, multiple septic tanks and french drains, etc. as well as diffuse pollution arising from fertilizer or manure application to land. For point sources control could for example be exercised by means of a permitting system, similar to that which was instituted for waste disposal sites. As in the case of waste disposal geohydrological and other studies should be required before a permit is issued. The effectiveness of the control measures should be confirmed by monitoring programmes and studies involving nitrogen isotope analysis. In the case of on-site sanitation a limit should be set for the density of sanitation units per unit area.

Information programme: A publicity programme should be aimed at the farming community, local and regional developers, local and regional authorities and industrial concerns active in farming related activities in order to create a public awareness of the nitrate problem, its causes, prevention and remediation. Farmers in particular should be made aware of the fact that many farming activities result in groundwater pollution and that it is in their own interest to protect their groundwater resources. Agricultural extension officers and others should be briefed on the groundwater nitrate hazards for them to further disseminate this information. At the same time guides, such as the one published by the Water Research Commission and the Department of Agriculture for the handling of manure from animal feeding units should be compiled for other polluting activities, as these guides can play a crucial role in protecting the environment, including groundwater.

9.2 Long-term trends

Long-term trends of the nitrate concentration in groundwater should be determined for various situations both where accumulation pertaining to natural conditions and to pollution occur. The need, extent and severity of control measures and enforcement actions required are subject to the established trends. There is less need for strict control measures in areas where the environmental conditions do not favour accumulation of nitrate in the groundwater. Conversely, strict control measures with proper enforcement will be needed in areas where rising nitrate levels have been established or for protecting vulnerable sole source aquifers. Knowing the actual nitrate trends will allow a more directed approach addressing the real issues. Nitrate in groundwater presents a special problem, often unrelated to increases in salinity and other quality problems, but the determination of trends should in some way or another be linked to the national groundwater quality monitoring strategy. However, it is essential that the trend analysis study be carried out properly (e.g. representative sampling of suitable and properly identified (marked) boreholes, correct sample handling, analysis by a reputable laboratory) so that the study will provide results that will be comparable even over a period of decades.

Models obtained from overseas should be evaluated and validated (or further developed) for simulating the generation of nitrate in the soil and the transport to the groundwater. This is essential for describing expected future trends in nitrate accumulation in groundwater. Input data for such models could be obtained from the detailed process and pollution studies as described below.

9.3 Delineation of vulnerable areas

The identification and delineation of areas and aquifers at risk due to cultivation and release of natural soil nitrogen is recommended. Those areas where the accumulation of nitrate in groundwater is favoured need stricter control measures for all potentially polluting activities, including farming practices, in order to allow protection of groundwater quality. For delineating such areas the information derived from the vulnerability map being compiled for the Water Research Commission could be used as a first estimate. Subsequently mapping of each of the factors enhancing subsurface nitrate accumulation should be carried out and the maps be combined through GIS to provide a nitrate specific vulnerability map.

9.4 Delineation and study of groundwater nitrate pollution

It is recommended that areas affected by nitrate pollution be delineated. Detailed studies should be undertaken at selected points within such areas, in order to identify the processes involved. Such studies should include

- confirmation of the origin of the nitrate by means of isotope identification;
- delineation of the extent of the affected area;
- establishment of any linkage to microbiological pollution/risk assessment;

- establishment of trend of nitrate concentrations;
- formulation of suitable measures to:
  - reduce inputs
  - find alternate sources
  - denitrify the supplies;
- investigation of epidemiological effects, particularly in areas where nitrate levels approach 50 mg/L or more.

The dolomitic area on the Ghaap Plateau south-west of Vryburg is considered a priority area for such a study. It could possibly provide an opportunity for studying nitrate accumulation due to both natural and anthropogenic factors.

9.5 Natural nitrate accumulation

Subsurface nitrate accumulation seems to occur widely in Southern Africa and its extent should be determined and the conditions enhancing this phenomenon defined. Evidently such accumulation occurs not only in the Kalahari but also in areas underlain by hard rock formations as for example at Prieska. Detailed studies similar to those for identifying the pollution processes should be carried out at selected sites.

9.6 *In situ* denitrification (aquifer restoration)

In due course when advances abroad justify its local application, *in situ* denitrification should be investigated as an alternative to treatment after abstraction as it could entail a number of advantages. In contrast to the general restoration of aquifers which has not been very successful *in situ* denitrification has at least shown some promise.

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