NITRATE IN GROUNDWATER

Why is it a hazard and how to control it?

Gideon Tredoux, Pannie Engelbrecht & Sumaya Israel

Report to the Water Research Commission by CSIR, Natural Resources and the Environment, Stellenbosch

WRC Report No. TT 410/09

August 2009

Obtainable from

Water Research Commission Private bag X03 Gezina, 0031 South Africa

orders@wrc.org.za

The publication of this report emanates from a project entitled *Managing Anthropogenic Nitrogen Input for Protecting Groundwater Resources: Conveying Research Results to Government Authorities, Water Supply Agencies, other Stakeholders and Consultants* (WRC Project No. K8/603

DISCLAIMER

This report has been reviewed by the Water Research Commission (WRC) and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the WRC, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

ISBN 978-1-77005-873-6

Printed in the Republic of South Africa

ABSTRACT

The occurrence of high nitrate levels in groundwater has to be recognised as a threat to humans and animals. Infant methaemoglobinaemia and nitrate poisoning of livestock occur at unexpected times and places. An important reason is that nitrate concentrations are variable, particularly under extreme climatic conditions. All instances of nitrate pollution related to anthropogenic sources can be managed to reduce or eliminate nitrogen inputs and for protecting groundwater resources. Hence the purpose of this book is to present the facts related to the health hazard, describe processes leading to nitrate pollution of groundwater, and to present strategies to eliminate nitrate pollution.

ACKNOWLEDGEMENTS

Research on nitrate in groundwater has been an on-going topic for decades and in the southern African region it was supported by several institutions while collaboration across country boundaries ensured progress in getting to grips with the issue.

Locally, funding for the research was provided by the Water Research Commission, CSIR and the Department of Science and Technology. Participants and collaborators are the Department of Geological Survey and the Department of Water Affairs, Botswana, the Federal Institute for Geosciences and Natural Resources (BGR), Germany, the Ministry of Agriculture, Water and Rural Development, Namibia, as well as the Department of Water Affairs and Forestry, South Africa, and the Department of Veterinary Science, University of Pretoria. All of these institutions made valuable contributions to the study of nitrate by providing data, logistics, and the funding of their own research.

NOTE

As it is customary in South Africa, nitrate concentrations in this publication are generally expressed as an equivalent quantity of nitrogen, i.e. NO_3 -N in mg/L. As some of the papers and maps were compiled also for use in the neighbouring countries using different conventions, some maps and graphs also show the equivalent concentrations expressed as nitrate (NO_3).

TABLE OF CONTENTS

Abstract	iii
Acknowledgements	iii
Introduction	1
Sources and distribution of nitrate in groundwater	1
Nitrogen cycle	1
Natural occurrence of nitrate in groundwater	2
Anthropogenic sources of nitrate in groundwater	3
Extreme variability of nitrate concentration in groundwater	4
Health hazards	5
Specifications for potable water and stocking watering	5
Nitrate toxicity	6
Methaemoglobinaemia	6
Nitrate poisoning: livestock losses	6
Action plan	7
Immediate action	7
Medium term action	8
Longer term action	9
Nitrate removal	9
Groundwater protection	9
Public awareness	10
Conclusion	11
Literature references	12
Appendix	13

INTRODUCTION

Elevated nitrate concentrations occurring in groundwater present a serious threat to infants and livestock. The presence of nitrates in groundwater is mainly perceived as a pollution problem, and in general this has been shown to be valid. However, nitrate deposits as well as high nitrate concentrations in groundwater are found in many arid and semiarid zones around the world. In most of these areas, recent anthropogenic impacts can be ruled out. Whereas nitrate pollution, which by definition is derived from anthropogenic sources, can be managed and be reduced, natural nitrate sources generally cannot be controlled and other means will have to be adopted for managing the nitrate content of the groundwater in such areas. This brochure describes the sources of nitrate in groundwater, lists the associated hazards, and provides guidance on the management of anthropogenic activities that cause nitrate pollution. In view of the complexity of the nitrogen cycle and the myriad of sources an understanding of the natural nitrate accumulation factors and pathways is essential. Such knowledge contributes to the successful management of nitrate concentrations in groundwater as the factors favouring natural accumulation are also expected to intensify the problems related to pollution-derived groundwater nitrate.

Nitrate in groundwater is a feature found in many regions and a significant part of the world population uses water with nitrate levels in excess of the World Health Organization (WHO) maximum drinking water standard. The WHO stated that evidence is accumulating that nitrate levels in many aquifers are increasing and that the problem of exposure of the world population to high nitrate inputs will become more pressing particularly in the developing nations (see WHO fact sheet in Appendix A). The increasing nitrate levels were recently demonstrated by a hydrogeological study at Ramotswa near Gaborone in Botswana (Staudt, 2003).

The full extent of the occurrence of methaemoglobinaemia amongst infants is unknown. Also, not all instances where livestock are lost due to nitrate poisoning are recorded either because the cause of death may not be recognised or due to the sensitive nature of livestock losses. It is the purpose of this booklet to bring the problem to the attention of the public at large in order to improve environmental management, to reduce groundwater pollution, and to prevent methaemoglobinaemia and stock losses.

SOURCES AND DISTRIBUTION OF NITRATE IN GROUNDWATER

Nitrogen cycle

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 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 viewed in terms of the nitrogen biogeochemical cycle (Diagram 1). Whereas nitrogen compounds in most environments play a beneficial role the presence of such compounds in water is generally detrimental.

Nitrogen inputs, whether due to natural fixation of nitrogen, fertilizer application, or pollution, all contribute to the pool of soil organic nitrogen. A series of (bacterially mediated) transformations are needed to convert the organic nitrogen to nitrate which could potentially be leached to the groundwater. Anthropogenic inputs increase the soil nitrogen pool to such an extent that leaching of nitrate is enhanced. This is also true for fertilizer application to land as well as the tilling of the soil which enhances the nitrification of soil organic nitrogen. Depending on the conditions in the unsaturated zone and in the aquifer, denitrification, i.e.

reduction of the nitrate to nitrogen is also possible. This is an important natural process which assists in maintaining the balance with respect to the nitrate in the groundwater.

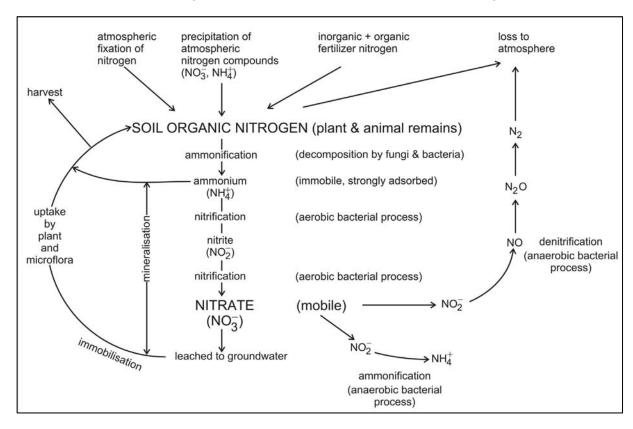


Diagram 1: The biogeochemical nitrogen cycle (Hiscock, Lloyd & Lerner, 1991)

Natural occurrence of nitrate in groundwater

Nitrate occurs extensively in groundwater in southern Africa. The map based on data for 50 000 groundwater sources (Figure 1) shows that elevated nitrate concentrations occur both locally at isolated points as well as in vast areas regionally extending over hundreds of kilometres. In the semi-arid to arid regions of the Northern Cape Province and Namibia significant groundwater nitrate occurrences are found in large areas where anthropogenic influences can be excluded. In these areas, the (human and animal) population density is very low but even confined groundwater with an apparent age of several thousands of years may have significant nitrate levels. Therefore, under natural conditions significant loss of nitrogen from the soil zone may occur in such climatic regions, causing enrichment of groundwater with high levels of nitrate. Various factors are involved, which may include the nature and thickness of surface deposits, rainfall quantity, and distribution, depth to the groundwater level, distribution of vegetation types and presence of nitrogen-fixing vegetation. High levels of "natural" nitrate only occur in groundwater, when most or all of the above factors are acting in unison. Natural disturbances of the plant cover, for example droughts (and possibly also bush fires) affect the nitrogen cycle, leading to nitrate leaching beyond the root zone, particularly during subsequent heavy rainfall events.

In the Australian arid zone nitrate occurrences were initially ascribed to biological nitrogen fixation, or a combination of nitrogen fixation and termite activity, and finally mainly to nitrate accumulation in termite mounds. Similarly, naturally high groundwater nitrate concentrations in the Sahel have been ascribed to leguminous vegetation and leaching of nitrate due to varying climatic cycles.

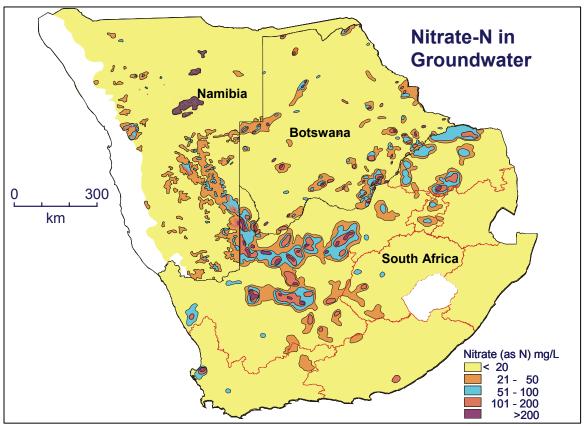


Figure 1: Map of southern Africa showing groundwater nitrate distribution

Anthropogenic sources of nitrate in groundwater

Apart from the natural sources of nitrate discussed above, most groundwater nitrates are derived from a wide range of anthropogenic sources. Anthropogenic generation of nitrate is well known and includes on-site sanitation, application of nitrogenous material to land, tilling of the soil, irrigation and other activities. Whereas agriculture is the main source of nitrate in the highly-developed countries such as Europe and the USA, on-site sanitation is seen as the main anthropogenic source of nitrate in Southern Africa. Groundwater pollution problems related to on-site sanitation have been known for decades in the southern African subcontinent and several studies have been carried out. These features can be seen in the nitrate map (Figure 1) as high nitrate levels around urban areas and also in the high-density rural settlements of the Northern Cape, Northwest, and Limpopo Provinces, South Africa, and in south-eastern Botswana.

In contrast, most other rural incidences are related to pollution point sources such as on-site sanitation, kraals, and other places where livestock congregate, especially at stock watering points, and feedlots. Non-point sources include manure and fertilizer application to land, and tilling of the soil, while deforestation and land clearing also provide significant nitrate addition to groundwater.

In the urban and peri-urban context sewage sludge drying beds at sewage farms and sludge "application" to land pose the greatest threat to groundwater, in addition to areas with inappropriate on-site sanitation.

Extreme variability of nitrate concentration in groundwater

The nitrate concentration in groundwater can vary over a very wide range depending on the aquifer and its recharge characteristics. Pollution derived from livestock congregation at feed troughs and watering points, as well as from on-site sanitation, generally enters into the unsaturated zone and collects above the water table. Only at the next rainfall event of sufficient magnitude the pollution is transported to the groundwater body and at that stage the groundwater quality may become degraded. In the semiarid to arid zones every one to two decades the seasonal rainfall far exceeds the mean annual precipitation. During such extreme events, large areas are flooded and the groundwater recharge processes are modified causing leaching of salts, including nitrates, which collected in the unsaturated zone over many years. This may affect the groundwater quality to such an extent that it becomes toxic to infants and livestock. Figure 2 shows an extreme example from Botswana where above average rainfall was experienced in the 1999/2000 rainy season and groundwater that was perfectly usable for stock watering became toxic to the livestock by September/October 2000. Some four years later the nitrate concentration returned to "normal".

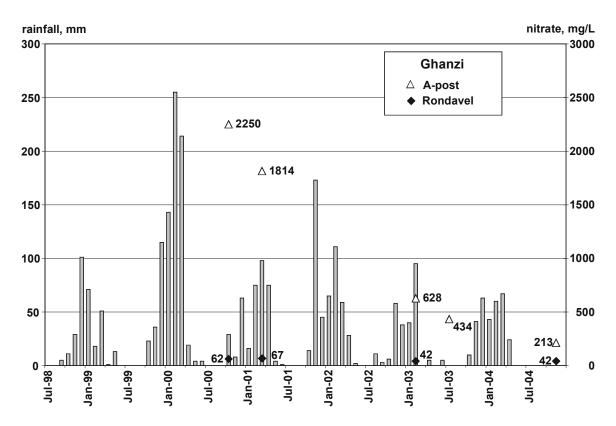


Figure 2: Rainfall and associated variation in nitrate concentrations (as NO₃) in groundwater

The extent of the rainfall event is shown in the pictures below where large areas in this arid landscape were flooded after the heavy rainfall (Figure 3). Groundwater recharge conditions differed totally from an average rainy season and caused the transport of nitrate from the unsaturated zone into the groundwater. Farmers and rural communities should be on the lookout for such events and be prepared to take action to protect their livestock and also other users of the groundwater.

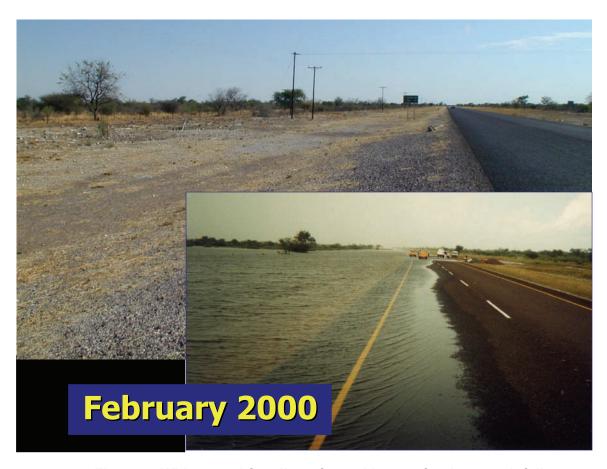


Figure 3: Widespread flooding of an arid area after heavy rainfall

HEALTH HAZARDS

Specifications for potable water and stock watering

The table below shows the specifications for nitrate in potable water in South Africa.

Nitrate-N specifications (mg/L) (DWAF)		
Potability class	ldeal	< 6
	Acceptable	6 - 10
	Marginal	10 - 20
	Poor	20 - 40
	Unacceptable	> 40
Livestock	Acceptable	< 110

The "ideal" and "acceptable" levels agree with the World Health Organization guidelines which are applied in most countries, and at these levels the health risk is negligible.

Nitrate toxicity

Nitrate as such is only not highly toxic to adults when ingested. The oral LD_{50} for sodium nitrate is 4300 mg/kg, which is equivalent to an intake of 300 g for a 70 kg person. On the contrary, nitrite, which is formed by reduction of nitrate, is highly toxic. The oral LD_{50} for sodium nitrate is 120 mg/kg, which is equivalent to an intake of only 8.4 g for a 70 kg person. Sodium nitrite, a salt used in meat processing, can, therefore, be fatal to **all**, i.e. also adults at intakes above the threshold.

Methaemoglobinaemia

Nitrate reduction happens in the digestive system of infants and livestock and hence they are at risk at high nitrate levels. The nitrite binds strongly to the haemoglobin in the blood causing the infant to suffer from methaemoglobinaemia which can be fatal. Should the water also be bacterially polluted, as is generally the case with pollution from on-site sanitation, e.g. septic tank overflow, the illness is often fatal. The condition can be recognised by the colouration of the lips and other body parts and hence the term "blue baby syndrome" is widely used. In the case of sub-lethal levels (nitrate-nitrogen < 20 parts per million, i.e. ppm or mg/L), children may show symptoms of "failure to "thrive", headache, fatigue, shortness of breath, and lack of energy. For mothers ingesting higher nitrate water there is an abortion risk or the chance of stillbirth.

The "blue baby syndrome" is often not recognised as such, however in mild cases if it is correctly identified the infant can be treated with methylene blue intravenously, or with ascorbic acid, and can make a full recovery. Alternative treatments include hyperbaric oxygen therapy, while in severe cases exchange blood transfusions are indicated.

NITRATE POISONING: LIVESTOCK LOSSES

In several instances nitrate poisoning has been identified as the cause of stock losses. This generally happened after periods of very heavy rainfall when some months after the event groundwater that was perfectly suitable for potable use becomes laden with nitrate and other salts, and often also harmful bacteria. Examples of recorded losses confirmed as nitrate poisoning are:

1969: Namibia: Tens of livestock 1969: Texas: 2 *HERDS* of cattle 1974: Namibia: hundreds of livestock 1989: South Africa: 147 heads of cattle 2000: Botswana: >356 heads of cattle 2001: South Africa: >60 heads of cattle 2002: Botswana: 48 heads of cattle

Not all instances where livestock are lost due to nitrate poisoning are recorded as the cause of death may not be recognised and in addition livestock losses are a very sensitive issue. It is therefore important for the public at large to be aware of the problem in order to improve environmental management, particularly to reduce groundwater pollution, and to prevent methaemoglobinaemia and stock losses.

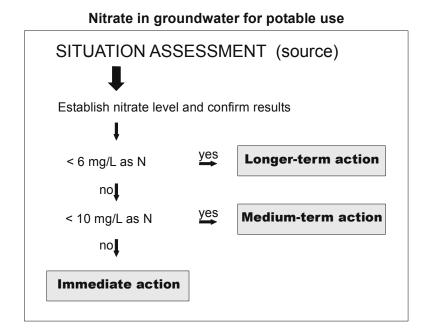
Nitrate poisoning is characterised by a brown colouration of the blood of the affected animal and the colour change can also be seen on mucous membranes and other body parts. At sub-lethal levels of nitrate (but often above 110 parts per million as nitrogen) abortion and poor milk production have been recorded for lactating cows.

ACTION PLAN

An action plan was devised for guiding the response to nitrate occurrences and for managing the nitrate concentration in groundwater.

Measuring nitrate:

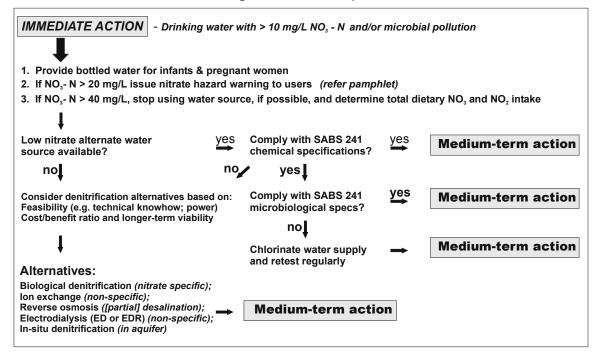
The action plan is based on the groundwater nitrate concentration. This is best determined by laboratory analysis. However, sample preservation between sampling and analysis is essential (consult with laboratory). For a rough, on-site indication of the nitrate level, nitrate test strips (obtainable from chemical companies) may be used but caution is needed as it is essentially a qualitative measurement while the value is indicated as parts per million of nitrate (i.e. not as nitrogen).



Immediate action

As set out in the specifications, if the groundwater nitrate exceeds 10 mg/L (as nitrogen) the water is of marginal quality. However, if the nitrate concentration exceeds 20 mg/L, or if the water is bacterially polluted, immediate action is needed. All users should be alerted to the risk and nitrate-free and bacterially safe bottled water provided for infants and pregnant women. If the nitrate exceeds 40 ppm, use of the source should be terminated and an alternative nitrate-free supply found (see below) or denitrification measures implemented. Bacterially polluted water should be disinfected, e.g. chlorinated.

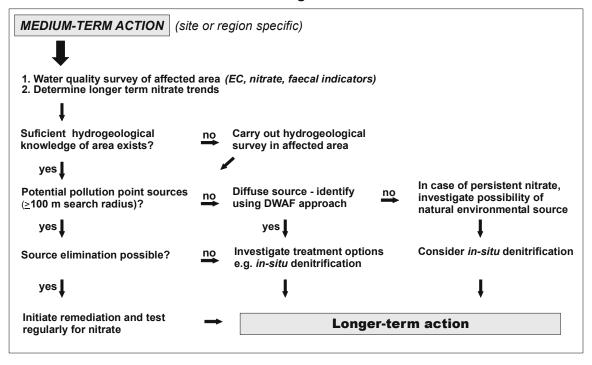
Nitrate in groundwater for potable use



Medium term action

When nitrate exceeds 10 mg/L but is less than 20 mg/L, it can still pose a threat to certain users, e.g. immune compromised individuals, particularly infants. In such cases, all potential nitrate sources, e.g. septic tank soakaways, stock watering points, etc., need to be identified. Should such pollution point sources exist then relocation of the borehole or well will be necessary.

Nitrate in groundwater



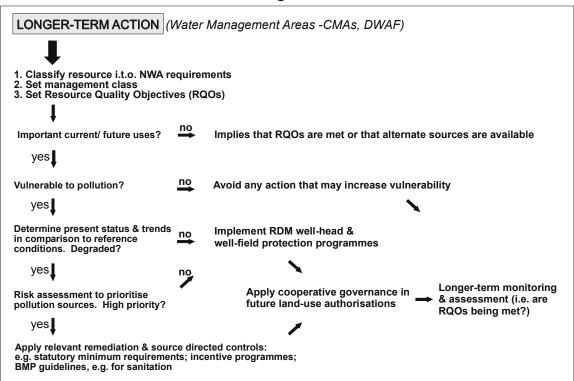
Longer term action

Should the nitrate concentration exceed the recommended potability level of 6 mg/L, and pollution sources can be identified, further action may be needed, e.g. relocation of the well or borehole, longer term monitoring of the nitrate levels, etc. In the case of regionally elevated nitrate in groundwater, other measures may be needed for which expert advice should be sought.

Nitrate removal

Removing nitrate from water is generally not easy. For potable purposes nitrate may be removed non-selectively by ion-exchange or by desalination, i.e. removing all salts from the water, e.g. by reverse osmosis. Biological denitrification, a nitrate-specific method, is used widely in treatment plants abroad but all these processes require considerable technical know-how. Therefore, for potable purposes in the rural situation it may be preferable to find an alternate supply as explained above. For town supply, denitrification, also by in situ treatment methods, i.e. in the aquifer, may be considered.

Nitrate in groundwater



GROUNDWATER PROTECTION

The management and reduction of groundwater nitrate levels depend on an understanding of the nitrogen sources and the pollution and nitrification mechanisms. A successful groundwater protection strategy has to consist of a dual approach, i.e. legislation and control consisting of pollution control legislation supported by effective law enforcement, as well as education and public awareness programmes for resource protection in rural areas. In rural areas the communities and farmers have to take their own resource directed protection measures as these are for their own benefit. That is also the purpose of this little flyer namely to distribute knowledge and to generate an interest in resource protection at all

levels. Communities and farmers are encouraged voluntarily to take all necessary steps that will ensure a reduction in environmental nitrogen inputs, particularly avoiding nitrate leaching to groundwater.

Public awareness

A public awareness and education programme forms an essential part of the groundwater protection strategy. This is a key component that will ensure the success of the legislative and pollution control approach for reducing nitrogenous inputs to the environment. The fact is that not all polluting activities in remote areas can be controlled by the authorities. For this reason, the public, including the farming community and other rural communities have to be convinced to own groundwater resources.

CONCLUSION

The occurrence of nitrate in groundwater is a serious problem. Nitrate in groundwater can be derived from various sources which can be grouped into two main categories:

- anthropogenic nitrogenous pollution, and
- natural nitrate accumulation, primarily present in arid and semiarid regions.

In the highly-developed countries the main anthropogenic source is agricultural nitrate, largely derived from excessive fertilizer and manure applications. Such sources are controllable and in Europe strict measures are in place for limiting the nitrogen fertilizer and manure application rates. In South Africa the data show that this widespread diffuse source generally only provides a relatively low background concentration of nitrate in the water, largely derived from the soil nitrogen pool due to the tilling of the soil. Pollution point sources are generally associated with specific activities, e.g. sewage sludge drying beds, land application of sludge, and irrigation of (partly) treated wastewater. At the large cities, high levels of sewage sludge application to land have caused serious groundwater pollution.

The above confirms that the main source of nitrate in groundwater is anthropogenic pollution but such nitrate inputs are manageable. In the rural setting voluntary action regarding nitrate management is essential, but overall legislation and control are also needed. Nitrate removal may be feasible in certain instances but generally expert advice and technological input will be required.

LITERATURE REFERENCES

- Hiscock, K M, Lloyd, J W & Lerner, D N, 1991. Review of natural and artificial Denitrification of groundwater. *Wat. Res.*, **25** (9), 1099 1111.
- Spalding, R. F. and M. E. Exner (1993). Occurrence of nitrate in groundwater A review. *Jour. Environm. Qual.*, **22**, 392 402.
- Staudt, M 2003. Environmental Hydrogeology of Ramotswa. Report by the Environmental Geology Division, 47 p., Dept of Geological Survey (DGS), Lobatse, Botswana.

AVAILABLE NITRATE RELATED WRC REPORTS

WRC Report 1058/1/04.

Tredoux G. Nitrate and associated hazard quantification and strategies for protecting rural water supplies.

WRC Report 1467/2/05

Cullis J; Rossouw JN; Görgens AHM. First order estimate of the contribution of agriculture to non-point source pollution in three SA catchments: Salinity, Nitrogen and Phosphorus.

WRC Report 1696/1/08

NZ Jovanovic, A Hon, S Israel, D Le Maitre, F Rusinga, L Soltau, G Tredoux, MV Fey, A Rozanov and N van der Merwe. Nitrate leaching from soils cleared of alien vegetation.

WRC Report 368/1/93

Tredoux G. A preliminary investigation of the nitrate content of groundwater and limitation of the nitrate input.

APPENDIX

World Health Organization (WHO)

Water-related Diseases: Methaemoglobinaemia

Water-related diseases

Methaemoglobinaemia

Methaemoglobinaemia caused by the decreased ability of blood to carry vital oxygen around the body. One of the most common causes is nitrate in drinking water. It is most important in bottle fed infants and water from wells in rural areas is of special concern. Controlling nitrate levels in drinking water sources to below around 50mg/litre is an effective preventive measure.

The disease and how it affects people

Methaemoglobinaemia is characterized by reduced ability of the blood to carry oxygen because of reduced levels of normal haemoglobin. It is uncommon. Infants are most often affected, and may seem healthy, but show signs of blueness around the mouth, hands, and feet, hence the common name "blue baby syndrome". These children may also have trouble breathing as well as vomiting and diarrhoea. In extreme cases, there is marked lethargy, an increase in the production of saliva, loss of consciousness and seizures. Some cases may be fatal.

In the body nitrates are converted to nitrites. The nitrites react with haemoglobin in the red blood cells to form methaemoglobin, affecting the blood's ability to carry enough oxygen to the cells of the body. Bottle-fed infants less than three months of age are particularly at risk. The haemoglobin of infants is more susceptible and the condition is made worse by gastrointestinal infection. Older people may also be at risk because of decreased gastric acid secretion.

Malnutrition and infection seem to increase the risk of methaemoglobinaemia (McDonald and Kay, 1988). The general health of the infant as well as Vitamin C intake may determine whether or not the condition develops (Super et al, 1981).

Others at risk for developing methaemoglobinaemia include: adults with a hereditary predisposition, people with peptic ulcers or chronic gastritis, as well as dialysis patients.

The cause

The most common cause of methaemoglobinaemia is high levels of nitrates in drinking-water. High nitrate levels may be present in drinking-water due to the use of manure and fertilizers on agricultural land. The natural level of nitrites and nitrates from the environment is normally a few milligrams per litre, although high levels may occur naturally in some areas. Intense farming practice may increase this to more than 50 mg/litre (WHO 1998). Levels greater than 50 mg/litre, are known to have been associated with methaemoglobinaemia in bottle fed infants. Nitrate is also found in vegetables. Methaemoglobinaemia can also be a side effect of some drugs (phenacetin and sulphonamides), although this is very rare with modern drugs.

Scope of the Problem

Methaemoglobinaemia is now rare in most of the industrialised countries due to control of nitrate contamination in water supplies, although occasional cases continue to be reported

from rural areas. It is a risk in developing countries, for example where the drinking water is from shallow wells in farming areas.

There is no reliable estimate of the extent of the problem worldwide. WHO is presently collecting information in order to make such an estimate.

Interventions

Control of nitrate in drinking water is an effective preventive measure. WHO's Guideline Value for nitrate in drinking water is 50 mg /litre and for nitrite is 3 mg/litre. This is relatively readily achieved in centralised, piped, supplies, but is difficult in rural and small supplies.

The group at greatest risk is bottle fed infants. Breastfeeding protects babies from methaemoglobinaemia. Boiling water does not remove nitrate.

For severely affected individuals, medical treatment is possible.

References

McDonald A T, Kay D. Water resources issues and strategies. UK: Longman Scientific and Technical, 1988, p 146-148

Super M, Heese HV, Mackenie D. An epidemiological study of well water nitrates in a group of South West African /Namibian infants. Water Research, 1981: 15: 1265-70

World Health Organization. WHO Guidelines for drinking water quality. 2nd edition, addendum to Volume 1: Recommendations. Geneva: WHO, 1998, p-8-10; and addendum to Volume 2: Health Criteria and other Supporting Information.

Prepared for World Water Day 2001. Reviewed by staff and experts from the Programme for Promotion of Chemical Safety (PCS), and the Water, Sanitation and Health unit (WSH), World Health Organization (WHO), Geneva.

Appendix: © Copyright 2004 World Health Organization

Appendix reprinted with permission from the World Health Organization