THE WATER RESEARCH COMMISSION
Pretoria, South Africa

WORKSHOP REPORT

FLUORIDE & NITRATES IN RURAL WATER SUPPLIES:

Health issues and removal techniques

March 9-10, 1999

WATER RESEARCH COMMISSION

WORKSHOP REPORT

ORGANISERS

Dr IM Msibi - Water Research Commission
Dr A Kühn - IWQS
Dr JJ Schoeman - CSIR
Prof F Schutte - University of Pretoria
Mr F Mafete - N-West Water Supply

1. Introduction

AIMS AND FORMAT OF THE WORKSHOP

The workshop had the following aims:

- The extent of fluoride and nitrate problems in rural water supplies
- Health effects of fluoride and nitrates in drinking water
- Processes & techniques for the removal of fluoride & nitrates from water

The first day will consisted of presentations by various researchers and specialists in the field to establish current status. During the second day the main focus was on Group Discussion which should lead to the formulation of a strategy for the way forward and establish urgent research needs.

PURPOSE OF THIS REPORT

The purpose of this report is to document the proceedings of the workshop held in Mmabatho from 9 t0 10 March, 1999. It will outline mainly the discussions and resolutions from that workshop. Further it is hoped that the details given in this report will help researchers identify priority areas for project proposal submission before the end of April, 1999.

2. Workshop Programme

9 March, 1999

08:45 Registration
09:30 Welcome **Dr M Sefularo** : MEC for Health & Developmental Social Welfare, NW

Session One: Water Quality and Health **Chair: Dr A Kühn**

09:40 "Fluoride and Health" *Prof Du Plessis*
10:10 "Nitrate and Health" *Dr P Kempster*

10:40 **TEA AND COFFEE**

11:00 Acute and chronic nitrate toxicosis in farm animals with special reference in clinical signs. *Dr J Myburgh*

11:30 An investigation into the fluoride status of ruminants in the North West Province. *Ms H Els*

11:50 Risk assessment modeling for commercial and rural livestock production systems exposed to fluorides & nitrates in drinking water *Dr JA Meyer / Prof NH Casey*

12:30 **LUNCH**

Session Two: The Extent of the Problem Chair: Dr N Mjoli

13:30 Dependency of communities on groundwater for water supply and associated nitrate and fluoride problems *Mr S Marais*

14:00 Effects of Fluoride on the self concept of the adolescence in the N/West Province. *Badu Mothusi*

14:30 Institutional arrangements and management of water quality problems in water supply. *Mr F van Zyl*

15:00 Utilizable ground water in the North-West Province. *Mr F Vogel*

15:30 **TEA AND COFFEE**

15:45 Fluoride concentrations in surface water. *Dr J Harris*

16:15 Nitrates in Groundwater. *Dr G Tredoux*

10 March, 1999

Session Three: Removal Processes & Techniques Chair: Mr J Bhagwan

8:00 Overview processes for the removal of fluoride from water; Case studies. *Dr JJ Schoeman*

08:40 Membrane and biological removal processes for the removal of nitrates from water; Case studies. *Prof CF Schutte*

09:10 Ion exchange resin for removal of nitrates from water. *Mr ED Hardwick*

09:40 Promising approaches in the removal of nitrates & fluoride in rural drinking water supplies *Mr C Chibi/Mr D Vinnicombe*

10:15 **TEA AND COFFEE**

Session Four: Group Discussion. Chair: Mr K Pietersen

10:45 Delegates will participate in discussions in any of the three groups:

Group A	Extent of the problem
Group B	Technological interventions and research needs
Group C	Institutional, Planning and Management issues. Capacity building and other considerations.

12:45 **LUNCH**

13:40 Report Back and Conclusion

15:00 **TEA AND COFFEE**

FACILITATORS:
J Bhagwan
N Mjoli
I Msibi
K Pietersen

3. Workshop Report:

Details, in the form of papers presented are given in appendix 1.

4. Discussion Sessions

A. EXTENT OF THE PROBLEM

Identifying the problem: Recommended Research issues.

- Identifying contribution factors and locating them
- monitoring fluorides over a time period.
- accessibility of data/interpreted results
- research into natural accumulation of NO_3
- investigate linkage between usage of pit latrines and NO_3 level.
- Research on people affected with skeletal fluorosis and also infants affected with blue baby syndrome
- Information on number of people affected by high levels of NO_3 including animals
- Intensive study to evaluate the socio-economic impact/implications of fluorosis
- Reduce the risk associated with high fluoride intake but without reducing the beneficial effect of fluoride in H_2O.
- Get more information on the prevalence of "blue-baby" syndrome and move research to be done in the nitrates level in different areas.
- Need for research to get data on people affected by skeletal florists
- No. of people affected and impact on animals on high nitrate/fluoride levels needed
- AWARENESS campaigns on problems of high nitrates and fluoride levels nationally, provincially and regionally.

B. TECHNOLOGICAL INTERVENTIONS AND RESEARCH NEEDS

1. Prevention

At source
-Economics
-Well-head protection
-Proper sanitation
-Training/education
-Borehole location

2. Treatment

O + M + C costs (research to reduce the costs)
Willingness to pay (when understanding reason)
Ease of operation - simplicity
Robustness
Aesthetics
Risk (pathogenic)
Appropriate quality (trace elements, organics)

3. Treatment Options

Use of

a) clays (sesquioxides, etc CAC/AEC)
b) Bone char - low cost sources?
c) Catalytic treatment (costs, risk?)
d) Biological treatment
   slow sand
   peat?
   anaerobic/anoxic/aerobic
e) Electrolytic processes - research costs etc.
f) Lime - alum treatment (Fl)
g) Naturally - occurring absorbents e.g. Bauxites, charcoal, dolomite, iron-oxide sands
h) Recycling of potentially suitable treatment media (eg. Eskom resins)
i) Point-of-use canisters
j) Membrane technologies - afford ability?

C. INSTITUTIONAL, PLANNING AND MANAGEMENT ISSUES. CAPACITY BUILDING AND OTHER CONSIDERATIONS

1. Community Awareness and Capacity Building

Fluoride & Nitrates how they affect:

- people/humans
- plants, &
- animals

Perception of the problem by community:

- cannot taste fluoride and nitrates
- cannot see fluoride and nitrates in water,

Information:

- community needs to be informed
- not only on fluoride and nitrates but on all aspects relating to water.

2. **What needs to be done**?

Monitoring:

- efficient monitoring
- convey results to communities
- involve students in monitoring
- use of portable water sampling kits

Appropriate tools:

- printed: posters, leaflets, guidelines, etc.
- electronic: panel discussions, talks, phone-in
- do not forget school children
- wider prog's:
  - competitions
- do not only focus on the negative aspects of water quality
- develop village structures
- strengthen community structures to address water problems at local level.

3. Institutional Problems and Recommendations

Lack of info/co-ordination

Fragmentation in sector

Lack of capacity, HR & info.

Prioritization of info

- Development of appropriate comm. process : Auth - comm.
- Development of tools
- Development of inter-sect. Strategies and process to facilitate in addressing the problem
- Development capacity at local level
- Develop <u>a model</u> to address the problem

4. Policy Issues

a To develop an integrated
- water
- health
- agriculture
- environment

database.

b Co-ordinate existing data bases

c Planning guides

d Involve DC's, VC's (protocols)

e Re-look at existing regulations; then develop new regulations

f Financial resources

g People-driven processes based on understanding.

APPENDIX 1

FLUORIDES AND HUMAN HEALTH

INTRODUCTION

According to the World Health Organization water fluoridation is the most cost-effective and safe preventive measure that can be implemented. The reason for this being that once implemented it reaches everybody in the target community at a minimum cost. It is very effective in that it will reduce the dental caries in any community by at least 50 to 80 percent. It is very safe in the sense that more than 200 million people are currently using fluoridated water, some for more than 50 years and not a single case of adverse effect could be proved. However, due to the fact that once implemented in a community, everybody is more or less forced to use the water, resistance against water fluoridation developed, and many objections and allegations as to its effectivity, safety and ethics have been made. The result is that many water fluoridation schemes never got further than the planning stage, and thus millions of people are still deprived of this wonderful preventive measure.

HISTORY

The role of fluoride in the development of dental fluorosis and in preventing dental caries was discovered over many decades during the first half of the 20th century. This was mostly done in the USA by people like Drs. F.S. McKay and H.T. Dean. In South Africa these developments were closely observed, and after pressure from the dental fraternity the Government of the day, in 1964, appointed a commission to investigate all the aspects of fluoridation. Of the seven members of the committee, only two had a dental background. The commission presented its report to the State President in 1966 and recommended the following:

1. Steps should be taken to encourage and assist local authorities to fluoridate the water supplies of their communities as soon as possible.

2. Local fluoridation schemes should aim to achieve an optimal concentration of fluoride in the drinking water for the prevalent weather conditions

3. Steps should be taken to assist local authorities in areas, where the fluoride content in the drinking water is more than double the maximum concentration, to reduce the fluoride content to the appropriate level.

4. In areas where drinking water containing more than double the maximum amount of fluoride is obtained from bore holes the consumers should be advised and helped to reduce the fluoride content.

5. Steps should be taken to inform consumers of fluoride deficient water of the best means of obtaining the beneficial effects of fluoride.

6. Where fluoridation is practiced the average fluoride concentration should be kept between the upper and lower control limits as set out in recommendation 2.

7. Regulations should be framed to control the practice of fluoridation.

8. Local authorities should be legally authorized to decide whether or not the public water supplies over which they have jurisdiction should be fluoridated. Their decision to fluoridate should not necessarily be subject to public voting.

Despite the many reminders and other efforts by the dental fraternity to get the government to act on this recommendations the government was reluctant to anything about this. It was only after the Government of National unity came into power in 1994 that a committee was appointed to prepare the regulations that would make water fluoridation a reality in South Africa.

FLUORIDE HOMEOSTASIS

The human body maintains the serum level of fluoride between 0,15 and 0,2 ppm. The main source of fluoride is the diet, and it is only in exceptional circumstances that fluoride in the air contributes significantly to the fluoride "intake" (In South Africa such a situation was encountered in Richards Bay in the vicinity of the aluminum foundry.) The main contributor of fluoride to the diet is the water we consume. Again it is only in exceptional circumstances that other foodstuffs contribute significantly to the fluoride intake. Up to the age of 5 years the optimal intake of fluoride is 0,05 mg per kilogram of body weight per day. After the age of 5 this amount can safely be quadrupled. Fluoride supplements to the diet is available in the form of tablets, drops and fluoride containing tonics and vitamin supplements.

When a normal dose of fluoride is taken, most of it is absorbed from the stomach into the circulating plasma. It happens as a passive diffusion process driven by concentration and pH gradients. The concentration in the plasma rises and fluoride quickly diffuses into the extra vascular fluid compartment and from there into the intracellular fluid compartment. At the same time the kidneys start to concentrate fluoride from the circulating plasma into the urine and soon most of the fluoride is excreted in this way. Fluoride in the intracellular fluid of the osteoblasts, odontoblasts and especially the ameloblasts is then incorporated into the new bone, dentine and enamel being formed by these cells. Apart from the fluoride excreted in the urine, fluoride is also excreted into saliva, digestive juices in the intestines, sweat, and in the case of pregnant women, through the placenta to the fetus and after birth into the milk. In periods between meals and/or drinks when no fluoride is taken in, fluoride is released from bone by osteoclastic activity and move into the intracellular fluid of the osteoclasts, form where it moves to the extra cellular fluid compartment and from there back to the circulating plasma, thus maintaining the normal fluoride concentration in the plasma. These homeostatic mechanisms can tolerate relative large single doses of fluoride. If the fluoride intake is spread evenly over the day, even larger doses can be tolerated over short periods. In general terms the body will accumulate fluoride until the age of about 55 (positive fluoride balance).There after the fluoride excretion equals the intake up to about the age of 75. At the older ages the body goes into a negative fluoride balance (excreting more fluoride than what is being taken in) as the skeleton begins to be less densely mineralized.

Fluoride derived from the water we consume forms the bulk of the total fluoride intake. It is therefore obvious that conditions that will lead to a higher consumption of water will significantly increase the fluoride intake. Such conditions are the normal variation in water intake due to the variation in the average maximum day air temperature of an area, and pathological conditions such as diabetes insipidus.

FLUORIDE TOXICITY

In the USA 1% of the deaths due to poisoning can be attributed to fluoride. For a 70 Kg person the minimum lethal dose (Mld.) of fluoride is 2,5 grams. The single dose that will kill 50% (ld50) of people of 70 Kg is 5 grams. Symptoms of acute fluoride poisoning occur when a single large dose of fluoride is taken. The smallest dose known to have caused acute poisoning was 200 mg. Symptoms of acute poisoning can last from a few minutes to two or three days, depending on the dose that was taken. In severe cases permanent damage can be done to the kidneys, liver and digestive tract.

Chronic fluoride poisoning can occur with the continuous intake of large quantities of fluoride. The smallest dose likely to produce soft tissue injury to the kidneys liver and intestinal tract is 100 mg per day for six months or longer. 20mg per day for 20 years or more will produce disabling skeletal fluorosis, while 8 mg. per day for 20 years or more will produce radiological evidence of skeletal fluorosis, without any clinical disability. The dose likely to produce objectionable dental fluorosis in a small percentage of children is more than 2 mg. per day for the duration of enamel formation in pre-eruptive teeth. (> 0,1 mg per kilogram of body weight before the age of 5.) It is generally accepted that children suffering from protein-carbohydrate malnutrition will be slightly more sensitive to the fluoride concentration and will develop dental fluorosis at a slightly lower dose. It is also postulated that children living at a higher altitude above sea level will also develop dental fluorosis at a slightly lower dose of fluoride.

OPTIMAL FLUORIDE DOSIS

The optimal amount of fluoride in the diet is that amount that will give maximum prevention of caries without causing objectionable dental fluorosis. Local circumstances can influence this optimal amount. More precisely, it can be defined as that amount that will ensure a fluoride intake of 0.05 mg/Kg body weight by children during the critical age of enamel formation. (That is from 0 to 5 years of age.)

FLUORIDES AND DENTAL CARIES

There are at least four different mechanisms by which fluoride prevents dental caries. Depending on the circumstances these mechanisms can act separately or jointly.

Firstly if the optimal amount of fluoride is consumed during the periods when tooth enamel is being laid down and while the enamel is being mineralised and matured by the ameloblasts, before eruption of the tooth into the oral cavity, some of the hydroxyl ions of the calcium hydroxy-apatite crystals are being replaced by fluoride ions. This tends to stabilize the crystals and make them more resistant to acid demineralisation. (Calcium hydroxy-apatite crystals will start to demineralise at a pH of 5,7, while calcium hydroxy-fluoro-apatite will only start at pH 5 or lower.) The initial stage of dental caries is a demineralisation of the enamel crystals as a result of the low pH created by acids produced by the oral microorganisms when they ferment sugars and refined carbohydrates. This process is retarded if not prevented by the fluoride in the enamel crystals.

Secondly, because of the high affinity of fluoride for calcium and phosphate, ionic exchange takes place on the surface of the enamel crystals after the eruption of the teeth in the mouth. Hydroxyl ions are being replaced by fluoride ions, thus making the enamel more resistant to demineralisation. This process is greatly enhanced if the enamel is first slightly demineralised by acid. This means that an initial carious lesion will be remineralised once the acid causing the demineralisation is removed. The resultant enamel crystals are now highly resistant to acid demineralisation. The fluorides responsible for this mechanism normally comes from the saliva and this process is very much enhanced by extra fluoride provided in the form of fluoridated toothpaste during tooth brushing.

Thirdly, the bacteria responsible for the acid production on the tooth surface is normally tightly packed in a thin layer on the tooth surface known as dental plaque. Plaque normally contains high concentrations of calcium and phosphates and as a result fluoride tends to accumulate in the plaque. The fluoride concentration in the plaque can reach such high levels that two very important enzyme systems of the bacteria are being blocked. Firstly the enzyme responsible for the formation of extra cellular dextrans is blocked. These dextrans which are now not being formed plays a very important role in keeping the plaque layer intact and attached to the tooth surface. With no dextrans the plaque bacteria are being washed off the tooth surface and swallowed with the saliva. Acids produced by the bacteria are also quickly diluted and neutralized by the saliva.

Fourthly the second bacterial enzyme being blocked by the high levels of fluoride is necessary for the acid production. Thus the fluoride actually retards acid production and therefore demineralisation of the enamel.

The question now is how effective is fluoride in preventing dental caries. When water fluoridation was first introduced in the USA and other Western countries, studies showed a 60 to 80 percent reduction in the caries experience of children. In all studies the permanent teeth benefited more than the primary teeth. After the introduction of other methods of fluoridating the mouth (such as the use of fluoride tablets, fluoride mouth rinses, fluoride applications, fluoridated toothpaste, fluoridated salt etc.) the effect of water fluoridation diminished to about 40 to 50 percent. The effect of these other methods singly or combined could reduce caries experience by 30 to 50 percent.

In South Africa the situation is that about 10 to 15 percent of the population is in a position where they can afford to buy the fluorides that they need in one form or another for the prevention of dental caries in themselves and their families. The other 85 percent of the population cannot afford to buy fluorides (which is at least 100 times more expensive than water fluoridation). They are in the same position where the people in the Western world was before water fluoridation was introduced. This was dramatically illustrated by the results of the National Oral Health Survey of 1989 and a survey conducted in the Free State Goldfields in 1991. In the White population the caries experience in the Free State Goldfields (fluoride content of the water = 0,54 ppm) was 45 percent lower than in the southern coastal areas (fluoride content of the water < 0.05 ppm). In the Black children the caries experience in the Free State Goldfields was 84 percent lower than in the southern coastal areas. It is therefore clear that the maximum benefit of water fluoridation will go to exactly the population group that needs it most.

WHAT IS THE OPTIMUM CONCENTRATION OF FLUORIDE IN THE WATER FOR SOUTH AFRICAN CONDITIONS?

Epidemiological work done in the Free State Goldfields during 1991 and 1992 revealed that for the high veld of South Africa, taking into account the annual average daily maximum air temperature, the altitude above sea level, the nutritional status of the children, and the availability of other forms of fluoridating the mouth, 0,55 ppm is the optimum concentration of fluoride. The safe maximum concentration is 0,7 ppm and at 0,9 ppm objectionable dental fluorosis will definitely occur. These values will be valid for the South African high veld areas, but it will have to be very carefully monitored in the hotter parts such as Pretoria, Soshanguve, Brits and Rustenburg areas where the climate is definitely hotter. It is expected that slightly higher concentration can be utilized in the southern coastal areas. Research is currently being done in Port Elizabeth to try to determine the exact values. The Natal coastal areas, especially Durban and the north coast will have to start with lower concentrations and slowly build up as evidence of safety is gathered.

Prof. J.B. du Plessis
Emeritus: Dept. of Stomatological Studies
Medunsa.
1998-05-19

Nafwork.doc

WHAT NITRATE CONCENTRATIONS ARE SAFE FOR AN INFANT TO DRINK?

Below 26mg/L NO_3 (6mg/L as N) is completely safe for all infants, even those at risk.

Below 44mg/L NO_3 (10mg/L as N) is safe for almost all infants. Mild symptoms may appear but will be extremely rare.

At 89mg/L NO_3 (20mg/L as N) is safe for all otherwise healthy infants. Mild symptoms (e.g., mild chronic effects) may occur in some susceptible infants. I.e., the severely malnourished infant is at slight risk.

At 177mg/L $N0_3$ (40mg/L as N) no effects in otherwise healthy infants, but more noticeable chronic effects in the susceptible group., Rare cases of the acute methaemoglobinemia syndrome may occur.

Above 177mg/L (i.e., >40mg/L as N) no effects in otherwise healthy infants, but group with achlorhydria definitely at risk of developing the acute sydrome, which can be life threatening.

Above 1800mg/L (i.e., >400mg/L as N) all people at risk of severe acute toxicity from the direct toxic effects on nitrate per se. Concentrations of this magnitude are uncommon in drinking water.

SUMMARY OF POTABLE WATER HEALTH EFFECTS ASSESSMENT GUIDELINES FOR NITRATE.

BLUE CLASS: <6 mg/L N (26 mg/L as NO_3) – ideal.
GREEN CLASS: 6 to 10 mg/l N - insignificant risk.
YELLOW CLASS: 10 to 20 mg/L N - slight chronic risk to some babies
RED CLASS: 20 to 40 mg/L N - Possible chronic risk to some babies.
PURPLE CLASS: >40 mg/L N - Increasing acute health risk to babies.

ACUTE AND CHRONIC NITRATE TOXICOSIS IN FARM ANIMALS WITH SPECIAL REFERENCE TO CLINICAL SIGNS

J G MYBURGH

INTRODUCTION

Nitrogen can exist in four states of oxidation. The level of toxicity varies with the state. Ammonia is a toxic gas; nitrogen is an inert, nontoxic gas. Nitrates are relatively nontoxic. Nitrites are more toxic. The toxicity depends on the ability to produce nitrite from nitrate. Acute or chronic nitrate poisoning can occur in various animals, including livestock.

MECHANISM OF ACTION

Reduction of nitrate to the more toxic nitrite is an intermediate step in the bacterially mediated biochemical sequence of the formation of fully reduced ammonia. This reduction reaction takes place in the large stomach (rumen) of ruminants and in plants.

Nitrate
↓ (*nitrate reductase*)
Nitrite – toxicosis/poisoning
↓
Ammonia

The relatively toxic nitrite ion can be absorbed into the blood stream where it oxidizes normal ferrous iron (Fe^{2+}) in hemoglobin to the ferric state (Fe^{3+}), forming methemoglobin. Methemoglobin is unable to carry oxygen.

CLINICAL SIGNS

Acute nitrate poisoning

When nitrite is ingested preformed, the effects are rapid. When conversion of nitrate to nitrite occurs in the rumen there is a delay of a few hours before clinical signs are apparent. In cattle maximum methemoglobinemia usually occurs about 5 hours after high levels of nitrate begin to accumulate. Nitrate levels of 1500 mg/l and higher in water could cause acute deaths.

In acute poisoning there may be sudden death without affected animals showing any clinical signs. Death usually occurs within 12 to 24 hours of ingestion of the toxic plant material. Pregnant animals may abort their foetuses.

Gastrointestinal disturbances

Salivation, abdominal pain, diarrhea (irritant effect of NO_3), vomiting (even in ruminants).

Oxygen deprivation

Increased respiratory rate and heart rate, dyspnea, gasping, cyanosis, mucous membranes: brown and pale.

Cerebral anoxia
Ataxia, muscle tremors, weakness, incoordination (cattle in particular are very reluctant to move), convulsions.

Chronic nitrate poisoning
Field reports and experimental studies have incriminated chronic sublethal nitrate poisoning as a causal or contributing factor in various clinical manifestations, including reproductive problems, interference with iodine and vitamin A metabolism and reduced growth and production. These disorders do not necessarily occur on every farm where nitrate containing feeds are used. Chronic poisoning by nitrates is evident on certain farms under certain conditions. Intake of water with 150 mg/l of nitrate, over a long period, could cause chronic nitrate poisoning.

Reproductive disorders
Excessive maternal exposure to nitrate/nitrite may be a cause of late gestation abortions. Feed nitrate concentrations of about 1% are considered potentially toxic to cattle. Field cases of bovine abortion have been associated with feed containing as little as 0.52 % nitrate. Heavy fertilization associated with cool, cloudy growing conditions is conducive to nitrate accumulation.

Placenta transfer of oxygen may be reduced severely with consequent hypoxia and intrauterine death of the fetus in nitrate poisoned cows. Further adverse effects of nitrite include its vasodilatory action.

Nitrite-induced fetal hypoxia could result in abortion due to anoxia death of the fetus as well as due to the activation of the fetal adrenals. Sodium nitrite given intravenously to pregnant cows at a dosage of 20 mg/kg body weight was fatal to two of eight fetuses within 24 hours.

In northern Georgia a herd of 120 Holstein cows was fed corn silage that contained levels of nitrate as high as 5000 ppm (dry weight basis). Reproductive problems included repeat breeders and early embryonic losses, however no abortions were reported. In another study, bovine abortion was associated with feed that contained 0.85% potassium nitrate. In farms in which abortion was enzootic, the drinking water contained 80 to 200 mg/L of nitrate and 1 to 2 mg/L of nitrite. Abortions can be related to the deficit in progesterone synthesis induced by nitrates.

Vitamin A deficiency
Nitrates have been determined to depress liver storage of vitamin A and affect carotene utilization. Carotene and vitamin A decrease with increasing amounts of nitrates in the diet.

Hypothyroidism

Nitrate and nitrite compete with iodine in the formation of thyroxine. In piglets, a diet that contains 3% potassium nitrate induces hypothyroidism.

Retarded growth

A diet that contains 3% potassium nitrate reduces daily weight gain by 38% to 55% in piglets. In ruminants, nitrate increases the relative concentration of acetic acid and reduces the relative concentration of propionic acid, butyric acid and valeric acid in the rumen.

NITRATES IN WATER

Nitrates and nitrites are water soluble. Thus, nitrate added to soil may be leached out, moving into ground water. The most common source of contamination to boreholes is surface water, usually in shallow, poorly cased boreholes.

Decaying organic matter, nitrogen fertilizers, animal wastes, silage juices and soil high in nitrogen-fixing bacteria may be sources of contamination to a borehole or surface water. The probability of high levels is much greater when the source is nearby. Deep, drilled boreholes might, occasionally, contain excess nitrates.

Dam water which collects feedlot or fertilizer runoff, may contain toxic levels of nitrates. Nitrates are not excessive in dams with abundant algae or other plants, the plant growth apparently utilizing the excess nitrate.

FURTHER READING

1. Bahri L E, Belguirth J, Blouin A, 1997. Toxicology of Nitrates and Nitrites in Livestock. Compendium on Continuing Education for the practicing veterinarian, 19, 643-649.
2. Choon Y, Brandow R A, Howlet P, 1990. An unusual cause of nitrate poisoning in cattle. Canadian Veterinary Journal, 31, 118.
3. Johnson J L, Grotelueschen D, Knott M, 1994. Evaluation of bovine perinatal nitrate accumulation in western Nebraska. Veterinary and Human Toxicology, 36, 467-471.
4. Jones T O, 1988. Nitrate/nitrite poisoning in cattle. In Practice, 10, 199-203.
5. Olson J R, Oehme F W, Carnahan D L, 1972. Relationship of nitrate levels in water and livestock feeds to herd health problems on 25 Kansas farms. Veterinary Medicine, 3, 257-260.
6. Page R D, Gilson W D, Guthrie L D, 1990. Serum progesterone and milk progesterone and composition in dairy cows fed two concentrations of nitrate. Veterinary and Human Toxicology, 32, 27-31.
7. Vermunt J, Visser R, 1987. Nitrate toxicity in cattle. New Zealand Veterinary Journal, 35, 136-137.
8. Yeruham I, Shlosberg A, Hanji V, Bellaiche M, Marcus M, Liberboim M, 1997. Nitrate toxicosis in beef and dairy cattle herds due to contamination of drinking water and whey. Veterinary and Human Toxicology, 39, 296-298.

AN INVESTIGATION INTO THE FLUORIDE STATUS OF RUMINANTS IN THE NORTHERN PROVINCE

[1] Heleen C. Els , [2] E. du Preez, [3] K.A. Ramsay, [4] A.. Mogale &. [5] P A Iloyazoglu.

1. The farm "Delftzyl" on which the research was conducted (24°35' - 24°43'S. 29°14' - 29°17'E; altitude approximately 850m - Boomker *et. al*; 1994) is situated near Roedtan in the Northern Province. The only source of water is from a borehole (28 000 l/hour). There is no municipal water nor irrigation on the farm. The average rainfall from 1994-1998 was 567mm per year, which mainly falls in the summer. The farm is divided into 26 camps of which 10 were randomly chosen to represent the conditions on the farm. Water, soil and plant samples were taken from the ten identified camps on a three-monthly basis to identify the possible cause of fluoride contamination. Water samples were taken from the drinking troughs. Eight bovines were used in the study. The animals were brought in from another farm to make sure they have not been subjected to high fluoride levels before. Indigenous goats were subjected to rib biopsies. Impala and warthog were culled and rib samples were obtained from them. Fluoride determination in the bone was done by using the fluoride electrode. Water and soil acted as the major contaminants of fluoride in this case. The concentration of fluoride in the water was significantly lower after the rains and very high just after winter. Certain camps on the farm appeared to have very high fluoride levels. Vegetation appeared not to be a source of fluoride contamination. The Bonsmaras seemed to suffer the most with prominent visible bone malformations. Of the four breeds used in the study, they were the most susceptible to fluorosis. In the Afrikaners the only visible sign of fluorosis was the growing out on the hooves. The Ngunis showed slight mottling of the teeth but no further clinical signs. They seemed to be affected the least. Simmentalers were very badly affected. They showed general mottling of the teeth, their growth was stunted and they never recovered completely afterwards when put on a lick. It seems if the indigenous animals show a higher tolerance for high fluoride levels than synthetic or exotic breeds. The indigenous goats also had high levels of fluoride in the bone. It is clear that game (impala, warthog) showed significant lower levels of fluoride in the bone than any of the domestic species. The building of earth dams could reduce the problem. Licks should be provided ad. lib. Municipal water will be the permanent solution. Waterpurifying apparatus can be installed at the borehole. Sheep and goats are better options than cattle under the circumstances. Game can be introduced on a permanent basis.

FLUORIDE AND NITRATE WORKSHOP - Mmabatho March 1999
Title

Risk assessment modelling for commercial and rural livestock production systems exposed to F and NO_3

JA Meyer & NH Casey
Dept of Animal & Wildlife Sciences, UP

Introduction

Inadequacies in existing water quality guidelines for livestock watering were described. Water quality norms affecting animal production were described for the water quality constituents fluoride and nitrate. Reasons were given for the necessity for differing modelling approaches for fluoride and nitrate.

Experimentation conducted

Main results from water quality studies in the Kruger National Park, Selati Game Reserve, Immerpan Resettlement Area, Barolong Resettlement Area, Delftzyl Agricultural Research Station and Vryburg District were presented. Correlations in groundwater between F, Ca, B, TDS and other water quality constituents were described for these areas, including the resultant toxicological and palatability implications.

Biological trials demonstrating the significantly beneficial effect of various salts and di-sodium tetraborate on alleviating fluorosis in sheep and cattle were presented. Clinical and growth results of an extensive region trial currently underway at Delftzyl were also presented.

In a toxicological trial in Dohne Merino ram lambs from birth to slaughter weight, it was concluded that adverse effects from the exposure to 20 mg F/l in the drinking water may be mitigated by the use of boron as an alleviator at a concentration of ca. 25 mg B/l . In palatability trials conducted in sheep and dairy cattle, it was found that the palatability of water may be improved significantly ($P<0.05$) by the addition of either sodium sulphate or sodium chloride, depending on the relative position of a zone of preference. Palatability tables and calculations were formulated to enable the prediction of the zone of preference and calculation of the required additions. The ramifications of these effects on the ingestion and toxicology of fluoride and nitrate was explained.

A chemical treatment of 25 mg/l B + 425 mg/l NaCl +600 mg/l $MgSO_4$ + 600 mg/l Na2SO4 + 375 mg/l CaCl2, with a SO4/TDS ratio of 0.296 and a [TDS] of 3000 mg/l, was significantly beneficial ($P<0.05$), in terms of final live weight achieved, as an alleviatory treatment administered in the drinking water to Afrikaner steers exposed to 20 mg F/l .

Results from trials investigating the effects of nitrate in the drinking water on blood-gas parameters and apparent digestibility in rams were presented. In a trial investigating the effects of nitrate on apparent digestibility and health no significant ($P<0.05$) adverse digestibility effects at 200 mg NO3/ to 400 mg NO3/ in the drinking water were detected in Dohne Merino sheep fed a standard commercial feedlot ration. No signs of methaemoglobinaemia were observed, although some significant ($P<0.05$) blood gas values indicated increased MetHb concentration for both treatments following NO3 exposure. It was concluded that 200 mg NO3/l to 400 mg NO3/l can be regarded as safe for use for sheep and was incorporated into the Generic guidelines developed.

Modelling for site-specific risk assessment
Relevant aspects that are included in modelling equations for livestock were described. The requirement for site-specific factors influencing animal, environmental and nutritional aspects was explained. Water quality guidelines were modelled for livestock watering and a water quality guideline index system, called CIRRA Version 1.03 (constituent ingestion rate risk assessment), developed in the format of a document driven interactive windows based software program, written in Clarion. The mechanism whereby CIRRA provides a site-specific risk assessment together with a help document containing supporting information, information regarding the main synergistic and antagonistic calculation results, and how these allow for solution driven management options was explained.

Communal livestock production systems and wildlife
Issues pertaining to both rural and wildlife water quality guidelines were presented, these being primarily multiple water source utilisation, multiple species utilisation and shared ingestion by animals and humans. The influence of these factors on modelling requirements were presented.

Conclusion
The need for a modelling approach in order to accurately perform risk assessment was highlighted. Reasons for using a software environment to conduct risk assessment were given.

FLUORIDE & NITRATES IN RURAL WATER SUPPLIES WORKSHOP

SESSION TWO: DEPENDENCY OF COMMUNITIES ON GROUNDWATER FOR WATER SUPPLY AND ASSOCIATED NITRATE AND FLUORIDE PROBLEMS

There are 11 761 rural communities and 1 439 urban communities excluding the Gauteng Province distributed throughout South Africa and the challenge to serve all these communities to the White Paper criteria over the next ten to twenty years. The available water resources are mainly major infrastructure development from dams or single community supplies from groundwater. Regional groundwater supply projects are scares due to the limited exploitation potential of aquifers in South Africa. The purpose of this talk is therefor to give a broad idea on the existing usage of groundwater as a supply source and to show the quality of this water in respect of nitrate and fluoride levels.

The best way to get perspective on the problems is to summarize the information firstly on a national level and then discuss the provincial distributions individually. It is of paramount importance to note at this stage that our main problem is not necessarily pollution of chemical elements but that the majority of our communities are using water of which no analysis have been documented in any database. This can only make the existing pictures worse and we really need to establish monitoring networks and systems that feeds information back to allow us to make decent planning decisions on water supply.

Included please find maps of National perspectives as well as provincial perspectives that state the source of existing usage as well as existing information on nitrate and fluoride levels as effected in our Community Water Supply and Sanitation database. Macro Planning and Information Systems is however in the process of establishing such networks and systems and this will be discussed with our provincial offices before the final project is launched. All the available data is already documented in groundwater planning manuals and is also printed on a provincial basis and it will be discussed with all the provincial role players in the near future.

PROVINCES	NUMBER OF COMMUNITIES	COMMUNITIES USING GROUNDWATER	COMMUNITIES OF NO INFORMATION	COMMUNITIES HIGH IN NITRATE AND FLUORIDE
NORTHEN CAPE	226	125	55	47
NORTH WEST	1297	1058	306	259
NORTHERN PROV	2067	2067	1380	191
MPUMALANGA	583	1850	1661	33
FREE STATE	251	528	286	72
KWAZULU/NATAL	1973	72	79	22
WESTERN CAPE	0	0	0	0
EASTERN CAPE	5677	4595	4594	1

SESSION TWO: INSTITUTIONAL ARRANGEMENTS AND MANAGEMENT OF WATER QUALITY PROBLEMS IN WATER SUPPLY

Mr. Marais on behalf of Mr. van Zyl gave this talk.

It id firstly important to understand water services in the total context and to realize that our responsibility does not begin or end only with technical issues but that we cover all other arrangements, e.g. environment, social, management, institutional and financial. In any one of these categories water quality plays a major role in setting standards and guidelines and also to regulate efficient and effective water supply to all our customers (domestic and industrial).

Macro Planning therefor needs to co-ordinate national standards and regulations through regional co-operation.

Although our role as government begins with standards and end with regulations the responsibility and accountability for water supply is rested in the hands of Local Government. We therefor see our role to support Local Government to understand water quality, to plan water quality, to commit and undertake to provide these customer services. Our help and support services can include activities such as monitoring, sampling, laboratories, control, maintenance and empowerment.

We also have to organize and lead NGO's, private sector, research and Industry with the technology required to deliver water quality goals. Issues closely related to the above-mentioned responsibilities include topics such as criteria (what is acceptable), technology (to treat), monitoring systems, interventions (what if things go wrong and if standards are not met), cost and financial management and operating systems.

To summarize our main actions to support Local Government will be to develop criteria and standards to build a reference system through the development of guideline documents, through development plans and through help systems.

THE EFFECTS OF FLUOROSED TEETH ON ADOLESCENTS IN THE NORTH - WEST PROVINCE

Badu Mothusi

"FLUORIDE & NITRATES IN RURAL WATER SUPPLIES" workshop
9-10 March 1999

INTRODUCTION

It is significant to me that the Fluoride and Nitrates workshop is held in the North west Province not because I am from the Province, not because I am the Head of Oral health Services but simply because it is ideal, it is appropriate and North west Province has unfortunately the richest deposits of fluoride in the country (Mc Caffrey 1994)

Dental Fluorosis is one of the major dental problems affecting the people on the North West province especially those in the Pilanesburg, Odi and Moretele regions (Zietman 1988).

People in these regions are hard hit by brown -stained that is mottled teeth due to an excessive amount of fluoride in their drinking water.

The development in this area has attracted a lot of people e.g. the Pilanesberg National Park which is the fourth largest park in South Africa (North -West Parks Board 1992).

The area also boast of a complex of hotels, sporting and entertainment facilities that rise out of rugged African bushes like an oasis (North West Parks board 1992)

These magnificent development brought changes to the life style of people in the region. What used to be normally brown -stained accepted teeth is now considered as abnormal and unwanted teeth.

The development in the area have attracted many people, who flock to Pilanesberg to seek employment. This affects the surrounding family members, as members of the family born in areas with low fluoride content have normal white teeth and while those born in these have fluorosed (brown stained) teeth.

In this region there is a high demand for these fluorosed teeth to be removed and replaced with dentures.
It would appear that having such teeth reduces the possibility that people might positively appraise themselves and / or might be positively appraised by others.

AIMS
The aims of the paper are;

To show that fluorosed teeth has some effect on self esteem of the people especially adolescents.
To place de fluoridation high on the priority list in areas where there is naturally high amount of fluoride the drinking water.
According to the figure from the department of water affairs Mankwe regions that is Sun City Area and Moretele region (Hammanskraal) area have exceptionally high amount of fluoride, some area had up to 13 parts per million parts of water.

Some of the bore - hole in the area had to be closed because of the high amount of fluoride and unfortunately some of these bore holes were in the school - yards.

OBJECTIVES

I believe in water fluoridation, I support fluoridation, I am an advocate of Water fluoridation, a Member of National Task team and we are preaching the Gospel of Water fluoridation.

But I believe that as long as we preach water fluoridation , we should at the same time talk about water de fluoridation in areas with high contents of fluoride especially in the North West Province.

We need to strike a balance between fluoridation and de-fluoridation. We need to adjust the level of fluoride in our drinking water.

FLUOROSED TEETH

Fluorosis is a mottling of teeth which in some cases can be unsightly, especially in this part of our country Pilanesberg. It occurs especially when the levels of fluoride are too high.

Slide .1

Horowitz (1986) defines dental fluorosis as a hypoplasia or hypo- mineralisation of tooth enamel, due to the ingestion of excess amount of fluoride during the period when teeth are developing.

Leverett (1986) studied prevalence of dental fluorosis in fluoridated and non fluoridated communities. In this area it proved that properly adjusted fluoride does not result in dental fluorosis that has reached an objectionable level.

PSYCHOLOGICAL EFFECTS

Most of the information available to date describes effects of excessive amount of fluoride on the teeth.

Most of the reviewed papers indicate the effects of fluoride in caries reduction, but few indicates the harmful effect of excessive amount of fluoride and none the psychological trauma caused by it.

SELF - CONCEPT / SELF ESTEEM

Self concept and self esteem will be used interchangeable in this paper to refer tot he image that each person has about himself.

Rungasamy (1979 , 5) talks about the incomprehensibility of trying to define self esteem. He says the more one tries to grasp it, the more it seems elusive like mercury, it slips and slide eluding the fingers of mind. In other words self - esteem is not something tangible and static, on the contrary self esteem is a dynamic mental picture that the person has person has about himself.

Burns (1984) says that the mouth and face are the focal points of a tremendous number of emotional conflicts and that dento facial deformities can constitute a source of emotional suffering varying from embarrassment to mental anguish.

Slide 2

Hall points out that people do not want to receive unfavourable information about themselves, for example to be informed about bad teeth as these will make them feel inferior and worthless, resulting in low self-esteem

slide 2
According to Penrod (1983) , self-esteem affects people's behaviour and the way they present themselves to others.He continues to say that people with low self esteem assume that other people will not like them. Such people anticipate rejection at every encounter with others and they are awkward and fearful in situations.

Goldstein (1976) says that an individual sense of what is beautiful influences how he desires to present himself to others, and that a desire to look well is no longer taken as a sign of vanity in a socially, economically and sexually competitive world. A pleasing appearance is literally a necessity. The physical aspect of one' s self concept is stressed here within the social context in which one lives.

Slide . 3

Vrey (quoted in Molefe , 1985:) states that " if personality is the radiant force emitted from the core of the person, the self - concept is the lens focussing this force on personality traits" . Molefe (1985) continues to say that positive or high self - esteem induces one to wear a happy face wherever one goes. He says the importance of acquiring a positive self - concept lies in the fact that it helps to promote self- actualisation provided the person is given essential educational help.

FACE

According to Patter (1985), the face is the most frequently used component in the physical attractiveness research. The face is interesting, enduring and informative. He says that consistent use of the face in evaluating physical attractiveness is justified. Because of its unique and powerful properties which appear to make it omnipotent and omnipresent. Thus people with fluorosed teeth keep on shielding their mouth thus hiding their faces.

Slide 4

According to Rubenstein (1983. 48) " Abraham Lincoln once stated in a campaign speech that, based on the appearance of his face, no one ever expected him to be president" handsome / good looking people are perceived to be leaders.

THE EFFECTS OF FACIAL APPEARANCE IN EMPLOYMENT

Signal and Arson (1969) suggest that it is more rewarding to please a physically attractive person than one who is not attractive.

Water (1985) suggests that attractive applicants are more favourably perceived than unattractive applicants.
Attractive applicants are attributed greater overall employment potential than unattractive applicants. He found that physical appearance plays an important role in the hiring process on all skills levels.

This is so true, as from to day observe receptionists in all the resorts.

FACIAL APPEARANCE IN ADVERTISING

In 1982 Joseph stated that advertisers believe that the beautiful are also credible, and that physical attractive sources can contribute to a communication's effectiveness.

Slide 5
observe all our News presenters and people used for / in advertising.
slide 6

slide 7

slide 8

CONCLUSION

The psychological effect in terms of the unsightly brown stained teeth has induced the adolescents with fluorosed teeth to the demand that these teeth be attracted and replaced with dentures.

Slide 9

Their demand suggests that the unsightly brown teeth negatively affects their appearance and their self concept.

Slide 10

Thus it is imperative that when we advocate water fluoridation, we should at the same time consider areas with high amount of fluoride causing dental fluorosis / brown teeth.

When all is said and done water fluoridation is the answer to tooth decay (dental caries) and it should be supported.

REFERENCES

Burns, R.B and Dobson, C. B(1984) . Introduction to Psychology . Langster . M. T. P. Press.

Goldtein, R .E (1976) . Esthecs in Dentisry , Esteem in children with special educational needs : Philadelphia.

Hall, J (1985). Psychology for nurses and health visitors: London. Mac Millian.

Horowitz, H. S (1982) . Indexes for measuring dental flourosis : **Journal of Public health Dentistry,**volume 46 179-182.

Joseph, W. (1982) : the incredibility of physically attractive communications. A reveiw. Journal of Advertising 11. 15-25.

McCaffrey , L.P (1994) . The Geohydrology of the Pilanesburg . Unpbl M .SC Diss. Wits.

Leverett, D (1986) Prevallence of dental flourosis in flouridated and non flouridated communities, a preliminary investigation. **Jounal public health in dentistry,** 46 184-187.

Molefe, R. D (1987). The meaning of self -concept for the academic achievement of Tswana teacher- trainees. M. SC thes. Un of Pretoria.

Patter, g. L (1985). The physical attractiveness phenomen. New York . Plenun Press.

Rubentein, C (1983). The face psychology today.

Rungasamy, P (1979). A study of the levels of depression in the physically ill. University of

Dublin, Tinity College.

Penrod , S (1983) Social psychology. Prentice Hall. Engelwood Cliffs.

Signal, H. and Aronson, E (1969) liking for and evaluation as a function of her physical attractive partner on person perception. **Journal of personality and social Psychology 31. 410-414.**

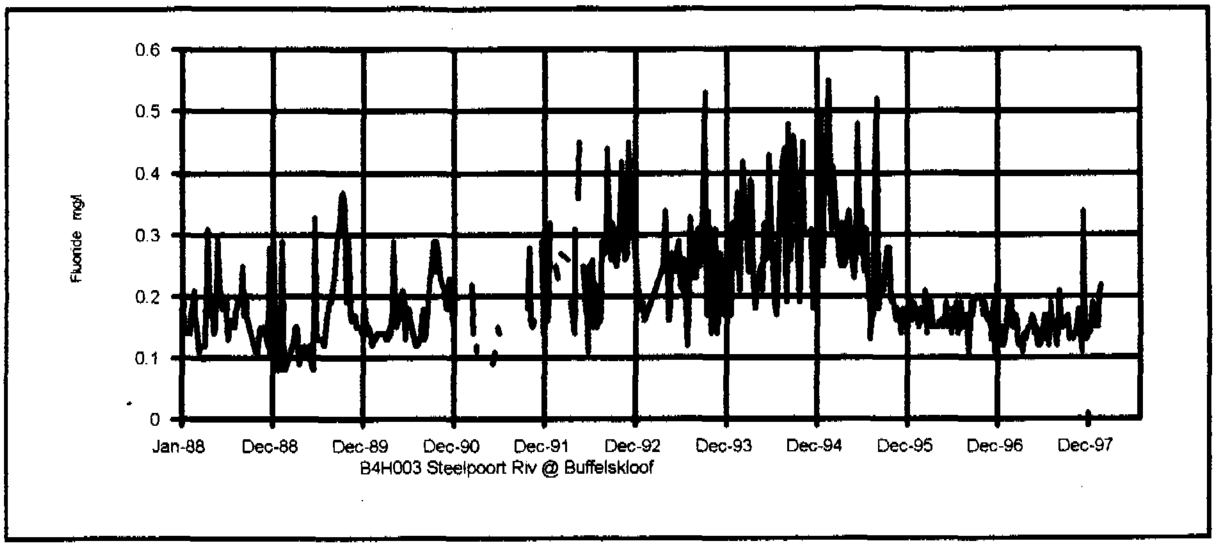
Waters, J (1985). Cosmetic and the Job Market in Graham J and Kliman's Psychology of cosmetic treatment : New York. Praegen.

Zietsman, S (1991) Spatial Variation of flourosis and fluoride content of water in an endemic area of Bophutatswana. **Journal of the dental association of South Africa,** 46, 11-15.

Fluoride concentrations in surface water

Jane Harris, Environmentek, CSIR

A preliminary survey of fluoride concentrations at water quality monitoring stations maintained by the Department of Water Affairs and Forestry indicates that a widespread pattern in magnitude and variability exists. The pattern is illustrated by the time series data given in Figure 1 for Station B4H003Q01, Steelpoort River at Buffelskloof in Northern Province.



The pattern can be described as a trend in increasing magnitude and variability, beginning during 1989-1991 then a sudden decrease in both magnitude and variability during 1995, lasting through the end of the data record. The spatial extent of the pattern is illustrated with a time series record, shown in Figure 2, of the Bree River at Witelsboom, Station H1H003Q01, in the Western Cape.

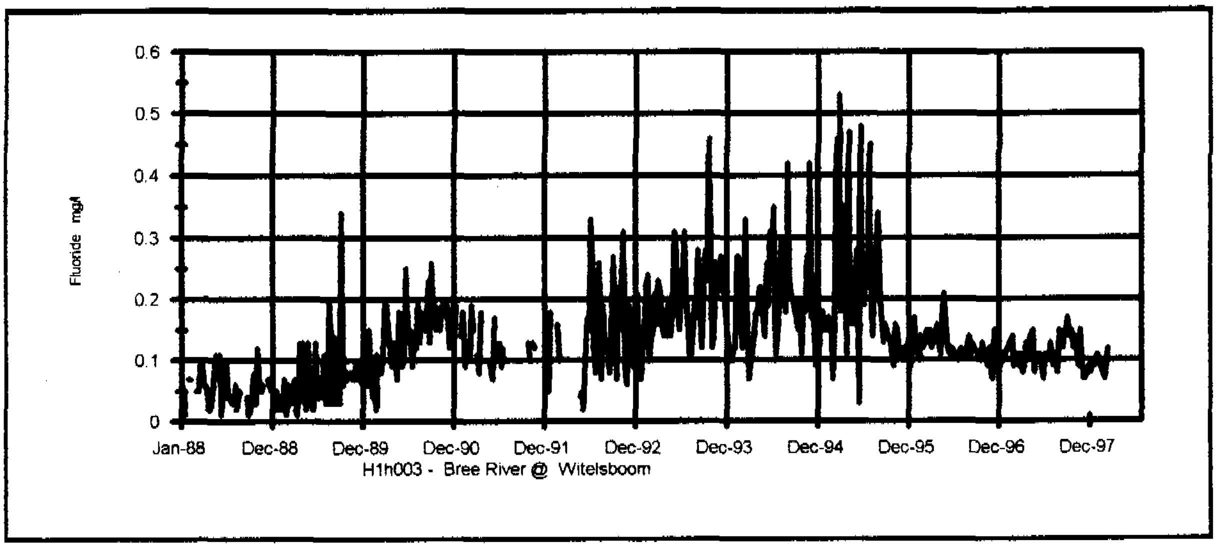


Figure 2 Time series of fluoride concentrations at Bree River gauge, H1H003, from January 1988 to May 1998.

The cause of the pattern is not immediately obvious. The fact that the pattern is widespread geographically seems to indicate a measurement effect. There has, however, been no fundamental change in the analysis method; an ion selective electrode method has been applied for at least the last ten years. No changes in reagent supplier or any other significant change has been identified.

Some stations do not show the pattern. Figure 3 shows the record from station C1H008, Waterval River at Elandslaagte, in Gauteng Province. The magnitude of fluoride

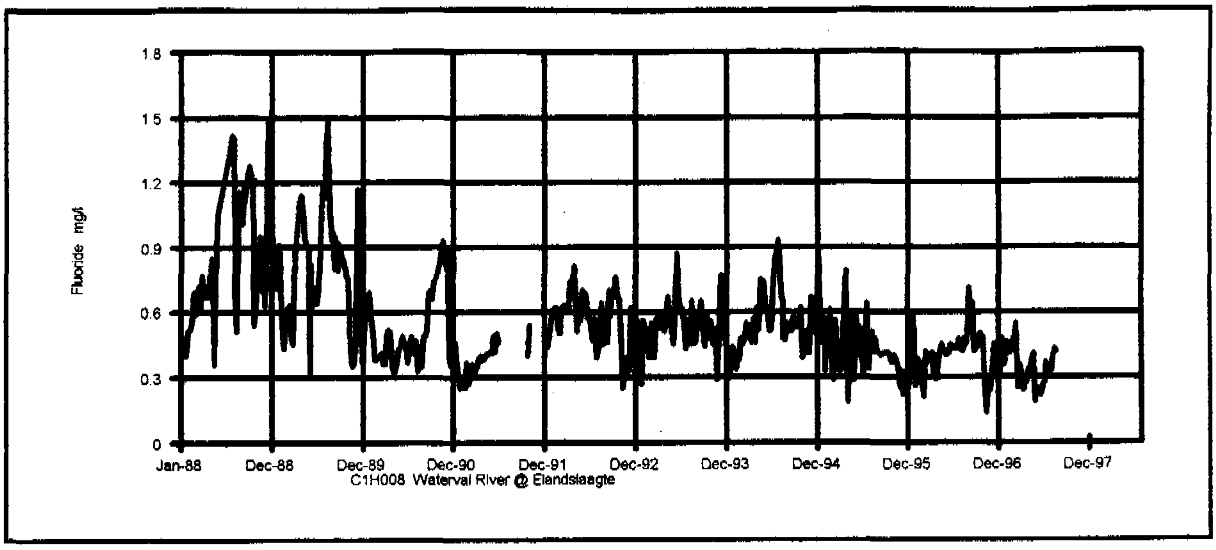


Figure 3 Time series of fluoride concentrations at Waterval River gauge, C1H008, from January 1988 to May 1998.

concentrations is higher than in the previous examples and possibly contributes to masking another pattern, however, neither the increasing trend nor the sudden decrease is displayed at this station.

Additional investigation into the origins of this pattern is strongly recommended.

The level of fluoride concentrations in water often given as the minimum required for healthy dental development in children is 0,8 mg/l (stated by Dr du Plessis at this conference). That concentration is attained at only a small proportion of the surface water stations examined in this investigation. The magnitude of the observed concentrations does not indicate that any threat to health exists. However, any prediction of management options that might affect fluoride concentrations in the environment must rely on accurate data.

Only with an understanding of the cause-effect relationships that created the existing data record can we hope to predict impacts of proposed activities. Basing management decisions on an estimate of impacts developed from misunderstood data can lead to unexpected, and unwanted, results.

Paper to be presented at the Workshop on ***Fluoride & Nitrates in Rural Water Supplies:*** *Health issues and removal techniques, Water Research Commission, Mmabatho, 9 - 10 March 1999*

NITRATE IN GROUNDWATER

G Tredoux

Cape Water Programme, CSIR, P O Box 320, Stellenbosch, 7599 South Africa

EXTENDED ABSTRACT

Introduction

The occurrence of nitrate in groundwater has been studied worldwide, particularly over the past five decades since Comly (1945) linked 'cyanosis' in infants to the presence of nitrate in the water ingested by such infants. In South Africa only anecdotal information is available in this regard and no statistics have been kept (Tredoux, 1993). There is no doubt that contamination is a significant source of nitrate in groundwater. Based on the literature and limited studies carried out locally, both pollution point sources and diffuse sources lead to nitrate occurring in groundwater. Furthermore, groundwater nitrate concentrations are increasing worldwide (WHO, 1985). A useful example is provided by a Danish groundwater study (Schroder *et al.*, 1985).

The pertinent question for this Workshop is whether groundwater nitrate poses a threat to rural water supply. In the attempt to arrive at an answer, this paper discusses the anecdotal information on the occurrence of methaemoglobinaemia and the loss of livestock, as well as the extent of the affected areas based on available information regarding the distribution of nitrate in groundwater in Southern Africa. Finally, management and control measures are proposed which are based on preliminary investigations and an interpretation of the nitrate accumulation mechanisms.

The nitrogen cycle

The prevailing opinion is that under natural conditions the nitrogen cycle in the soil is closed. Nitrogen is converted from one oxidation state to another and into other chemical compounds without any loss of nitrogen to the subsurface. Nitrogen compounds, and particularly nitrate, are generally not expected to occur in groundwater. The occurrence of nitrate in groundwater is, therefore, usually ascribed to pollution. Anthropogenic nitrogen sources include fertilizer application to land, sludge application to soil, wastewater irrigation, deforestation, as well as oxidization and mobilization of natural soil nitrogen by ploughing. This scenario is considered to be valid for the humid and temperate regions of the world.

In semiarid to arid regions, significant groundwater nitrate occurrences have even been reported from areas where anthropogenic influences can be excluded (Barnes *et al.*, 1992; Edmunds & Gaye, 1997; Heaton, 1984; Mueller, 1960; Tredoux & Kirchner, 1985; Tredoux, 1993). This would seem to indicate that nitrogen losses from the soil zone and accumulation of nitrate in the subsurface could take place under natural conditions encountered in arid regions. When considering the nitrate occurrences in groundwater, natural nitrate accumulation and the factors expected to favour such accumulation needs to be taken into account when formulating management options for arid regions.

Nitrate occurrence

The hydrochemical data contained in the national groundwater database of the Department of Water Affairs and Forestry was the only data set available covering the country as a whole. The distribution of sampling points is very uneven and would at least partly introduce 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 the present drinking water guideline value of 10 mg/L, some15 per cent exceeded the earlier guideline of 20 mg/L and 4,3 per cent 50 mg/L.

The groundwater quality surveys showed that nitrate often occurred in small isolated areas including one or more wells, sometimes attaining relatively high concentrations. Such occurrences are ascribed to pollution and this can generally be confirmed by nitrogen isotope determinations. However, in certain cases vast areas are affected, which could not be solely due to pollution. Examples of such areas with higher nitrate levels (usually > 20 mg/L, but mostly > 50 mg/L) are the following:

- the Kalahari Beds in the Gordonia District adjacent to the Namibian border;
- the Asbestos Hills Formation, Griquatown Group, in the vicinity of Prieska;
- the Ghaap Plateau, south-west of Vryburg;
- 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 thought to be related to anthropogenic activities. The extensive Ghaap Plateau nitrate occurrences could be due either to anthropogenic inputs or to natural phenomena or possibly both.

Anthropogenic activities disturbing the nitrogen cycle can cause accumulation of nitrate in the groundwater over larger areas. This was postulated to be the case in the Springbok Flats (Grobler, 1976) and was confirmed by nitrogen isotope determinations (Heaton, 1985). Also, Faillat & Rambaud (1991) concluded that deforestation in Côte d'Ivoire caused the appearance of nitrate in the groundwater in that area. Kinzelbach *et al.* (1992) came to a similar conclusion when modelling the regional nitrate transport at Bruchsal-Karlsdorf in the Upper Rhine Valley.

At this stage no definite trends related to nitrate occurrence in groundwater in South Africa have been established with any degree of certainty. Data spanning a period of two to three decades is required for any meaningful answer. Two earlier attempts ((Van der Merwe & Levin, 1990; Orpen & Fayazi, 1991) have been unsuccessful. This is largely due to the uncertainty regarding older analyses. Even a decade ago it was reported that many laboratories generate incorrect nitrate results (Smith, 1989).

Conclusions

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. 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.

Rural water supplies are under threat and *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.

Informing the public, and particularly the rural and farming communities 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. Presently, the impacts of a variety of anthropogenic activities causing groundwater pollution are 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.

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*, i.e. denitrification in the aquifer itself, is being applied abroad and a number of plants are successfully in operation. The robustness of this technique warrants investigation for adaption for local application in this country.

References

Barnes, C J, Jacobson, G & Smith, G D, 1992. The origin of high-nitrate ground waters in the Australian arid zone. *Journal of Hydrology*, **137**, 181 - 197.

Comly, H.H. (1945). Cyanosis in infants caused by nitrates in well water. *J. Am. Med. Ass.*, **129**, 112 - 116.

Edmunds, W M & Gaye, C B, 1997. Naturally high nitrate concentrations in groundwaters from the Sahel. *J. Environ. Qual.*, **26**, 1231 - 1239

Faillat, J P & Rambaud, A, 1991. Deforestation and leaching of nitrogen as nitrates into underground water in intertropical zones: The example of Côte d'Ivoire. *Environ. Geol. Water Sci.*, **17**, 133 - 140.

Grobler, D C, 1976. Report on the investigation into the causes of the high nitrate content of the groundwater in certain parts of the Springbok Flats *(in Afrikaans)*. *Technical note 74*, Dept of Water Affairs, Pretoria.

Heaton, T H E, 1984. Sources of the nitrate in phreatic groundwater in the Western Kalahari. *J. Hydrol.*, **67**, 249 - 259

Heaton, T H E, 1985. Isotopic and chemical aspects of nitrate in the groundwater of the Springbok Flats. *Water SA*, **11**, 199 - 208.

Kinzelbach, W., Van der Ploeg, R.R., Rohmann, U. & Rödelsperger, M. (1992). Modelling of regional transport of nitrogen: case study Bruchsal-Karlsdorf. *In:* Kobus, H. (Ed.) (1992), *Schadstoffe im Grundwasser: Band 1: Wärme- und Schadstofftransport im Grundwasser*, DFG, VCH, Weinheim, 413-470.

Mueller, G, 1960. The theory of formation of North Chilean nitrate deposits through "capillary concentration". Int. Geol. Congress, **21**, pages 76 - 86.

Orpen, W. R. G. & Fayazi, M. (1991). Aquifer systems and groundwater chemistry of the Springbok Flats, *Biennial Ground Water Convention* (Midrand), *Paper No 5.*

Schroder, H., Harremoës, P. & Simonsen, J. F. (1985) Water pollution caused by nitrogen from urban wastewater and from agriculture. Paper presented at Conf. *Nitrates in Water*, Paris.

Smith, R. (1989) Organization and evaluation of interlaboratory comparison studies among Southern African water analysis laboratories (1976 - 1987). *CSIR Research Report 676*, Pretoria.

Tredoux, G & Kirchner, J, 1985. The occurrence of nitrate in groundwater in South West Africa/Namibia. *Paper presented at Conference Nitrates in Water, Paris.*

Tredoux, G, 1993. A preliminary investigation of the nitrate content of groundwater and limitation of the nitrate input. *Report to the Water research Commission*, Report **No 368/1/93**, ISBN 1 86845 009 0.

Van der Merwe, P. J. & Levin, M. (1990) *An application of geostatistical methods to the hydrochemistry of the Springbok Flats*. Atomic Energy Corporation, Pretoria.

World Health organization (WHO) (1985) *Health hazards from nitrates in drinking water*. Copenhagen, 102 p.

WATER DEFLUORIDATION

J J SCHOEMAN
Environmentek, CSIR, P O Box 395, PRETORIA, 0001 South Africa

SUMMARY

The presence of fluoride in drinking water may be beneficial or detrimental to public health, depending on its concentration. Fluoridation of drinking water to a level of 1 mg/ℓ has been shown to reduce dental cavities among children. No known deleterious effects of drinking defluoridated water have been observed when the concentration of fluoride is kept within prescribed limits. However, when water supplies contain excessive fluoride concentrations, the teeth of most young consumers become mottled with a permanent black or grey discolouration. Children who have been drinking water containing 5 mg/ℓ or more fluoride are invariably afflicted and, for many, the enamel becomes so severely pitted that they eventually lose their teeth. Bone changes and crippling fluorosis may also result from the long-term consumption of water containing 8 to 20 mg/ℓ fluoride, or from a total intake of 20 mg of fluoride per day for 20 years or more.

Many groundwaters in the Republic of South Africa are unfit for human consumption, because they contain more than the maximum allowable limit of 1,5 mg/ℓ fluoride recommended by the South African Bureau of Standards for potable water. The fluoride concentrations vary from about 2 to 20 mg/ℓ, with levels up to 10 being fairly general. Some industrial effluents also contain high fluoride concentration levels (approximately 4 to 30 mg/ℓ).

A number of methods can be used for the removal of fluoride from water. These can be divided into three categories - those based on the addition of chemicals to cause precipitation or co-precipitation during coagulation; those based on ion-exchange or adsorption; and those based on membrane separation.

The chemical methods include the use of lime, magnesium, aluminium sulphate and polyaluminium chloride. Theoretically, lime can reduce fluoride to no lower than 8 mg/ℓ, while aluminium and magnesium sulphate can reduce fluoride to lower than 1,5 mg/ℓ. Cases have been demonstrated where aluminium sulphate could reduce fluoride from 30 mg/ℓ to less than 3 mg/ℓ, and from 5 mg/ℓ to approximately 0,5 mg/ℓ. However, excessive and costly dosages are required and a sludge disposal problem also arises. A case has been demonstrated where polyaluminium chloride could reduce fluoride from 19 mg/ℓ to 2,4 mg/ℓ.

Adsorption methods include the use of activated alumina, activated carbon, strong-base anion exchange resins, bone char and tricalcium phosphate. Of these methods, the activated alumina process appears to be the most attractive, because alumina is somewhat specific for fluoride, and has a relatively high fluoride exchange capacity. Activated alumina is not very friable, and is not seriously affected by the concentrations of chlorides and sulphates usually encountered in waters. Regeneration, which can be performed with caustic soda, is fairly straightforward, and the process is reliable, safe and relatively simple to use. Cases have been demonstrated where fluorides in the concentration range from approximately 4 to 20 mg/ℓ in borehole waters could be reduced to potable standards with activated alumina treatment.

Membrane separation methods include the use of reverse osmosis and electrodialysis. Both these processes can remove fluoride effectively from water. A case has been demonstrated where fluoride in a borehole water of approximately 12 mg/ℓ could be reduced to potable standards with reverse osmosis treatment.

MEMBRANE AND BIOLOGICAL PROCESSES FOR THE REMOVAL OF NITRATES FROM WATER

FRIK SCHUTTE

Dept of Chemical Engineering
University of Pretoria

Membrane processes for nitrate removal: The two membrane processes that can be used for nitrate removal from water for domestic use are reverse osmosis (RO) and electrodialysis (EDR).
RO is a presssure-driven process in which relatively pure water is forced through a semi-permeable membrane which rejects dissolved salts including nitrates. In addition to rejecting dissolved salts the membrane also rejects bacteria, virusses and other colloidal material. The product water is therefore of excellent quality.

EDR is an electrically-driven membrane process in which ions are removed from water under the action of an electrical potential. The membranes are electricall charged, and positively and negatively charged membranes are put alternately in a stack to form cells. Only charged ions and particles are removed leaving potential contaminants in the product water.

Biological nitrate removal involves using micro-organisms to reduce nitrates to nitrogen gas by using a carbon source as electron donor and the nitrate as electron acceptor. The disadvantage of this process is the need to add a carbon source such as methanol to the water which adds to the cost and also may cause problems of microbial growth in the distribution systems.

Hollow fibre or capillary membranes may be used as bioreactors in which the micro-organisms are separated from the water by the membrane.

A case study of the removal of nitrates by RO at Zawa in the Northern Province confirmed the feasibility of RO for removal of nitrates as well as high TDS (1200 mg/l) from ground water for human consumption. The CSIR/DWAF project has been running for more than two years. The RO plant is operated bu two local operators with supervision by the CSIR on a once a month basis. The capacity of the plant is 100 kl/d and it is operated at a water recovery of 50%. The low recovery minimises potential problems of membrane fouling. The membranes showed a nitrate and TDS rejection of about 98%. Because the recovery is only 50% the brine concentration is not excessive so that it may be used for stock watering.

Both RO and EDR can be used to remove nitrates to very low levels from domestic water. However, the costs of removing nitrates are relatively high and it is concluded that membrane processes would only be economically viable if desalination of water is also required in addition to removal of nitrates.

Subject: ION EXCHANGE RESIN FOR THE REMOVAL OF NITRATES FROM WATER

AUTHOR: E.K. HARDWICK CHEMATRON PRODUCTS

Ion exchange is the removal of one ion from water and its replacement by another. For nitrate removal an anion resin in the chloride form is used. For high sulphate waters the nitrate selective resin Wofatit SN 36 L is used. For low sulphate waters Lewatit M 500 is preferred.

Ion exchange is an established and proven technology with operation plants world-wide. It has low capital and operating costs, with low maintenance requirements and simple operation .

Disadvantages are that an effluent is produced and that the corrosiveness of the water may increase. Taste may be affected but this is more likely to be positive than negative.

The cost of treating a water containing 100 mg/; No3- and 50 mg/l SO4= is about 26 c per 1000 litre. Capital costs vary from R 1000.00 per m3 per day for smaller plants down to R100.00 per m3 per day for bigger units.

Effluent handling is possible by solar evaporation in arid areas. Biological treatment allows the re-use of the brine regenerant and is applicable for municipal scale operation. Tanker removal my be considered for small units.

Promising Approaches in the Removal of Fluoride and Nitrate in Rural Drinking Water Supplies.

C Chibi * and D A Vinnicombe **
* Options to Solutions CC.
** ERWAT Laboratory Services.

INTRODUCTION

Since 1994 South Africa has embarked on a ambitious infrastructure roll-out programme called the Reconstruction and Development Program (RDP). A key component of this program aims to address large backlogs in the supply of easily accessible and good quality water to residents, particularly those who live in rural outlying areas of the country. Recent estimates put this figure at about 11 million people. These areas are frequently the ones that lack basic infrastructure and economic activity, and once infrastructure has been delivered, face the largest challenges in ensuring that it stays functional and is operated and maintained in a sustainable manner.

Different agencies are involved in the funding and implementation of water supply schemes, ranging from the Department of Water Affairs and Forestry (DWAF), government/private sector partnerships (eg, BOTT), non-government organizations such as The Mvula Trust and the Independent Development Trust as well as local self-help development structures. The approaches, design philosophies and policies adopted are scheme-specific. However, fundamental principles are still influenced by world-wide experience gained during the United Nation's Water Decade of the eighty's. These have been refined as more and more policy research and findings as well as local experience have come to the fore.

Community water supply schemes (populations typically < 10 000 people), which are characteristically found in outlying rural areas, are generally designed to be as simple as possible in order to minimize operations and maintenance (O+M) requirements. This is in view of the lack of skilled operators in those environments, and the need to make O+M requirements low cost, thus affordable to users.

In practice, translating the requirements mentioned above means that schemes which find preference to develop from a community water supply point of view, frequently have the following sources;

ground water supplies,
spring water
connections to bulk supply developments in the area

The reasons are not difficult to figure out as the common denominator to be found amongst the three sources above is the relative good quality of water to be expected from any of these sources. Whist access to minimum quantities of water per individual per day is still the primary consideration (access to increased quantities of water reportedly singularly provide the largest health benefits according to WHO reports), the associated water qualities provided are still of major concern.

Microbial contamination remains the most important health risk, but inorganic and organic compounds are increasingly in the spotlight due to advances in sophisticated analytical techniques for their detection
and, newer understanding from recent epidemiological studies regarding their potential health effects.

Nitrates and Fluorides are two inorganic compounds which occur widely in South African waters, albeit in concentrations most oftenly within the recommended guidelines. In certain areas of the country, however, they occur in varyingly high concentrations above guideline standards such that they could be a threat to the health of the indigenous users. This is particularly true for some ground water sources in the country, which are used as sole sources of water supplies by the local populace. From a CWSS point of view, these contaminants are viewed with increasing attention (and concern) due to the fact that the costs for removing these contaminants can be prohibitive using the current techniques of ion exchange, membrane technologies as well as chemical precipitation removal.

To date the occurrence of nitrates and fluorides, especially in ground water, has only been studied on an ad hoc basis. Tredoux (1993) has summarized the important studies that have been carried out in South Africa on the occurrence of Nitrates. McCaffery (1998) has written extensively on the distribution and occurrence of fluorides in ground waters of South Africa.

Current worldwide trends indicate that groundwater concentrations of these contaminants will continue to increase, particularly in the case of nitrates. This is attributable mainly to natural geologic formations and/or antropogenenic activities. In addition, nitrates are a normal part of the human diet and are found in numerous foodstuffs including vegetables, meat and fish.

In the current drive to increase the access of safe clean water to outlying smaller communities, there is a need to evaluate new and innovative approaches, which will enable the removal of contaminants such as nitrates and fluorides. This must be done without greatly complicating the operation and maintenance requirements of schemes, or greatly increasing the running cost burden for rural dwellers.

This document summarizes findings from a desktop study on some approaches that appear promising, and are considered worthy of further investigation. For ease in presentation, the research findings for nitrates and fluorides are presented separately.

FLUORIDES

General Chemistry

Fluoride is the lightest and most reactive of all the halogens (Dictionary of Chemistry, 1980). The chief commercial ore is fluorite, CaF2, but many silicates contain some fluorine. Fluorine gas, HF and fluorides are toxic in large amounts, but essential to life and beneficial in the prevention of dental caries. Fluorine compounds find use in many applications including the preparation and handling of metals, the manufacture of inert plastics, in refrigerants, toothpaste additives, etc.

Fluorine forms a single series of compounds in the -1 oxidation state. High oxidation state compounds such as WF6 and SF6 are covalent., with low oxidation state compounds such as NaF, being ionic.

Fluoridation of Water

The fluoridation of water remains a highly controversial subject, with a paper recently published by the Department of Health giving (among many) the following recommendations regarding the fluoridation of water (Muller WJ et al, 1998).

The decision to fluoridate a public water supply must be a community decision taken after public consultation. However, the decision can only be taken after the public has properly been informed about the issue.

Optimum levels of fluoride for human health should range from 0.4 -0.7 mg/l F, depending on maximum mean annual temperature.

Accordingly, it is recommended that in areas where natural fluoride concentrations in drinking water exceed 0.7 mg/l F, steps should be taken to defluoridate the water.

Fluoridation should be considered only as a short-term measure, until economic conditions are such that all South Africans have access to proper dental health care facilities.

Current Removal Methods

A number of techniques have been proven as effective in removing fluorides from water. These can be divided into two groups (Benefield et al, 1982) –

(i) those based on the addition of chemicals to cause precipitation or co-precipitation duration coagulation, and
(ii) those based upon ion exchange or adsorption. Specifically, these are ion exchange, activated alumina, bone char and activated carbon, respectively.

Ion Exchange

Ion exchange is a well-established and precise method for the removal of dissolved ionic constituents from water. Synthetic ion exchange media has been engineered to have the property to release one or more ions in their structure in exchange for ions in solution (Benefield et al, 1982). Ion exchange media is continually being developed to have increasingly large exchange capacities as well as selectivity in certain cases towards the removal of specific target ionic constituents. Naturally, certain IX media has been developed which has a high affinity for fluoride ions.

Ion exchange treatment has the advantage that no sludge is produced, but it must be remembered that when the ion exchange capacity has been exhausted, the material must be regenerated. This gives rise to a concentrated waste stream of the original contaminant which must be disposed of safely. Regenerant chemicals used are frequently a brine solution with either caustic or concentrated acid solution depending on the ionic species being treated.

From a rural water supply point of view, ion exchange treatment has a number of important disadvantages:

high capital costs,
high operation and maintenance costs,
high skills levels required for plant operation, and
a concentrate stream is generated which may need to be safely disposed.

Activated Alumina

Of the adsorption processes, the activated alumina one appears to be the most attractive because alumina is somewhat specific for fluoride, and has a relatively high fluoride exchange capacity (Schoeman and Botha, 1985; Van Duuran, 1997). The affinity for common ions on acid treated activated alumina is in the following order:

$$OH^- > PO_4^{3-} > F^- > SO_3^{2-}; (Fe(CN)_6)^{4-}; CrO_4^{2-} > SO_4^{2-} > (Fe(CN)_6)^{3-}; CrO_7^{2-} > NO_2^{2-} > Br^- > Cl^- > NO3^- > MnO_4^{2-} > ClO_4^- > CH_3COO^-$$

In addition, activated alumina costs are relatively cheaper at about 10% those of ion exchange resin, and is not seriously affected by the concentrations of chlorides and sulphates usually encountered.

Regeneration, performed with either caustic soda or alum (Savinelli and Black, 1958), is fairly straightforward with the process being reliable, safe and relatively simple to use. A disadvantage, especially in the South African rural water supply context, is that the process needs a neutralization step with acid after caustic soda regeneration. The pH of the inlet water must also be adjusted to between 5 and 6 so as to create optimum fluoride adsorption conditions (Rubel and Woosley, 1979; Schoeman and Botha, 1985).

Generally speaking, it is the opinion of the authors that there is a need to do an in depth study on alumina availability juxtaposed against areas where fluoride occurs abundantly in rural drinking water supplies. Economic assessments need to be carried with regard to the financial impact added by the activated alumina process on rural water supply schemes. A manual summarizing design and operation would also be useful.

Bone Char

Prior to the use of activated alumina, bone char was originally used, with the process being described as an ion exchange on the surface of the bone, in which the radical on the surface of the apatite component was ($Ca(PO_4)_6.CaCO_3$) was replaced by fluoride to form insoluble fluorapitate (Benefield et al, 1982):

$$Ca(PO_4)_6.CaCO_3 + 2F^- \rightarrow Ca(PO4)_6.CaF_2 + CO_3^{2-}$$

Bone char, produced by carbonizing at 1100 - 1600 °C, had superior removal properties compared to the previous bone char used. When exhausted, the char is regenerated with sodium hydroxide (1%) to exchange the fluoride component to hydroxyapatite. Soluble sodium fluoride is produced as a by-product.

Essentially, bone char in operation is similar to activated alumina, and by-and-large also shares the same advantages and disadvantages as alumina (albeit to a larger extent) from a community water supply point of view.

Activated Carbon

Activated carbon is made up of random amorphous graphite plates, which give the carbon its very large surface area and unique property of adsorbing many different compounds. Nitrate is one of them, however, not as efficient as alumina. A study was carried out between four activated carbons, three activated bauxites, and two activated aluminas in there fluoride removal properties with optimum operating pH (Chang, 1953). Waters used were distilled water, sea-water and simulated geothermal water, and similar conditions were used for all tests. The following table summarizes the results obtained, and shows that the activated alumina and bauxite were superior to that of the activated carbon.

	Activated Carbon				Activated Alumina		Activated Bauxite	
Adsorbent	1		2		6		9	
Solution	Opt. pH	Rem. Ef	Opt. pH	Rem. Ef	Opt. pH	Rem. Ef	Opt. pH	Rem. Ef
Distilled water	6.2	84	6.0	45	4.9-8	95	5.5-6.8	95
Sea-water	6.2	72	6.0	24	4.9-8	95	5.5-6.8	95
Simulated Geo-water	6.2	72	5.9	24	4.9-8	95	5.5-6.8	95

Opt.pH = Optimum pH after 48 hr of contact between adsorption and solution.
Rem.Ef = Percentage maximum removal efficiency.

Membrane Processes

Reverse osmosis membranes are universally accepted for their ability to remove ionic constituents in water, including substances such as fluoride and nitrate (Montgomery, 1978). This is carried out by physical means, through the pressurization of water through a semi-permeable membrane, with pore sizes such as to prevent the passage of contaminants.

Similarly to ion exchange, however, from a rural water supply point of view, membrane treatment has a number of important disadvantages;

high capital costs,
- high operation and maintenance costs,
- high skills levels required for plant operation, and
- a concentrate stream is generated which may need to be safely disposed.

New advances in membrane technology indicate potential for the future in lower *trans-membrane pressure operating membrane systems* as well as more hardy and scale resistant membranes. These will reduce running costs, and the operating requirements making them more amenable to rural application.

Chemical Precipitation

The chemical precipitation methods include the use of lime (Boruff, 1934; Maier, 1947; Zabban and Jewett, 1970), magnesium (Sorg, 1978) and aluminium sulphate (Culp and Stoltenberg, 1958). Theoretically, lime can reduce fluoride to no less than 8 mg/l, while aluminium and magnesium sulphate can reduce fluoride to lower than 1.5 mg/l (Benefield, 1982). Combinations of these methods, especially in other treatment processes such as the ettringite process (Vinnicombe et al, 1994), as well as the precipitation of a sodium phosphate aluminium fluoride (Miller, 1986), has shown very good removal rates. However, the disadvantages are numerous and significant;

excess and costly dosages are required,
- a sludge disposal problem also arises,
- operation and maintenance costs rise dramatically, and
- the skills complement required to run the scheme gets increased.

NITRATES

General Chemistry

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 (Dictionary of Chemistry, 1980). 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, 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 ground water) 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 (Tredoux, 1993).

Health Effects of Nitrate in Drinking Water

Nitrate per se is considered to be relatively non-toxic and is readily excreted by the kidneys. The secondary products of it, namely nitrite and nitrosamines, however, present a health hazard to humans. Nitrites are known to cause methemoglobinaemia in infants, while nitrosamines are carcinogenic and may play a role in the induction of certain gastro-internal cancers (Hill et al, 1973; Fan et al, 1987).

CURRENT REMOVAL METHODS

Ion Exchange and Membrane Processes

Both of these have been covered previously in the section on fluoride removal, however, it must be mentioned that ion exchange resins have been developed that are highly selective to nitrates (Hellmig; Jackson et al, 1990; USEPA, 1983). The pros and cons remain the same as for fluoride removal, in the requirements needed to operate the systems, disposal requirements and capital and operating costs.

VARIOUS PROMISING NEW APPROACHS IN REMOVING NITRATES AND FLUORIDES

In determining promising approaches it is worth defining criteria and the basis on which particular techniques are being suggested as worthy of further investigation. In order for a process to be cited, it has to have the following attributes;

it should be effective in removing the offending contaminant of interest,
- it should have relatively low operation and maintenance costs,
- it should have low or comparatively priced capital costs, and
- it should be relatively simple to operate, and certainly operable at the local level.

From that point of view, therefore, the approaches or techniques which have been identified as having good potential, for rural application, can be broadly described as being those either of a biological nature, or those that rely on adsorption/desorption mechanisms to remove fluorides and/or nitrates from drinking water supplies.

It is important to note, however, that the fact that while certain "low level" complexity techniques are promoted suitable for application in rural environments should not mean that they are of necessity restricted there. In almost all cases, these are frequently also the most logical processes utilized in urban schemes. Examples are slow sand filtration and the utilization of natural aeration in order to remove iron and manganese, which are technological techniques popularly used both in urban and rural water supply schemes.

1. Bacterial Removal of Nitrates

Microbiological means have generally been used in the past as an alternative process for the removal of nitrates. An increasing number of reports have documented the successful utilization of denitrifying bacteria for the removal of nitrates from drinking water (Anonymous, 1985; deMendonca et al, 1992; Hogrewe, 1990; Cook, 1990). The Electric Power Research Institute (EPRI) has published findings emanating from one of their funded demonstration projects where-by drinking water for a small rural community (pop. approx. 650) was successfully denitrified in the Town of Wiggins, Colorado (EPRI, 1998). Wiggins is located 75 miles North West of Colorado. In this case the system was designed for a capacity of 76 liters per minute. The nitrate levels were brought down from 20-25 mg/l NO3 (as N) to less than 3 mg/l in the effluent. Sand filters were subsequently used to remove residual suspended bio-solids, with a final treated water that was always less than 0.5 NTU, which is a very good quality standard for drinking water. The project reportedly demonstrated that the process can function reliably with relatively unattended operation. In this instance, food grade corn syrup was added to provide an adequate food source for the bacteria, which adhered to plastic porous media.

From the study at Wiggins, a company was initiated to commercialize the process. The company is Nitrate Removal Technologies (EPRI, 1998), and the process is called BioDenTM (NRT, 1998). The process is commercial with the removal of nitrates by bacterial action, converting it to nitrogen and carbon dioxide gases. Bacteria utilized are naturally occurring and non-pathogenic. However, their activities are stimulated by the addition of substrate with a carbon source such as acetic acid, molasses, etc.

A farmer at Settlers in the Springbok flats has claimed that after implementing a similar denitrification process, he was able to bring down nitrate levels from 34.3 mg/l to 0.2 mg/l (Anonymous, 1985). High nitrate concentrations in ground water on the Springbok Flats are a common phenomenon. The farmer reported that after implementing this process, his livestock units increased from nine to the forty units at the time of publication of the article (1985).

The farmer described the denitrification unit as one utilizing molasses. Inoculation with sludge was reportedly superfluous. Costwise, the unit seldom required more than 1 kW to function, the investment required largely confined to a motor, 2 positive displacement pumps, a speed control system, a stone/sand filter as well as an air introducer to render the water even more palatable.

From a South African context and point of view it is necessary to investigate appropriate, indigenously occurring substrates which could be utilized especially in rural communities without greatly impacting negatively on the operating and maintenance costs of nitrate removal reactors. Bacterial processes have generally found widespread use in wastewater treatment. From a drinking water purification point of view, their largest application has probably been in the *schmutzdecke* on slow sand filters. It is the authors' opinion that design and operating guidelines also still need to be developed for this process. However, as mentioned previously this process appears to hold good promise for rural application in South Africa.

2. Extended Operation Adsorption/Ion Exchange Media

In recent years, due to the demand for more effective removal of fluoride from water, new and improved high yield activated aluminium oxide media have been formulated. These have a high surface area (350 m2/g), produced by controlled pore size distribution from 30–100 Angstrom (TES, 1998). This provides greater accessibility to the surface active sites through bulk diffusion.

Commercial systems using either activated alumina, carbon or ion exchange are available. An important disadvantage with these systems is the interference of other compounds and chemical substances on the media. Micro-filters assist in the removal of particles, but do not impart any protection against reactive and/or fouling chemicals. This also includes bacteriological fouling.

An approach that needs to be investigated, is the extension of the above mentioned adsorption and ion exchange techniques by using redox media. Commercial systems using this media with activated carbon are available and are used for the removal a wide-range of contaminants from water (PureEarth Tech.,1998; Solid State Tech., 1998). The media, produced from two dissimilar metals, uses redox (reduction-oxidation) reactions on the surface of the media to "clean-up" the water prior to processes like activated carbon, activated alumina or membrane treatment systems. Reduction-oxidation reactions are those in which atoms undergo changes in oxidation number. In general, these reactions involve the transfer of electrons from one atom or molecule to another. The potential that is formed during the process is a redox potential.

The redox media works by producing a redox charge or "shock" that kills micro-organisms, remove metals, and destroy reactive components such as chlorine. The media may not remove chemical components such as fluoride or nitrate, from water, but will enhance the quality of the water prior to systems such as absorption media, thus reducing fouling and prolonging the life of the absorbent/ion exchange material. It can also act as a particle filter prior to the adsorption media.

3. The Low Cost Sri Lankan Defluoridation Approach

In recent years, a lot of work has been carried out on low cost domestic defluoridation. Most of this work has been carried out in Sri Lanka, due to the fact that Sri Lanka has a similar fluoride problem to South Africa, with over 40 % of wells in parts of the country being high is fluoride. The defluoridation system which has been tested in Sri Lanka comprises of either a PVC pipe or a square column, with the inlet pipe situated in the center of the container, with the flow of water from the bottom to the top. The containers are then packed with broken pieces of freshly burnt bricks to a height of 75 cm. Initially the filter is filled with the high fluoride concentration water for 12 hours. This is to obtain equilibrium. During operation, the water if fed into the pipe, allowing the water to flow through the brick media and then over-flow for usage.

The percent removal efficiency of these low cost defluoridators, based on the results from Sri Lanka, varies from 85 % at the beginning of the run, to 25 % near the end, depending on the run time for each tests. The removal of fluoride by defluoridators, used in the rural areas, has consistently shown removal efficiencies of approximately 80 %, with 70-100 day trials. A vast majority of the defluoridators in operation in Sri Lanka are showing the sustainability and acceptability of this technique on a domestic level.

The theoretical mode of removal is based on the fact that low temperature burnt clay brick pieces consists of silicates, aluminates and hematites. These oxides are converted to oxyhydroxides of iron, aluminium and silica, when soaked in water for several hours. As the geochemistry of the fluoride ion is similar to that of the hydroxyl ion, these are readily exchanged. Other possible formations are with aluminium in the formation of aluminium fluoride, and also the adsorption onto aluminium hydroxide.

CONCLUSIONS AND RECOMMENDATIONS

The challenge facing scientists, design engineers and policy managers has come to the fore, to come up with appropriately proven techniques for the removal of nitrates and fluorides from community water supplies. This is particularly important in view of the current RDP infrastructure roll-out programme currently taking place in South Africa which has a particular focus on rural previously unserviced areas in the country.

A desk-top review on promising approaches for the removal of these contaminants from drinking water has yielded at least three techniques which are deserving of further investigations with regard to their potential applicability for South Africa. These fall into the two main categories of biological processes and adsorption/desorption techniques. Pressure driven membrane process also continue to show promise as newer systems are developed which have lower operations and maintenance requirements.

Biological reactors packed with porous media have steadily demonstrated good results in the treatment of high nitrate containing drinking water. The media support a biofilm containing denitrifying bacteria. These non-pathogenic organisms convert nitrate to harmless nitrogen gas that is discharged to the atmosphere. These systems show good potential for rural application due to simplified operation and low capital and O+M costs.

Adsorption/desorption processes such as activated alumina, ion exchange also show good promise for application due to their relatively easy mode of operation as well as their effectiveness. The extremely wide variations in media from the capital intensive ion exchange to the "lowly" clay bricks utilized in Sri Lanka means that there is opportunity to investigate appropriately priced media for the South African rural environments, as well as natural occurrence patterns.

In both instances, once the techniques have been proven as appropriate, there will be a need to develop design guidelines as well as operation manuals.

ACKNOWLEDGEMENTS

This paper is an excerpt from a report currently being compiled on behalf of the Water Research Commission which summarizes the status of South African research regarding the removal of nitrates and fluorides in drinking water as well as details promising new techniques for their removal in rural water supplies. We gratefully acknowledge support from the Commission for funding the study.

REFERENCES

Benefield LD, Judkins, JF and Weand BL, "Process chemistry for water and wastewater treatment", Prentice-Hall, Inc, 1982.

Boruff C, "Removal of fluoride from drinking water", Water Ind. Engng. Chem., (**26** 69), 1934.

Chang SL and Morris JC, Industrial Engineering Chemistry, 45:1009, 1953).

Cook NE, Silverstein J, Hogrewe WJ and Hammad KA," Denitrification of Potable Water in a Packed Tower Biofilm", Environmental Engineering, ASCE EE Div Conf., 1990.

Culp R, Matson J and Kennedy R, "Fluoride reduction at La Cross, Kan", J. Am. Wat. Wks. Ass. (**50** 423), 1958.

DeMendonca MM, Silverstein J and Cook NE, "Short and Long-Term Responses to Changes in Hydraulic Loading in a Fixed Denitrifying Biofilm", Wat. Sci. Tech., 26, 1992.

Dictionary of Chemistry, Sharp DWA, Penguin Books, 1980.

EPRI, "Demonstration of Biological Denitrification of Drinking Water for Rural Communities", Report CR-108884, 1997.

Fan AM, Willhite CC and Book SA, "Evaluation of the nitrate drinking water standard with reference to infant methemoglobinaemia and potential reproductive toxicity", Regulatory Toxicol. Pharmacol. (**7** 135-148), 1987.

Hill MJ, Hawksworth G and Tattersall G, "Bacterias, nitrosamines and cancer of the stomach", Br. J. Cancer (**28** 562-567), 1973.

Hellmig R, " Wofatit Anion Exchangers for Removing Nitrates from Potable Water", Chemie Ag Bitterfeld-Wolfen.

Hogrewe WJ, "Biofilm Denifrification of Drinking Water: Kinetics, Oxygen Inhibition and Biomass Removal", PhD thesis, Civil Engineering, University of Colorado, Boulder, CO, 1990.

Jackson MB and Bolto BA, "Effect of Ion-exchange Resin Structure on Nitrate Selectivity", Reactive Polymers, 12, 1990.

McCaffrey LP, PhD Thesis, UCT, 1998

Miller DG, "*Fluoride precipitation in metal finishing waste effluent*", 1986.

Montgomery JM, "Water Treatment: Principles and Design", John Wiley & Sons, 1978.

Muller WJ, Heath RGM, and Villet MH, "Finding the optimum : Fluoridation of potable water in South Africa", Water SA, Vol 24, No. 1, January 1998.

NRT, Nitrate Removal Technologies, http://www.nitrateremoval.com/.

Pure Earth Technologies, http://www.pure-earth.com/.

Rubel F and Woosley RD, "Removal of excess fluoride from drinking water", Technical Report No. EPA 570/9-78-001, Washington DC, 1978.

Savinelli EA and Black AF, "Defluoridation of water with activated alumina", J. Am. Wat Wks. Ass. (**71**, 45), 1979.

Schoeman JJ and Botha GR, " An evaluation of the activated alumina process for fluoride removal from drinking-water and some factors influencing its performance", Water SA, Vol 11, No 1, January 1985.

Solid State Technologies, http://pw1.netcom.com/~owensva/.

Sorg TJ, "Treatment technology to meet the interim primary drinking water regulations for inorganics', j. Am. Wat. Wks. Ass. (**70** 105), 1978.

TES, Private communication with Tempest Environmental Systems, tempest@aquapura.com.

Tredoux G, "A preliminary investigation of the nitrate content of groundwater and limitation of the nitrate input", WRC Report No. 358/1/93.

USEPA, "Nitrate Removal for Small Public Water Systems", 1983.

Van Duuran FA, "Water Purification Works Design", Water Research Commission, TT 92/97, 1997.S

Vinnicombe DA and Conlin JB, " Sulphate removal from mine, ash and cooling water", Aquafrica, 1994.

Zabban W and Jewett H, "The treatment of fluoride wastes", Proc. 23rd Ind. Waste Conf., Purdue Univ., Lafayette, Indiana,, J. Ind. Engng. Div. Am. Soc. Civ. Engrs. (**96**, 1031), 1970.