

**FLUORIDES AND NITRATES: THEIR OCCURRENCE IN RURAL
SOUTH AFRICA, CURRENT REMOVAL TECHNOLOGIES AND
PROMISING NEW APPROACHES**

by

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Extent Of Fluoride and Nitrate Contamination Problems In Rural Drinking Water
Supplies And Promising Appropriate Technologies For Removal"

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TABLE OF CONTENTS

EXECUTIVE SUMMARY

1. INTRODUCTION

2. FLUORIDES

- 2.1 General Chemistry
- 2.2 Distribution and Causes of High Fluoride Concentrations in Groundwater
- 2.3 Fluoride and Health
- 2.4 Metabolism of Fluoride
- 2.5 Dental Fluorosis
- 2.6 Fluoridation of Water

3. CURRENT REMOVAL METHODS

- 3.1 Chemical Precipitation
- 3.2 Lime Softening
- 3.3 Magnesium Co-precipitation
- 3.4 Alum Coagulation
- 3.5 Ettringite Formation
- 3.6 Membrane Processes
- 3.7 Ion Exchange
- 3.8 Activated Alumina
- 3.9 Bone Char
- 3.10 Activated Carbon

4. PROMISING APPROACHES FOR FURTHER DEVELOPMENT

- 4.1 Extended Operation of Adsorption/Ion Exchange Methods
- 4.2 Low Cost Sri Lankan Defluoridation Approach

5. NITRATES

- 5.1 General Chemistry
- 5.2 Health Effects of Nitrates in Drinking Water
- 5.3 Nitrate Occurrence in South African Groundwater

6. CURRENT REMOVAL METHODS

- 6.1 Ion Exchange
- 6.2 Membrane Processes

7. BACTERIAL NITRATE REMOVAL AS A PROMISING TECHNIQUE FOR

8. FURTHER DEVELOPMENT

9. SUMMARY OF PROMISING APPROACHES AND RATIONALE

10. CONCLUSIONS AND RECOMMENDATIONS

EXECUTIVE SUMMARY

This report reviews the occurrence of nitrates and fluorides in South African drinking water through previous reports and publications from other workers. It also reviews the current methods and technologies utilized for their removal taking particular regard to the needs of rural communities. The advantages and disadvantages of each technology are considered. Finally, the report outlines some emergent techniques and approaches, which the authors consider to hold good promise for rural application, are recommended for further research and investigations.

From a South African perspective, several researchers have noted the high fluoride content of certain groundwaters in South Africa, especially in the Pilanesburg and Bushveld complex. Hydrochemical data from the national groundwater database has been analyzed by Tredoux in a report published in 1993. In that study, the median nitrate concentration was found to be 4.5 mg/l with 15 percent of the samples (out of 18827) indicating fluoride concentrations in excess of 20 mg/l. Certain groundwater maps detailing high fluoride and nitrate have been published by certain researchers, the most recent by Marais (1998) which details each province excluding Gauteng and the Western Cape. These depict concentrations according to a classification system, which indicates the suitability of water for domestic use, or else, treatment options to make it suitable. Nitrate occurrences on these maps shows broad agreement with findings from earlier researchers, and in addition, shows newer previously un-monitored areas. Out of a sample number of communities totaling 12 074, 10 295 were found to be utilizing groundwater. Amongst these where information was available, 625 were found to be utilizing drinking water high in nitrates and/or fluorides.

Currently utilized techniques for the removal of these contaminants, which were reviewed, include ion exchange and other adsorptive processes, membrane processes, chemical precipitation as well as the microbiological denitrification of nitrates, specifically.

Based on the nature of the fluoride and nitrate problems, and the unique requirements of rural supply and treatment, the following is recommended:

- Biological systems should be investigated with respect to nitrate removal. This should include pilot scale on a specific source, and then full scale on a problem source, so as to obtain long term experience and knowledge. Naturally occurring substrates should also be investigated with respect to nitrate removal capabilities.
- Fluoride removal research effort should concentrate on absorption methods. This will include activated alumina, with and without redox media. The activated alumina should first be evaluated in the laboratory to identify the benefits of redox media, and then to evaluate each on a problem source, so as to obtain long term operating needs. The method described by Sri Lankian researchers should also be investigated on pilot plant scale (small scale) before a larger investigation. The source of adsorption material should be investigated with respect to the types of brick to be used, as well as clay, minerals and carbons. These will include dolomite, charcoal and different types of clays, bauxites and zeolites. The study should include the areas where the minerals are present, compared to that of the problem waters. This will assist in evaluating the feasibility of using these minerals and clays.

1. INTRODUCTION

Since 1994 South Africa has embarked on an ambitious infrastructure rollout 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 (e.g., Build, Operate, Train and Transfer (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 worldwide 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. Whilst 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 World Health Organisation (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.

Nitrate (NO_3^-) and Fluoride (F^-) are two inorganic compounds which occur widely in South African waters, albeit in concentrations usually within the recommended guidelines. In certain areas of the country, however, they occur in varying 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 Community Water Supply

System (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 NO_3^- and F^- , 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 NO_3^- . McCaffery (1998) has written extensively on the distribution and occurrence of F^- 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 NO_3^- . This is attributable mainly to natural geologic formations and/or anthropogenic 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 NO_3^- and F^- . 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 the occurrence of the contaminants in South African waters, commonly used removal techniques as well as some approaches that appear promising, and are considered worthy of further investigation. For ease in presentation, the research findings for NO_3^- and F^- are broadly presented separately over three parts. The first being on F^- ,

the second on NO_3^- and then the third on various promising technologies, covering both F^- and NO_3^- removal techniques.

2. FLUORIDES

2.1 General Chemistry

Fluorine (F) is the lightest and most reactive of all the halogens [Dictionary of Chemistry, D W A Sharp, Penguin], with an electronic configuration $1s^2 2s^2 2p^5$. The chief commercial ore is fluorite (CaF_2), but many silicates contain some fluorine. It is obtained by electrolysis of a KF-HF melt using a carbon anode. Hydrogen is liberated at the cathode and must be kept rigidly separated from the fluorine. Fluorine can be handled in metal (copper, nickel, etc) apparatus and stored as a gas in cylinders or as liquid fluorine. Elemental fluorine consists of F_2 molecules but they have relatively low dissolution energy and react with most elements (metals tend to be coated by a coherent film of fluoride). Fluorine gas (F_2), hydrofluoric acid (HF) and fluorides (F^-) are toxic in large amounts, but essential to life and beneficial in the prevention of dental caries. Fluorine compounds are used in the preparation and handling of metals, in inert plastics, refrigerants, aerosol propellants, toothpaste, and water treatment.

Fluorine forms a single series of compounds in the -1 oxidation state ($E^\circ = -2.82 \text{ V}$). High oxidation state compounds such as WF_6 and SF_6 are covalent, with low oxidation state compounds such as NaF , being ionic.

2.2 Distribution and Causes of High Fluoride Concentrations in Groundwater

Global. Many countries of the world have significant areas where groundwater contains elevated concentrations of fluoride (F^-). The United States of America, Canada, China and India are amongst countries in the northern hemisphere that experience high F^- groundwater (Cobertt and Manner, 1984; Yong and Hua, 1991; Gupta and Sharma, 1995; Boyle and Shagnon, 1995; Hitchon, 1995, Yong and Hua, 1991) attributed to several causes: high F^- content on aquifers; low groundwater flow rates; arid and semi-arid climate leading to increased potential evaporation; and water with high pH.

In a detailed study in the Alberta basin of Canada, Hitchon (1995) found formation waters with up to 22 mg/l F^- . He noted a trend of increasing fluorite (CaF_2) saturation from shallow, cool, low Ca, fresher waters to deeper, hotter ($73^\circ C$), more saline and calcium (Ca)-rich water. He noted the importance of the MgF^+ complex, and that the complexes NaF° , VO_2F° and AlF_2^+ were of minor importance. He stated that the F^- concentration in groundwater is controlled by an intricate relation between saturation with respect to CaF_2 and the concentration of ions which form F^- complexes, all of which are controlled by ionic strength and temperature. It was calculated that many possible F^- complexes were not in fact of quantitative importance, e.g., aluminium complexes from AlF^{2+} to AlF_6^{3-} , vanadium complexes VOF^+ and VOF_2 , FeF^{2+} and SiF_6^{2-} .

Kraynov et al. (1969) found that waters with up to 15 g/l F^- had been in contact with villiamite (NaF), an abundant accessory mineral in the deep zones of the Lovozero Massif. The massif is composed of alkalic rocks, similar to those of the Pilanesburg Complex. The author noted that evaporation had increased the F^- concentration in the groundwaters. The waters are highly alkaline ($pH > 12$)

and are characterized by very high concentrations of Na (up to 26 g/l), Si (up to 13 g/l) and virtual absence of Ca.

Africa. In Africa, high F^- groundwaters have been studied in some detail in Kenya (Gaciri and Davies, 1993; Davies, 1994), in Ethiopia (Ashley and Burley, 1994; Gizaw, 1996), and in Tanzania (Smet, 1992). The abundance of F^- in Rift valley groundwater has been attributed to weathering of alkaline volcanic rocks rich in F^- and the interaction of groundwater with volcanic HF exhalations (Gaciri and Davies, 1993); outgassing of CO_2 , geothermal heating and low groundwater Ca and salinity (Gizaw, 1996) and ion exchange processes (Ashley and Burley, 1994). Botchway *et al.* (1996) attributed high F^- concentrations in the groundwater of Accra in Ghana to the decay of plant material. Other countries which have F^- enriched groundwaters include Sudan (Ibrahim *et al.*, 1995), Nigeria, Senegal, Algeria, Egypt, Zimbabwe, Morocco, Uganda and Somalia (Smet, 1992).

South Africa. Several researchers have noted the high F^- content of certain groundwaters in South Africa, especially in the Pilanesburg and Bushveld Complexes. Shand (1928) gave a description of the hydrology of the Pilanesburg Complex and commented on spring water composition: "high level" springs being pure, and "low level" springs being high in soda. Orckse (1943) measured rock, soil and groundwater concentrations of F^- in an attempt to understand the causes of endemic dental fluorosis. His study covered the whole of South Africa but unfortunately gave the western Bushveld only superficial attention. He did, however, single out the Pilanesburg, Warmbaths and Pretoria Saltpan areas with endemic dental fluorosis deserving greater investigation. He suggested F^- in groundwater of the Springbok flats came from the Eccu formation, and suggested detrital fluorapatite as the source. Grobler and Dreyer (1988) determined F^- concentrations in drinking water from surface waters and groundwaters from 162 towns and cities across South Africa. Forty

percent of the groundwaters had F^- concentrations below 0.1 mg/l, and less than 7% had fluorides greater than 1.0 mg/l. Of the groundwaters, 84% had significantly lower concentrations than that of surface waters. Raubenheimer *et al.* (1990) determined F^- concentrations in rivers flowing through the Kruger National Park. Their main conclusion was that all 5 rivers (the Oliphants, Levuhu, Letaba, Sabie and Crocodile rivers) had higher concentrations of F^- during the latter part of the dry winter season. The Oliphants river had differences of up to 2 mg/l F^- between wet and dry season flows. Changes in mean F^- concentration in each of the 5 rivers over 5 years was very slight, and not significant. Fayazi (1995) suggested that the Karoo sedimentary strata contained CaF_2 derived from the surrounding Bushveld Granites during episodes of arid erosion. He suggested that F^- concentrations in groundwater hosted by the Karoo formations is strongly controlled by the geochemistry of the rock.

McKenzie *et al.* (1966) published a map of groundwater with a F^- concentration above 1.5 mg/l, prepared by the Soil Research Institute. The map was based on unspecified data sources and is at variance with the current known distribution as presented in Figure 1a and 1b. These figures are based on unpublished distribution maps calculated from the SA National Groundwater Database. It can be seen that large areas of the country are subject to F^- concentrations in groundwater in excess of 1.5 mg/l, especially in the arid western and south-western Cape.



Figure 1a South African groundwater with F^- concentration greater than 1.5 mg/l. (Source: McCaffery, 1998)

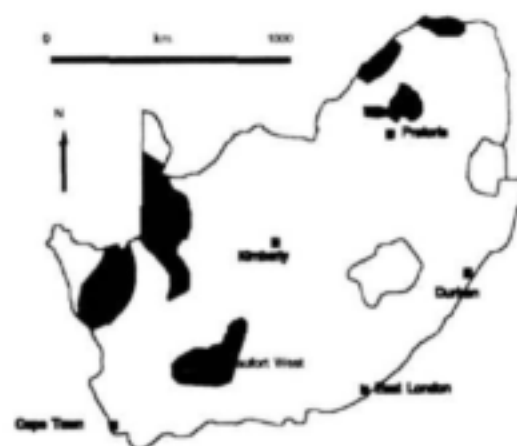


Figure 1b South African groundwater with F^- concentration greater than 3.0 mg/l. (Source: McCaffery, 1998)

Bond (1947) was the first worker to extensively discuss chemical analyses of groundwater from the Pilanesburg Complex. He noted the "high soda alkalinity and the consistently high F^- content". He stated that the highest recorded concentration of F^- in ground water so far discovered in the Union of South Africa was 67.2 mg/l in spring water from the farm Doornhoek, although the exact location was not given. Ritief (1963) published 9 analyses of groundwater, which were only analyzed for F^- and chloride (Cl^-). F^- was consistently high in his analyses. Lurie (1974) gave a full chemical analysis of water from an artesian borehole in Tuffs, which showed a F^- concentration of 2.4 mg/l. Bond (1947) described groundwaters occurring in other lithologies in the field area, based on a fairly limited sample set. He stated that Pilanesburg groundwater was similar in chemical composition to those of the 'Red Granites' (Lebowa Granite Suite) which are also characterized by high F^- concentrations. The 'Old Granite' (Archaean Granite) occasionally has an appreciable F^- content, whilst in some samples it is absent. Both Bond (1947) and Ockerse (1943) stated that F^- was present in solution as "sodium fluoride".

Marais (1998) has subsequently published the newest set of F^- (and nitrate (NO_3^-)) concentration maps covering each province excluding Gauteng and the Western Cape. These depict concentrations according to a classification

system which indicates the suitability of water for domestic use, or else, treatment options to make it suitable. This classification is according to the Assessment Guide Vol1: Quality of Domestic Water Supplies published by DWAF, the WRC and the Dept. of Health (See Appendix 1 and 2 for the fluoride and nitrate concentration maps, respectively). NO_3^- occurrences on these maps show broad agreement with findings from earlier researchers, and in addition, show newer previously un-monitored areas. A brief summary of findings is as follows;

Table 1: Communities with High Occurrences of F^- and NO_3^- in Drinking Water

Provinces	No. of Communities	Communities using Groundwater	Communities with no Information	Communities High in NO_3^- and F^-
N Cape	226	125	55	47
N West	1297	1058	306	259
N Province	2067	2067	1380	191
Mpumalanga	583	1850	1661	33
Free State	251	528	286	72
KZN	1973	72	79	22
W Cape	0	0	0	0
E Cape	5677	4595	4594	1
TOTAL	12074	10295	8361	625

2.3 Fluoride and Health

F^- is an excellent example of the principle: *"All substances are poisonous; there is none which is a poison. The right dose differentiates a poison and a remedy"*. It is one of a group of trace mineral which are beneficial at low dosages, but which are harmful (and even fatal) at higher doses. F^- not only affects humans, but livestock as well. The first recorded outbreak of recognizable fluorosis in

farm animals took place after the eruption of the volcano Hekla in the eighteenth century. Mass mortality of livestock due to acute F^- poisoning caused starvation and a 25% reduction in the human population of Iceland (Fridriksson, 1983). Chronic fluorosis in animals is manifested by severe dental lesions, lameness and exostoses. Fluorosis in animals has been recorded from just north of the Pilanesburg, Warmbaths, Kalkheuvel and Pretoria Saltpan areas (Botha *et al.*, 1993). Also affected are wildlife (Fourie *et al.*, 1996) and plants.

2.4 Metabolism of Fluoride

F^- passes into the blood plasma by absorption through the lungs or gastrointestinal tract. In contrast to the other halogens, fluoride is rapidly absorbed from the stomach; plasma F^- concentrations peak approximately 1 hour after ingestion. The free F^- ion is converted to HF in the stomach (Jenkins, 1990). In the blood, three quarters of the total F^- is found in the blood plasma, with the balance taken up by red blood cells. Fluorine in plasma exists primarily as the free F^- ion, whilst the rest is present as lipid-soluble organic fluorocompounds. The kidneys rapidly remove F^- from the blood, so that a typical background concentration is only 0.02 mg/l F^- (Jenkins, 1990). Approximately 50% of absorbed F^- is eliminated from the body within 24 hours, primarily in urine. The residue becomes associated with calcified tissue, where 99% of the total F^- in the body is found. Whilst Jenkins (1990) states that F is firmly bound to the bone, Whitford (1996) states that F^- is not irreversibly bound to the surface bone crystallites, so that F^- concentration in bone can eventually reflect changes in the amounts of F^- ingested chronically. The F^- half-life in bone is approximately 8 years (Schlatter, 1978). F^- is not accumulated in the thyroid gland and is eliminated many times faster than the other halogens. Urinary pH affects the efficiency with which the kidneys remove F^- from the body, so chronic acid-base disturbances are important in F^- metabolism. Acid-

base status is influenced primarily by diet, as well as certain drugs, metabolic and respiratory disorders, physical activity and altitude (Whitford, 1996). Fluoride freely passes through the placenta, so that foetal F^- plasma levels are directly proportional to those of the mother.

The cariostatic effect of F^- is probably due to its ability to promote enamel remineralisation and to inhibit acid production by plaque bacteria (F^- is a potent inhibitor of many enzymes. F^- has the ability at low levels to inhibit soft tissue calcification and may decrease the chances of death due to cardiovascular disease, particularly ischemic heart disease (McCaffery, 1998).

2.5 Dental Fluorosis

Since the fifty's it has been shown that high concentrations of F^- in drinking water can cause deleterious effects in human dentition (Senewiratne *et al.*, 1973). It has also since been shown that a moderate intake of F^- , often facilitated by fluoridation of drinking water, is beneficial to dental health by causing a reduction in dental caries (Arnold *et al.*, 1953; Newbrun, 1989). F^- deficiency is marked by an increased incidence of dental caries.

The incidence and severity of dental and skeletal fluorosis are influenced by other factors apart from the concentration of fluoride in drinking water. A dietary content in vegetables and fruit has been suggested as a factor (Dodd *et al.*, 1960). The increase in the availability of fluoridated toothpaste and F^- supplements has caused an upsurge in dental fluorosis in communities with optimally fluoridated water (Pendrys, 1995). The increases in dental fluorosis with increasing altitude (Shortt *et al.*, 1937 and average temperature (Galagan and Lamson, 1953; Brouwer *et al.*, 1988) are due to increased water consumption, thus increasing total F^- intake.

Ockerse (1941 and 1943) and Ockerse and Meyer (1941) were the first workers to report on the occurrence of endemic dental and skeletal fluorosis in South Africa. Ockerse (1943) found evidence of the condition in the Pilanesburg, Warmbaths, Kalkheuveld and Pretoria Saltpan areas. Not all occurrences were large; only 3 cases were located around the Saltpan, and the cases at Kalkheuveld were found only in the workers of a certain quarry. However, he stated that the Pilanesburg was *"one of the worst affected endemic fluorosis areas in the Transvaal"*, and that *"some of the worst cases of mottled enamel are found among school children who were born and grew up in Warmbaths"*. He stated that 144 endemic areas had been identified in the Transvaal, mostly in areas underlain by the Bushveld Complex.

Zietsman (1985, 1989 and 1991) carried out a study encompassing several villages in the Nebo district. She sampled 120 boreholes, and found much spatial variation of F^- concentrations, ranging from 0.1 to 5.5 mg/l. Importantly, she found that 33% of children drinking groundwater with a F^- content of <0.5 mg/l had dental fluorosis.

Rudolph et al., (1995) have investigated dental fluorosis in four villages near the Pilanesburg Complex. Two of the villages had high F^- groundwater, whilst the two control villages had low F^- groundwater. They found that severe dental fluorosis occurred in 28% of subjects drinking groundwater with a F^- concentration of 7 to 8 mg/l, whilst 41% had moderate dental fluorosis. Every person in the two villages with high F^- groundwaters showed some evidence of dental fluorosis. Three people in the two villages with low F^- also had dental fluorosis. In 1991, 95% of the inhabitants of Bophuthatswana received their drinking water from groundwater (Pelpola et al., 1992).

According to du Plessis et al. (1995), race was found to be a factor in the severity of dental fluorosis. They found that 39% of white children in the

Bloemfontein area had evidence of dental fluorosis on the maxillary central incisors, compared to 16% of black school children drinking water of the same concentration (0.54 mg/l F⁻). Ritief *et al.* (1979) showed that a positive association existed between F⁻ concentration in tooth enamel and the degree of fluorosis in the individuals of the town of Klenhardt in the Northern Cape, supplied with high F- content drinking water (3.2 mg/l). The study of van der Merwe *et al.* (1979) reached similar conclusions.

Other effects of F⁻ on the human body (and livestock) include skeletal fluorosis (Jenkins, 1990; Meunier *et al.*, 1989; Shortt *et al.*, 1937; Ockerse, 1941), goitre (Day and Powell-Jackson, 1972; Yang *et al.*, 1994; Kalk *et al.*, 1997) as well as acute F⁻ poisoning (Gessner *et al.* (1994). Large amounts of F⁻ must be ingested to induce acute F⁻ poisoning. Gessner *et al.* (1994) reported death conditions after ingestion of 18 mg/kg body weight, although other workers have quoted an LD₁₀₀ (the dose which is 100% lethal to a specified group of subject, in this case human males of 70kg mass) of a quarter of this value.

2.6 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, it can only be reached when the public is properly informed about the issue.
- Optimum levels of F⁻ for human health range from 0.4 - 0.7 mg F⁻ /l, depending on the maximum mean annual temperature. *The maximum level of 0.7 mg/l F /l should not be exceeded.*

- Accordingly, it is recommended that in areas where natural F^- concentration in the drinking water exceeds $0.7 \text{ mg } F^- / l$ steps be taken to defluoridate the water.
- As an interim measure, a scale of temperature-adjusted optimum fluoride levels should be adopted in South Africa, rather than a single level covering the wide-ranging ambient temperatures (and corresponding consumption rates of drinking water) in the country. A sliding scale would mean that the community within supply regions can determine its own F^- consumption within the optimum range.
- 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.

The major point of the above abstract is the correct and absolute education of the public as to the advantages and disadvantages of the addition of F^- into potable water. It must also be noted that the correct dosing of the water means the absolute and accurate measurement of F^- , at and below the control point.

The controversy can also followed on the world wide web (internet) concerning dental and skeletal fluorosis. Following is the summary of the main points discussed on abstracts answering the question: "Are the claimed benefits of ingesting fluoride worth sky-rocketing fluorosis rates?". Even though the articles are mainly from fluoride proponents, several clear messages on either case emerge:

- There has been a significant rise in dental fluorosis rates and the severity of fluorosis since fluoridation was introduced and other F^- products captured the marketplace,
- Children are ingesting too much F^- from heretofore unknown sources,

- True dental fluorosis rates and it's corresponding severity is probably underestimated in the population.
- According to the proponents, fluoridation is responsible for about 40% of all fluorosis,
- There is no safe level of F^- intake below which the effects of F^- on enamel will not be manifest,
- Under-nourished children are at a much higher risk of developing dental fluorosis (the very children whose parents probably won't be able to afford the sometimes expensive cosmetic repairs needed),
- Together with the F^- ingested with fluoridated water or supplements, high protein diets, caffeine intake, tea intake, residence at high altitude, certain metabolic and respiratory disorders, and some drugs and medical conditions can significantly increase a child's risk of developing dental fluorosis,
- The magnitude of the benefits (if any) which dentistry attributed to ingested F^- was vastly overblown,
- Recent studies show no clinically relevant differences in tooth decay rates between those children who take F^- supplements and those who do not,
- It was once believed that the more F^- a child received, the fewer cavities he/she would have. However, studies now show that there are no clinically relevant differences in decay rates between children with fluorosis and those not affected,
- Dental researchers now believe that F^- action is predominately topical (i.e. acts on the surface of teeth, not from inside the body),
- F^- proponents are now starting to question the inadequate standards of previous dental research, which led to the uncritical and mostly indiscriminate use of fluoride supplements for young children. This begs an answer to the following question: *are scientific standards for dentistry any better today?*

- Fluorosed enamel is subject to increased attrition and erosion and post-eruptive damage increases with time. Severely fluorosed enamel is structurally weak,
- Contrary to dental rhetoric, laypeople are fully capable of diagnosing the different degrees of dental fluorosis,
- The cosmetic ramifications of dental fluorosis may have profound effects on self-conscious teenagers, and
- While dentistry is called on toothpaste manufacturers to lower the F^- content in children's toothpaste, it's unclear whether they are actually doing anything about it.

3. CURRENT REMOVAL METHODS

A number of techniques have been proven as effective in removing F^- 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.

The above classification does not include membrane treatment which is a physical water treatment method, removing contaminants in water in general.

3.1 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 F^- 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 and Conlin, 1994), as well as the precipitation of a sodium phosphate aluminium fluoride (Miller, 1986), has shown very good removal rates.

Although detailed further below, it is worth noting that the disadvantages of chemical precipitation as a method to remove F^- are many 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.

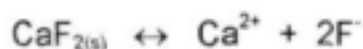
3.2 Lime Softening

This is carried out by the addition of lime to the water, with the mode of action being both the formation of an insoluble precipitate, and the co-precipitation with magnesium hydroxide (Boruff, 1934; Maier, 1947; Zabban and Jewett, 1970).

Although the precipitation by lime is usually used when the concentrations of F^- is extremely high, and initial removal needed, an equation has been calculated for the precipitation of insoluble CaF_2 . The reaction is:



The theoretical concentration of F^- should be subject to the solubility of the CaF_2 , but the equilibrium is also affected by the protonated species and ion pairs produced (Benefield, 1982). The approximate equilibrium constants are as follows:



$$K_s (\text{CaF}_2) = 4.0 \times 10^{-11}$$



$$K (\text{CaF}^+) = 10$$



$$K (\text{HF}) = 1.5 \times 10^3$$



$$K (\text{HF}_2^-) = 3.9$$

Using the above constants, the theoretical total soluble F^- concentration can be calculated by the equation, with the F^- concentration being a function of the calcium and pH:

$$[\text{F}]_T = \left[\frac{10^{-10.4}}{[\text{Ca}^{2+}]} \right]^{\frac{1}{2}} \cdot \{1 + (10)[\text{Ca}^{2+}] + (1.5 \times 10^3)[\text{H}^+] + (3.9)(1.5 \times 10^3)[\text{H}^+] \left[\frac{10^{-10.4}}{[\text{Ca}^{2+}]} \right]^{\frac{1}{2}}\}$$

If calcium hydroxide is the source of lime used, the pH of the water will increase with the increased addition of lime. This will form calcium carbonate if the water has alkalinity, and the pH is high enough. Temperature, ionic strength, and common ion effect also influence the removal of F^- . Soluble complexes with substances such as Fe^{3+} are frequently formed.

3.3 Magnesium Co-precipitation

The co-precipitation of F^- with magnesium hydroxide can reduce the F^- to low concentrations, as the softening of the water would be necessary (Sorg, 1978). A theoretical equation has been developed to predict the amount of magnesium required in order to reduce the F^- level to a given value.

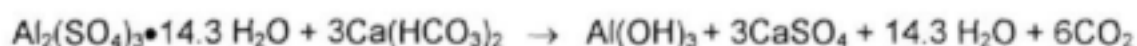
$$F_{\text{residual}} = F_{\text{initial}} - (0.07 F_{\text{initial}} \times \sqrt{\text{Mg}})$$

This equation suggests the reduction of fluoride from 5 to 1.5 mg/l requiring a magnesium concentration of 100 mg/l. In general, the utilization of this method is impractical, unless a high concentration of magnesium exists naturally and

needs to be treated. Large amounts of sludge are also produced by this method.

3.4 Alum Coagulation

The reduction of F^- by alum requires a large amount of alum. For instance, it has been shown that 250 mg/l alum is needed to reduce F^- concentrations from 3.6 to 1.4 mg/l (Culp and Stoltenberg, 1958). Operating pH is as with normal treatment, but large amounts of sludge are produced. Alum reacts with the alkalinity in the water to produce insoluble $Al(OH)_3$ as is shown by the reaction:



It has been suggested that the F^- ions are removed by adsorption onto the $Al(OH)_3$ particles. This would then be removed from water by sedimentation.

3.5 Ettringite Formation

This was also noticed in the removal of sulphate from water using the precipitation of Ettringite (Vinnicombe and Conlin, 1994). Ettringite formation is a little known method for the removal of sulphate from water, but has got a lot of attention worldwide over the last decade. Ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31-32 H_2O$) can be formed through the addition of calcium aluminate ($CaO \cdot Al_2O_3$) in solution at high pH. The reaction is as follows:



This reaction will take place using any soluble aluminium source at the right pH.

During the investigations on the removal of sulphate from ash, mine and cooling waters, the co-removal of F^- was also noted. The F^- concentration decreased from 200 ppm to approximately 1 ppm, within a one hour period.

In the above reaction, aluminium and calcium (lime) sources are used in the formation of ettringite. It can, therefore, be hypothesized that the F^- was either removed by its incorporation in the Ettringite structure, or by precipitation with the aluminium hydroxide or calcium as has been highlighted above.

3.6 Membrane Processes

Membrane processes are a physical method for the removal of unwanted material or contaminants from water, based on their specific size, shape or charge (Van Duuran , 1997). These include (in order of decreasing membrane pore size) micro-filtration, ultrafiltration, nanofiltration and reverse osmosis, as well as electrodialysis.

Reverse osmosis membranes are universally accepted for their ability to remove ionic constituents in water, including substances such as F^- and NO_3^- (Montgomery, 1978). Osmosis is commonly known as the diffusion of water through a membrane from a low concentration solution, to a highly concentrated solution, thus increasing the volume of water on the highly concentrated side of the membrane (concentration gradient). Reverse osmosis, as the name indicates, is the reversal of what is noticed in osmosis, hence the diffusion of water from a high concentration to a low concentration solution. This is produced by the application of a pressure to the highly concentrated solution, larger than that of the osmotic pressure, thus forcing the water through the osmosis membrane.

For reverse osmosis, a number of essential components are required, other than the membrane, so as to ensure the membrane lasts for an optimal length of time. These include:

Pretreatment: this is to ensure that the reverse osmosis membrane is not fouled by organic material or chemical deposition, as well as not chemically degraded. This usually includes the removal of suspended solids, pH adjustment, dechlorination, as well as possible scale inhibition chemical addition.

Stabilisation: the product water is usually corrosive due to the removal of salts. pH adjustment is therefore required before distributed for domestic applications.

Brine disposal: this is a serious problem, especially in domestic and rural applications, and must be considered right up front.

Another membranes process, electrodialysis, is based on the basis that dissolved salts are present in the water in the ionic form. These ions can be manipulated through the use of charged electrodes. The cationic species in the water will be attracted to the cathode (negatively charged electrode), with the anionic species being attracted by the anode (positively charged electrode). If charged membranes are also placed between the electrodes, the ionic species that can pass through a specifically charged membrane will, and will be prevented from passing through the membrane that is not suitable. For example, cationic species will pass through a cation membrane, but will be retained from passing through an anion membrane, and visa versa.

If this principle is used in a stacked system, desalination of water occurs, producing, like reverse osmosis, a desalinated stream, and a concentrated stream. The same pretreatment, stabilisation and brine disposal problems are present, as with reverse osmosis.

Nanofiltration and the other treatment processes are variations of the basic membrane treatment concept used for specific applications which are frequently of an industrial nature.

Reverse osmosis and electrodialysis desalinates the water to such a degree that it may also remove essential salts and trace elements required for potable use. This can also be a danger that must be identified when considering such treatments.

From rural water supply point of view, therefore, 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.

However, 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. Brine disposal will always be a problem.

3.7 Ion Exchange

Ion exchange (IX) is a well-established and precise method for the removal of dissolved ionic constituents from water. Synthetic ion exchange media has been engineered from mainly divinyl- benzene and styrene, with an attached functional group. This functional group is where the ion exchange takes place between the ion joined to the functional group, and the ion in the water that is

needed to be removed. In other words, IX resins have the property to release one or more ions in their structure in exchange for ions in solution (Benefield *et al*, 1982).

The exchange reaction occurring on the surface of the IX resin can be illustrated as follows, with the B^+ cation being in a solution that contains a resin with A^+ cations attached:



The presence of the equilibrium sign shows that an equilibrium will occur, depending on the selectivity of one ion compared to the other ion.

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 F^- ions.

Defluoridation of water can be carried out using two distinct beds, one containing cation exchange resin that exchanges the sodium fluoride for hydrogen ions, and the second containing anion exchange resin used to remove the F^- . Regeneration is also required. The two processes can be graphically shown by:



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 resin material must be regenerated. This gives rise to a concentrated waste stream of the original contaminant which must be disposed of safely.

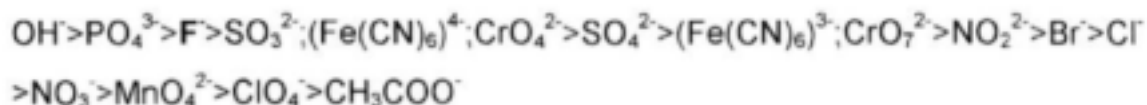
Regenerant chemicals used are frequently a brine solution with either caustic or concentrated acid solution depending on the ionic species being treated. The caustic and acid solutions can be considered hazardous in untrained hand.

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.

3.8 Activated Alumina

One of the most frequently used methods of treatment for high F^- water is an adsorption process with media such as activated alumina, bone char or granular tricalcium phosphate. Of these adsorption processes, the activated alumina appears to be the most attractive because alumina is somewhat specific for F^- , and has a relatively high F^- exchange capacity (Schoeman and Botha, 1985; Van Duuran, 1997). The affinity for common ions on acid treated activated alumina is in the following order:



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.

These advantages can be summarized as:

- ♦ relatively specificity for F^- ,
- ♦ high capacity for F^- ,
- ♦ not affected by SO_4^{2-} , or Cl^- in the water, and
- ♦ relatively low cost (approximately 10 % of the cost of a synthetic anion resin).

Alumina has an optimal operating pH for the removal of F^- , which is between pH 5 and pH 8, with the most rapid uptake of F^- at a pH of 5.5. The kinetics of the adsorption of F^- onto the alumina is 5 minutes.

The capacity of a continual-flow column of alumina is dependent on:

- initial F^- concentration: the higher the initial concentration, the greater the capacity of the adsorbent, as it will allow greater penetration of the ions to unused sites.
- pH: the optimal pH range for F^- removal is between pH 5 – 8, with the most rapid up-take being at pH 5.5.
- particle size: the smaller the particle size of the alumina, the more rapid the uptake of the F^- . This is due to the relatively slow kinetics of the media. The size most often used is 28-48 mesh.

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 F^- adsorption conditions, as mentioned previously (Rubel and Woosley, 1979; Schoeman and Botha, 1985). As with other techniques, the disposal of the regeneration effluent may be a problem.

A comprehensive study concerning activated alumina for the removal of F^- from water, as well as the determination of factors influencing its performance, was carried out in South Africa (Schoeman and Botha, 1985). The objectives of the study were to compare regeneration methods, the importance of influent water pH, as well as to determine the economics of a 518 m³/day plant. The conclusions of were:

- ♦ F^- can be reduced to below 1 mg/l from an influent concentration of 8 mg/l.
- ♦ Sodium hydroxide was found to be better as a regenerant, compared to alum.
- ♦ The adsorption capacity of the alumina is adversely influenced by the formation of a partially soluble aluminum-silica-fluoride complex when using alum as a regenerant.
- ♦ Optimal pH is between 5 and 6, as silicates and hydroxyl ions compete strongly with the F^- ions.
- ♦ Readjustment of the pH must be carried out on the product water.
- ♦ Greater than 90 % recovery can be achieved.
- ♦ Provision must be made to dispose the regenerant and rinse water. High levels of sodium hydroxide, sodium sulphate and sodium fluoride will be present.
- ♦ Defluoridation costs were calculated out at being R0.33/m³ of treated water.

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

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 F^- 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.

3.9 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 ($Ca(PO_4)_6.CaCO_3$) was replaced by F^- to form insoluble fluorapatite (Benefield *et al*, 1982):



Bone char, produced by carbonizing at 1100 - 1600 °C, has 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. Typical properties of bone char can be seen in Table 2.

Table 2: Typical properties of bone char.

Constituent and Properties	Content
$Ca_3(PO_4)_2$	73.50 %
$CaCO_3$	8.50 %
Iron and Aluminium oxide	0.40 %
Magnesia	0.20 %
Acid insoluble ash	0.30 %
Total volatile	16.50 %
Apparent density (lb/ft ³)	40 - 46

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.

3.10 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. F^- is one of them. It does so, however, not as efficiently as alumina. A study was carried out between four activated carbons, three activated bauxites, and two activated aluminas to investigate their F^- removal properties as well as optimum pH operating conditions. Waters used were distilled water, seawater and simulated geothermal water. Similar conditions were used for all tests. A 48 hr contact time was used for all tests, even though adsorption was completed in about $1/4$ of the time. Table 3 summarizes the results obtained, showing the final pH of the solution, as well as the maximum removal efficiency. As can be seen, the activated alumina and bauxite removal results were superior to that of the activated carbon.

Table 3: Results obtained comparing the removal of fluoride capabilities of various activated carbons, activated alumina, and bauxites.

Adsorbent	Activated Carbon				Activated Alumina		Activated Bauxite	
	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.

Activated carbon, however, is very effective when more than one contaminant of the water needs to be removed. For example, in systems designed to

remove such contaminants as pesticides and other harmful organics, NO_3^- , as well as F^- .

4. PROMISING APPROACHES FOR FURTHER DEVELOPMENT

Two techniques presented below have been proven elsewhere as feasible, and it is the opinion of the authors that they deserve further investigation, as they may be the most appropriate for rural application in South Africa.

4.1 Extended Operation of Adsorption/Ion Exchange Methods

Commercial systems using either activated alumina, carbon or ion exchange is available, with one of the target removal contaminants being F^- . One disadvantage with these systems is the interference of other compound and chemical substances on the media. Micro-filters assist in the removal of particles, but do not provide any protection against reactive/ fouling chemicals or bacteriological fouling.

An approach that the authors feel needs further investigation, is the extension of the above-mentioned media's adsorption runs by using redact media as pretreatment. Commercial systems using this media with activated carbon are available and are used to remove 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, as well as ion exchange processes. 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 electrical potential that is

formed during the process is a redox potential. This is the main principle behind batteries.

The redox media works by producing a redox charge or "shock" that kills microorganisms, removes metals, and destroy reactive components such as chlorine. The media may not remove chemical components such as F^- or NO_3^- , from water, but will enhance the quality of the water prior to downstream treatment systems such as absorption media, thus prolonging the life of the absorbent/ion exchange material during individual filtration runs. It can also act as a particle filter prior to the adsorption media.

4.2 Low Cost Sri Lankian Defluoridation Approach

In recent years, a lot of work has been carried out on a "low cost" domestic defluoridator of water, with most of this work has being carried out in Sri Lanka. This is due to the fact that Sri Lanka has a similar F^- problem to South Africa, with over 40 % of wells in parts of the country being high in F^- (Padmasiri, 1997).

The disadvantages or shortcomings of most defluoridation methods, as indicated previously, are:

- high cost of plant,
- high operational and maintenance costs,
- low capacity for removing F^- ,
- lack of selectivity for F^- ,
- undesirable effects on water quality,
- generation of sludge that is difficult to handle, and
- complicated procedures.

The defluoridation system developed in Sri Lanka is illustrated in Figure 2. The filter system comprises of a reactor made of either a PVC pipe or a square column. The filters are packed with broken pieces of freshly burnt bricks of the size of 8-16 mm, to a height of 75 cm. At the centre of the reactor is a perforated pipe funnel. Initially the filter is filled with the high F^- concentration water for 12 hours. This is to obtain equilibrium, as well as hydration of the burnt media. During operation, the water is fed into the pipe funnel, allowing the water to flow through the brick media and then over-flow for usage.

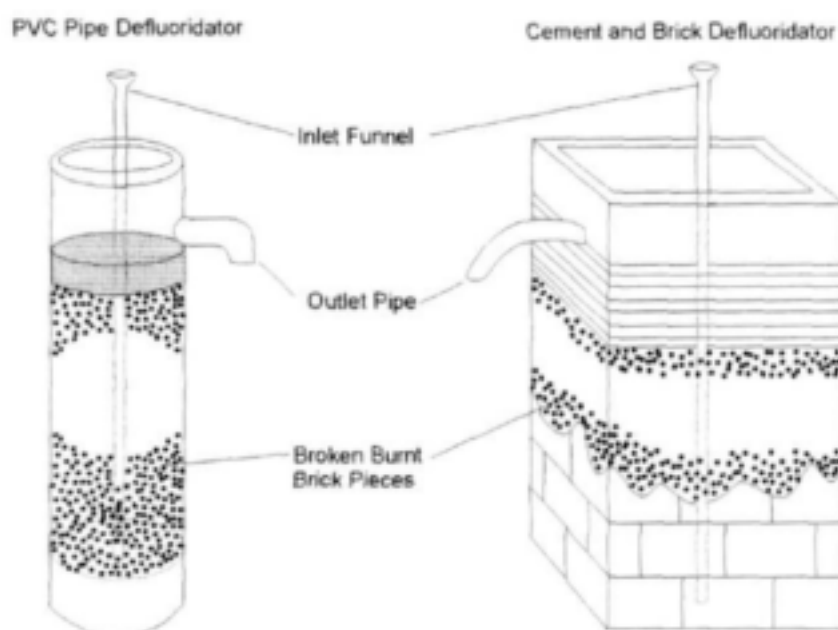


Figure 2: Design of the low cost defluoridator (column and brick style).

The efficiency of these low cost defluoridators, based on the results from Sri Lanka, varies from 85% at the beginning of a filter run, to 25% at the end, depending on the length of time taken for each run. The removal of F^- by one such defluoridator can be seen in Figure 3. As can be seen, this was from four runs of the same defluoridator, over 70-100 day trials, each run. The removal averaged at 1 mg/l from an initial concentration of 5 mg/l.

A vast majority of the defluoridators in operation in Sri Lanka are reported as still showing the sustainability and acceptability of this technique on a domestic level.

The mode of action is relatively simple. The 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 F^- 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 on to aluminium hydroxide. The mechanism of the exchange can be seen in Figure 4.

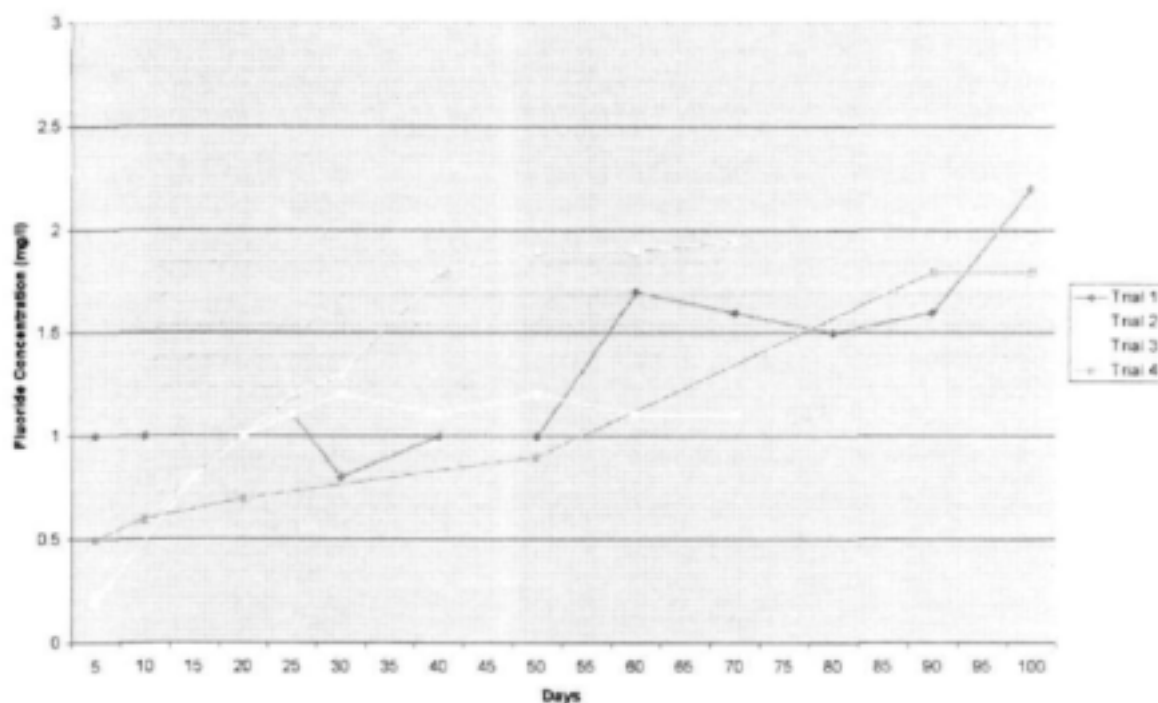


Figure 3: Removal capacity during 4 trials of one defluoridator.

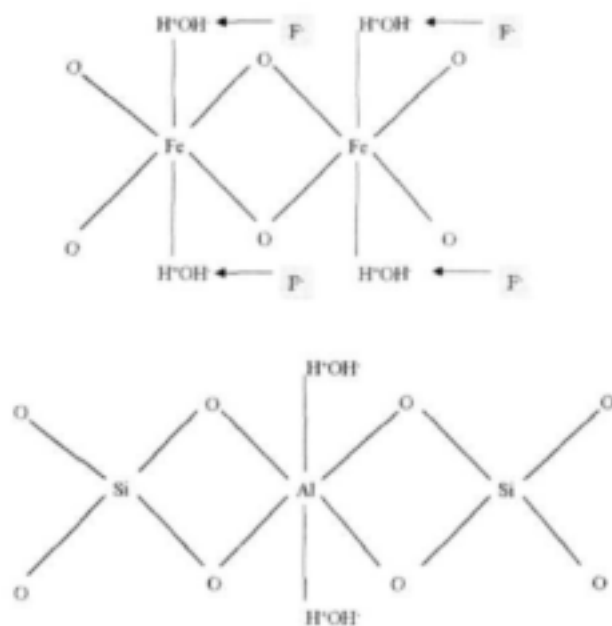


Figure 4: Mechanism of exchange of F^- ions.

This method of F^- removal needs to be investigated further, especially with respect to the type of bricks used, as well as alternative minerals that may be present in the areas of need, or can be very inexpensively obtained and transported to the required areas.

The method provides a potentially very important breakthrough for South African application in rural areas.

5. NITRATES

5.1 General Chemistry

Nitrogen can exist in a range of oxidation states at ambient conditions. This gives rise to a series of stable nitrogen compounds occurring in the environment (Dictionary of Chemistry, 1980) which include nitrogen gas, ammonia and nitrate (NO_3^-). NO_3^- itself has a low primary toxicity but the partially reduced form, nitrite (NO_2^-), which can be 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).

5.2 Health Effects of Nitrate in Drinking Water

NO_3^- 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. NO_3^- are known to cause methemoglobinaemia in infants, while nitrosamines are carcinogenic and may play a role in the induction of certain gastro-intestinal cancers (Hill et al, 1973; Fan et al, 1987).

Methemoglobinaemia is a condition resulting from the conversion of hemoglobin (Hb), the oxygen carrier of mammalian blood, to methemoglobin (MetHb) which is unable to transport oxygen. Several chemicals such as nitrites, perchlorates, sulphonamides, aniline dyes, bismuth and others (Adam,

1980) can cause conversion of Hb to MetHb, in which the iron is in the ferric (Fe^{3+}) state, rendering the molecule unable to bind oxygen. The exact mechanism of this conversion is still not known (Adam, 1980).

NO_3^- , unlike NO_2^- , does not convert hemoglobin but can, under certain conditions, be reduced to NO_2^- by intestinal microflora, with subsequent formation of methemoglobin. NO_3^- is thus indirectly toxic in that it is the precursor to NO_2^- , which is poisonous owing to its property to form methemoglobin.

Many workers accept that, under normal circumstances, less than 2% of the total Hb exists as MetHb (Shuval and Gruener, 1977). No external signs or symptoms are generally noted under 5% MetHb, whereas the first signs of cyanosis can be seen between 5% and 10% (Knotek and Schmidt, 1964). Hypoxic signs and symptoms may develop at levels above 20%, while death results at levels of 50% and higher (Shuval and Gruener, 1977).

The finding that NO_3^- poisoning is limited to infants may be explained as follows (Adam, 1980);

- ✓ Conditions in the gastrointestinal tract of infants are favourable for bacterial conversion of NO_3^- to NO_2^- . The capability to secrete gastric acid is incompletely developed in infants: consequently, their stomach pH of 4.6 to 6.5 is higher than that of adults (pH 2.0 to 5.0), permitting the presence of NO_3^- -reducing bacteria in the stomach and upper intestine.
- ✓ Foetal Hb, which is still present in the newborn (60 to 80 percent of the total Hb, decreasing to 20 to 30% in three months) is more readily converted to Met Hb than adult Hb.
- ✓ Infants are also deficient in two enzymes in their red blood cells, namely Met Hb reductase and diaphorase, which convert Met Hb back to Hb

(ISCWQT, 1974). Met Hb is normally present in human blood, but is kept at low, steady state levels (1 to 2% of the total hemoglobin) due to the action of these enzymes.

- ✓ Babies consume about three times more fluid per unit body mass than adults (Winton et al, 1971); this contributes to the hazard of NO_3^- -induced methemoglobinaemia, especially in arid climates where the fluid intake is higher than in moderate climates.
- ✓ A certain proportion of infant methemoglobinaemia has been traced to NO_3^- -rich vegetables such as spinach and carrots. Microbial reduction of NO_3^- to NO_2^- often takes place in infant food preparations prior to intake, especially when stored in room temperature (Klotter, 1969).

5.3 Nitrate Occurrence in South African Groundwater

In a report by Tredoux (1993) hydrochemical data was analyzed from the national groundwater database maintained by the Department of Water Affairs and Forestry (DWAF). The data largely contains information obtained from boreholes drilled by the Department as well as large numbers of private boreholes. In that study, a total of 18 827 analyses were available for scrutiny. The median NO_3^- concentration from these analyses was found to be 4.5 mg/l. forty five percent of the sources exceeded 5 mg/l, 27 percent 10 mg/l and 15 percent 20 mg/l. Due to the investigations in the Springbok Flats and the Northern Cape Province, where extensive occurrences of elevated NO_3^- concentrations are found, a slight bias could have been introduced because of the inclusion of virtually all boreholes in those areas. The large number of sources (814, that is 4.3% of the total) having NO_3^- concentrations is thus not necessarily representative of the country as a whole.

The geographical distribution of the 18 827 sampling points is shown on the map in Appendix 3. The sampling points provided reasonable coverage of most

of the country except for the eastern and south-eastern areas where sample numbers were very low – on average there were 150 data points in each square degree.

In Appendix 4 the areal NO_3^- distribution from the study has been summarized for each square degree. In each square degree the number of sampling points, the median NO_3^- concentration and the 90th percentile nitrate values are shown. The inner and outer rectangles in certain square degrees highlight those in which the median value exceeds 10 mg/l and the ninetieth percentile exceeds 50 mg/l, respectively. This clearly depicts the areas in the northern Cape Province (Kalahari, Prieska and Vryburg) and the northern Transvaal (Springbok Flats) where elevated NO_3^- concentrations are known to occur. The population affected by these high NO_3^- occurrences is essentially the farming community and people living in rural settlements and towns supplied by groundwater in the indicated areas.

Marais (1998) has subsequently published the newest set of F^- and NO_3^- concentration maps covering each province excluding Gauteng and the Western Cape. These depict concentrations according to a classification system which indicates the suitability of water for domestic use, or else, treatment options to make it suitable. This classification is according to the Assessment Guide Vol1: Quality of Domestic Water Supplies published by DWAF, the WRC and the Dept. of Health (See Appendix 1 and 2 for the fluoride and nitrate concentration maps, respectively). NO_3^- occurrences on these maps show broad agreement with findings from earlier researchers, and in addition, show newer previously un-monitored areas. A brief summary of findings has been shown in Table 1 earlier.

6. CURRENT REMOVAL METHODS

Certain Techniques effective in the removal of NO_3^- from water are the same as those utilized in defluoridation and hence, have been covered to a certain extent in earlier sections on F^- removal. These include ion exchange and membrane processes, for instance.

6.1 Ion Exchange

The principles of ion exchange resin have been covered previously in the section on F^- removal, however, it needs to be added that certain ion exchange resins have been developed that are highly selective to NO_3^- (Hellmig; Jackson *et al*, 1990; USEPA, 1983).

Ion exchange offers the following advantages over biological and membrane systems:

- fully developed process engineering,
- standardized apparatus and ion exchangers, and
- process easy to automate.

The systems are mainly suitable in particular for small and medium-sized plants, and can be operated both centrally and remotely.

Normal IX resins have the following affinity gradient, meaning that for the removal of NO_3^- , sulphate (SO_4^{2-}) is also removed:



New strong base resins have been produced, and are commercially available for the removal of NO_3^- from water. The following affinity gradient applies with these resins:



The pros and cons remain the same as for F^- removal, in the requirements needed to operate the systems, disposal requirements and capital and operating costs. Again, 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.

6.2 Membrane Processes

The principles of ion exchange resin have been covered previously in the section on F^- removal. As already mentioned, the rejection of salts through a process such as reverse osmosis and electrodialysis is well over 80 - 90% plus, which means that, for drinking purposes, extra salts will then need to be added in the treated water, especially in waters that initially had a low concentration of salts.

Other disadvantages include:

- pretreatment and stabilization systems are usually required,
- 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.

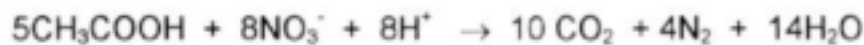
7. BACTERIAL NITRATE REMOVAL AS A PROMISING TECHNIQUE FOR FURTHER DEVELOPMENT

Microbiological means have generally been used in the past as an alternative process for the removal of NO_3^- . An increasing number of reports have documented the successful utilization of anaerobic, non-pathogenic bacteria for the removal of NO_3^- from drinking water and ground water (Anonymous, 1985; deMendonca *et al*, 1992; Hogrewe, 1990; Cook, 1990, Green *et al*, 1994)

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). In this case the system was designed for a capacity of 76 liters per minute. The carbon source was either corn syrup or acetic acid. The NO_3^- levels were brought down from 20-25 mg/l NO_3^- (as N) to less than 3 mg/l. Sand filters were subsequently used to remove residual suspended bio-solids. A schematic of the plant can be seen in Figure 5.

From the study at Wiggins, a company was set up to commercialize the process. The company is Nitrate Removal Technologies (EPRI, 1998), and the process is called BioDen™ (NRT, 1998). The process removes NO_3^- through 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 a substrate with a carbon source such as acetic acid, molasses, etc. The system can be automated, and resembles the original plant that was used during the EPRI tests.

The energy-generating portion of the denitrification reaction, neglecting cell synthesis can be shown as:



One slight disadvantage about this type of system is build-up of biofilm that has to be periodically removed.

A farmer at Settlers in the Springbok flats also claimed that after implementing a similar denitrification process, he was able to bring down NO_3^- levels from 34.3 mg/l to 0.2 mg/l (Anonymous, 1985). High NO_3^- 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. Cost-wise, 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.

As denitrification of ground water has been investigated for years, a study was carried out to model the process and to determine the reasons for discrepancies between theoretical and practical cell yields per carbon source. Findings were reported in a publication by Green *et al* (1994). The paper discussed the experimental procedures used, and the related operating parameters. The predominant bacteria species present was *Pseudomonas spp*. The model, although "crude" gave theoretical data close to those previously predicted.

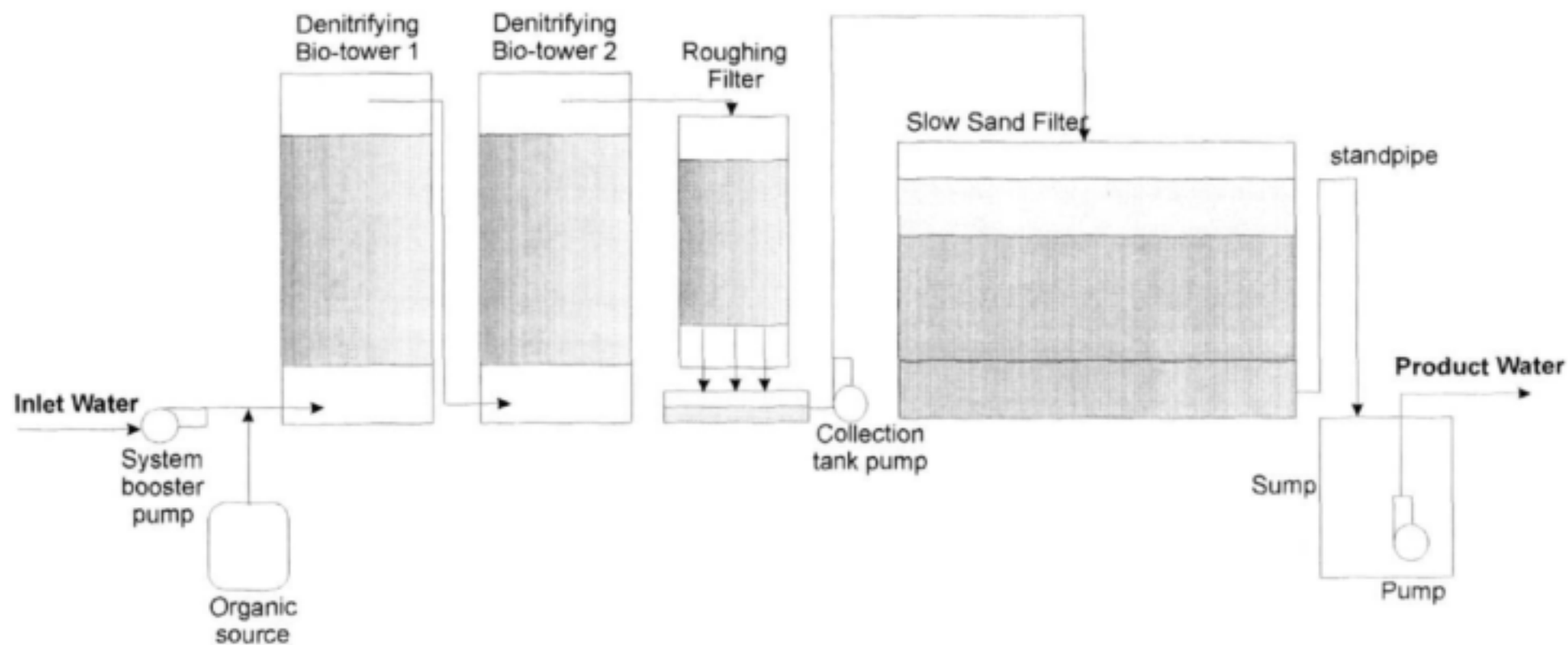


Figure 5: Schematic of the test rig used during the EPRI trials on Denitrification of ground water for domestic use.

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 NO_3^- removal reactors. Bacterial processes have found widespread use in wastewater treatment. From a drinking water purification point of view, their largest application has probably been in slow sand filters where they are utilized as the *schmutzdecke*. 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.

8. SUMMARY OF PROMISING APPROACHES AND RATIONALE

In determining promising approaches it is worth defining the rationale and 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 the point of view of rural requirements, 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 (for NO_3^- removal),
- or those that rely on adsorption/desorption mechanisms (for F^- removal), also using redox media,

to remove F^- and/or NO_3^- from drinking water supplies.

9. CONCLUSIONS AND RECOMMENDATIONS

Elevated NO_3^- and F^- concentrations occur extensively throughout South African waters. These are highlighted in maps shown in Appendices 1 and 2.

There are various methods for the removal of both NO_3^- and F^- from water. These vary from chemical, to adsorption and ion exchange, to physical, to biological processes. The advantages and disadvantages of each system are illustrated, from a rural community application perspective.

Process	Summary
Ion exchange	This is mainly a broad-spectrum removal technique, although specially selective resins have been produced for NO_3^- removal. Disadvantages include high cost, high expertise required, and disposal of regeneration effluent.
Adsorption	This is mainly a specific removal technique specially selective for F^- removal. Disadvantages include high cost, high expertise required, and disposal of regeneration effluent. High capacities, however, can be produced.
Membrane	This is mainly a broad spectrum removal technique with desalinates the water. Disadvantages include high cost, high expertise required, and disposal of concentrate. Salt addition may be need is the initial water was low in salinity.
Chemical Precipitation	This is specific for F^- , and has been successful. Disadvantages include high capital and chemical cost, and the need to dispose relatively high quantities of precipitate.
Extended Process Operation	This method does not remove F^- or NO_3^- from water, but will condition the water before processes like ion exchange, adsorption or membrane techniques.
Sri Lankian Process	This is a specifically designed method for the removal of F^- in rural communities. These systems are relatively cheap to run and maintain.
Biological	This system is specifically for NO_3^- removal, and uses anaerobic bacteria, with a carbon source, to change NO_3^- to nitrogen. This has been proven on the treatment of water for the use by a small town.

Based on the nature of the problem, and the unique requirements of rural supply and treatment, the following is recommended:

- Biological systems should be investigated with respect to NO_3^- removal. This should include pilot scale on a specific source, and then full scale on a problem source, so as to obtain long term experience and knowledge. Peat should also be investigated with respect to NO_3^- removal capabilities.
- F^- removal should concentrate on absorption methods. This will include activated alumina, with and without redox media. The activated alumina should first be evaluated in the laboratory to identify the benefits of redox media, and then to evaluate each on a problem source, so as to obtain long term operating needs. The method described by Sri Lankan researchers should also be investigated on pilot plant scale (small scale) before a larger investigation. The source of adsorption material should be investigated with respect to the types of brick to be used, as well as clay, minerals and carbons. These will include dolomite, charcoal and different types of clays, bauxites and zeolites. The study should include the areas where the minerals are present, compared to that of the problem waters. This will assist in evaluating the feasibility of using these minerals and clays.

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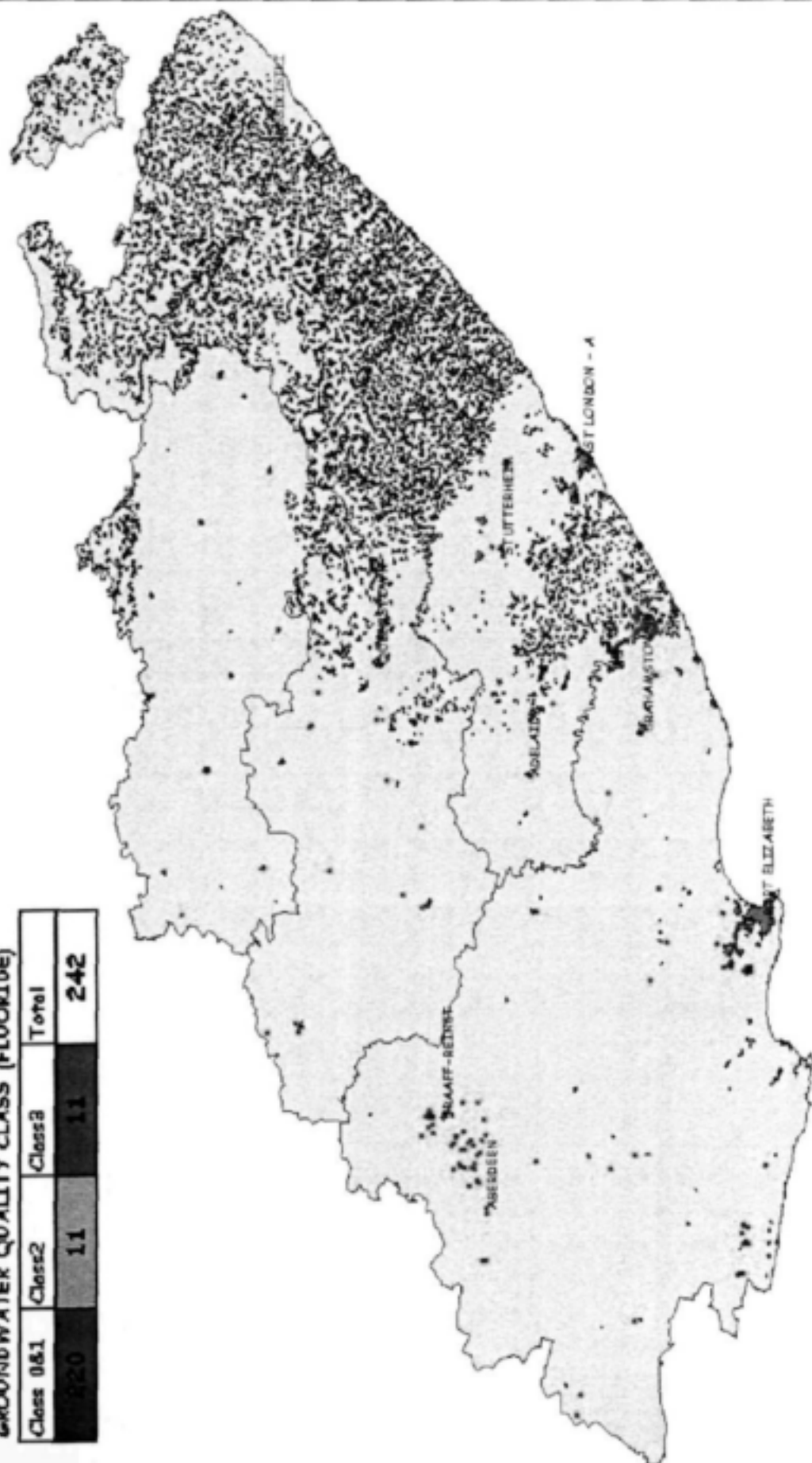
APPENDIX 1

Boreholes with fluoride classification

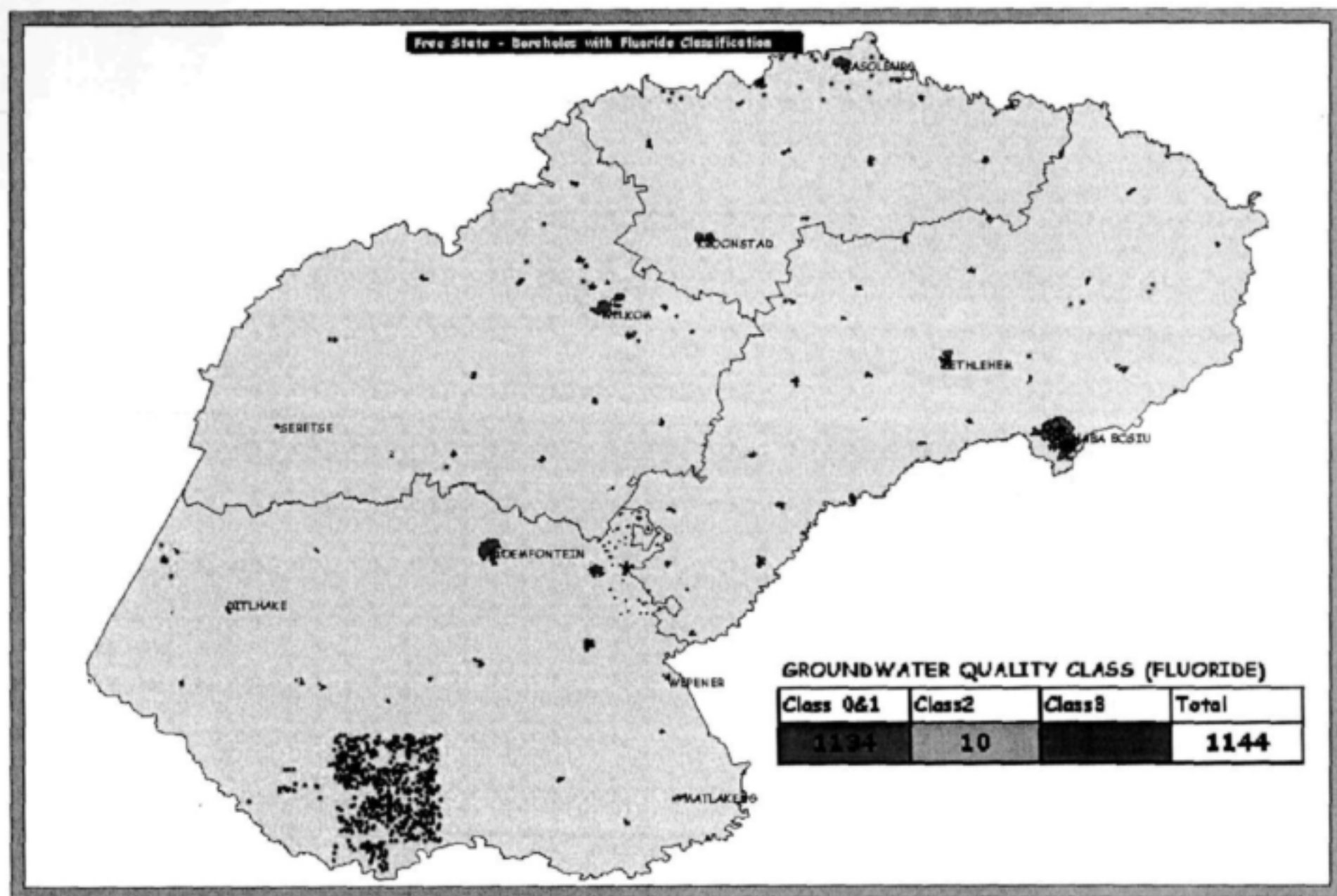
Eastern Cape - Boreholes with Fluoride Classification

GROUNDWATER QUALITY CLASS (FLUORIDE)

Class 0&1	Class2	Class3	Total
220	11	11	242



Boreholes with fluoride classification



Owazulu Hotel - Boreholes with Fluvial Classification

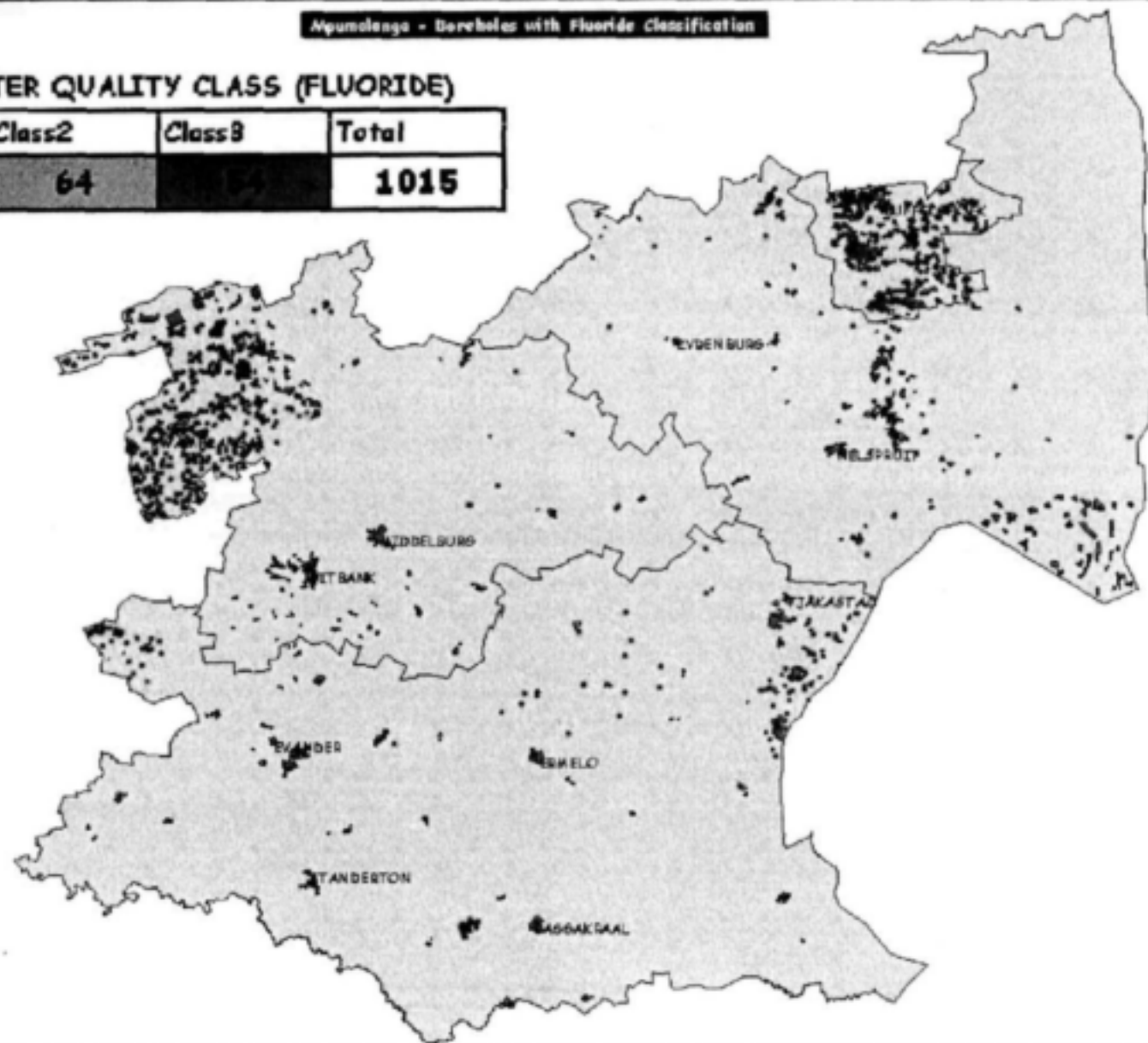
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Boreholes with fluoride classification

Agumoleng - Boreholes with Fluoride Classification

GROUNDWATER QUALITY CLASS (FLUORIDE)

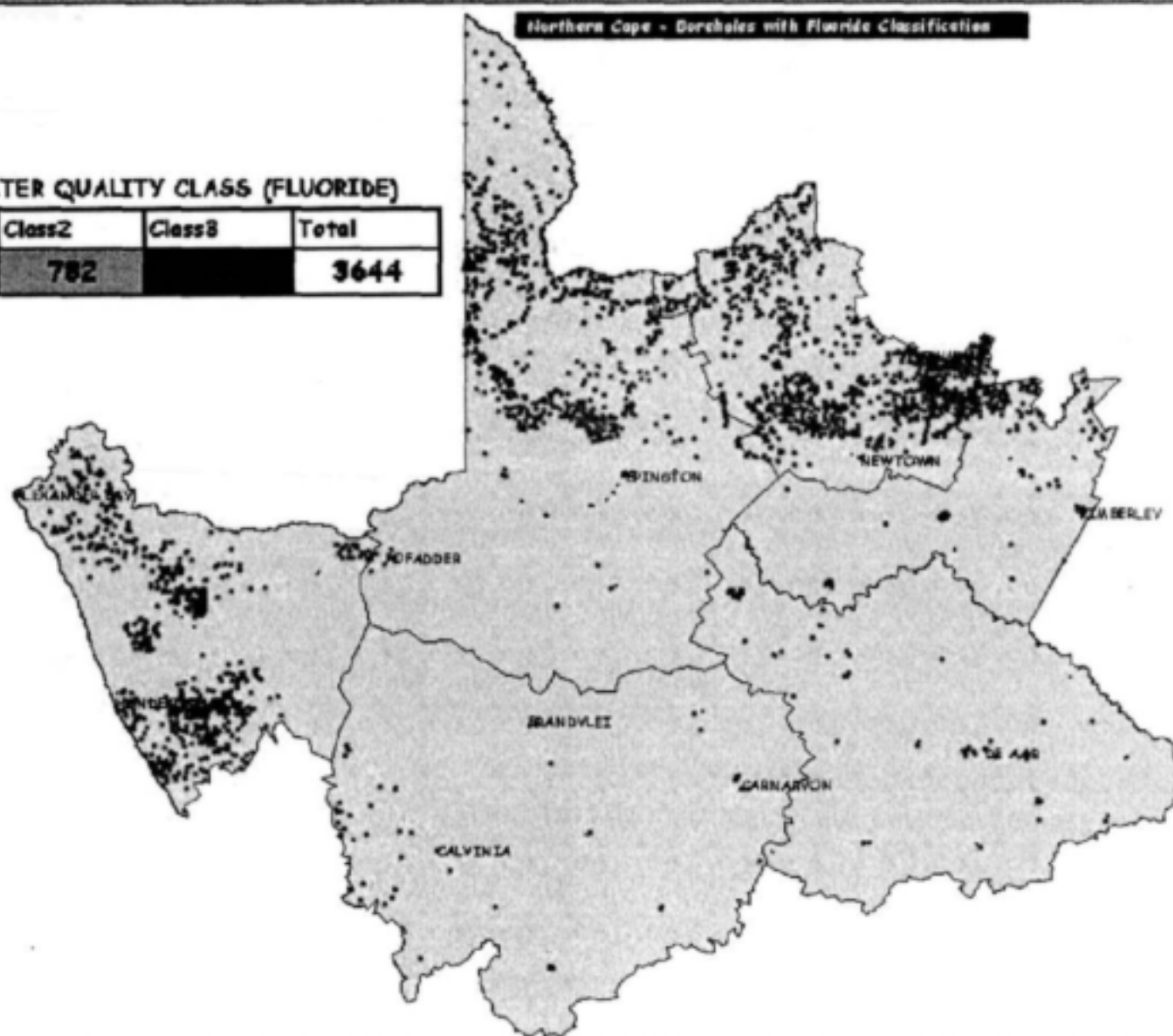
Class 0&1	Class2	Class3	Total
997	64	54	1015



Boreholes with fluoride classification

GROUNDWATER QUALITY CLASS (FLUORIDE)

Class 0&1	Class2	Class3	Total
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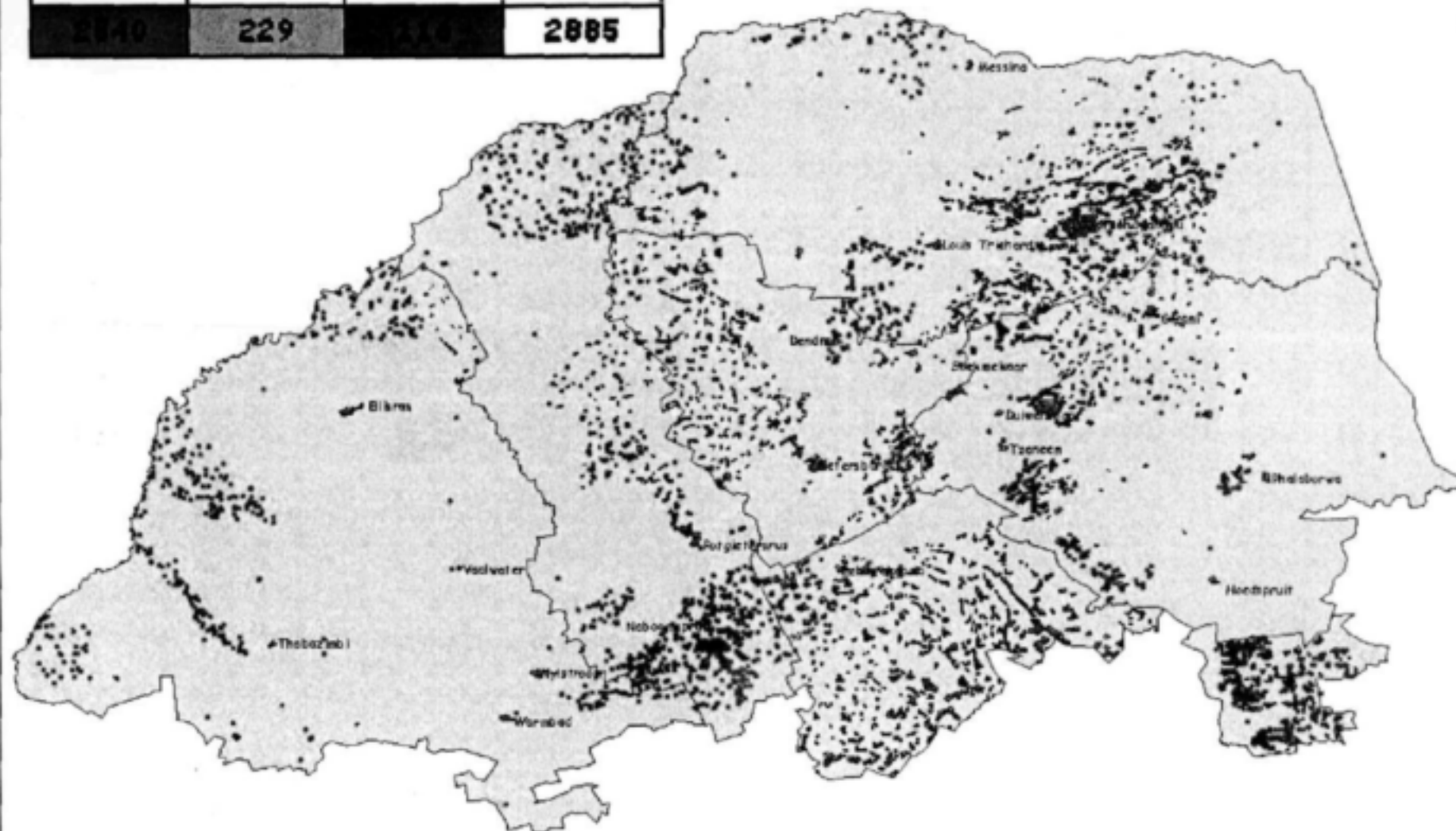


Boreholes with fluoride classification

Northern Province - Boreholes with Fluoride Classification

GROUNDWATER QUALITY CLASS (FLUORIDE)

Class 0&1	Class2	Class3	Total
2040	229	116	2885



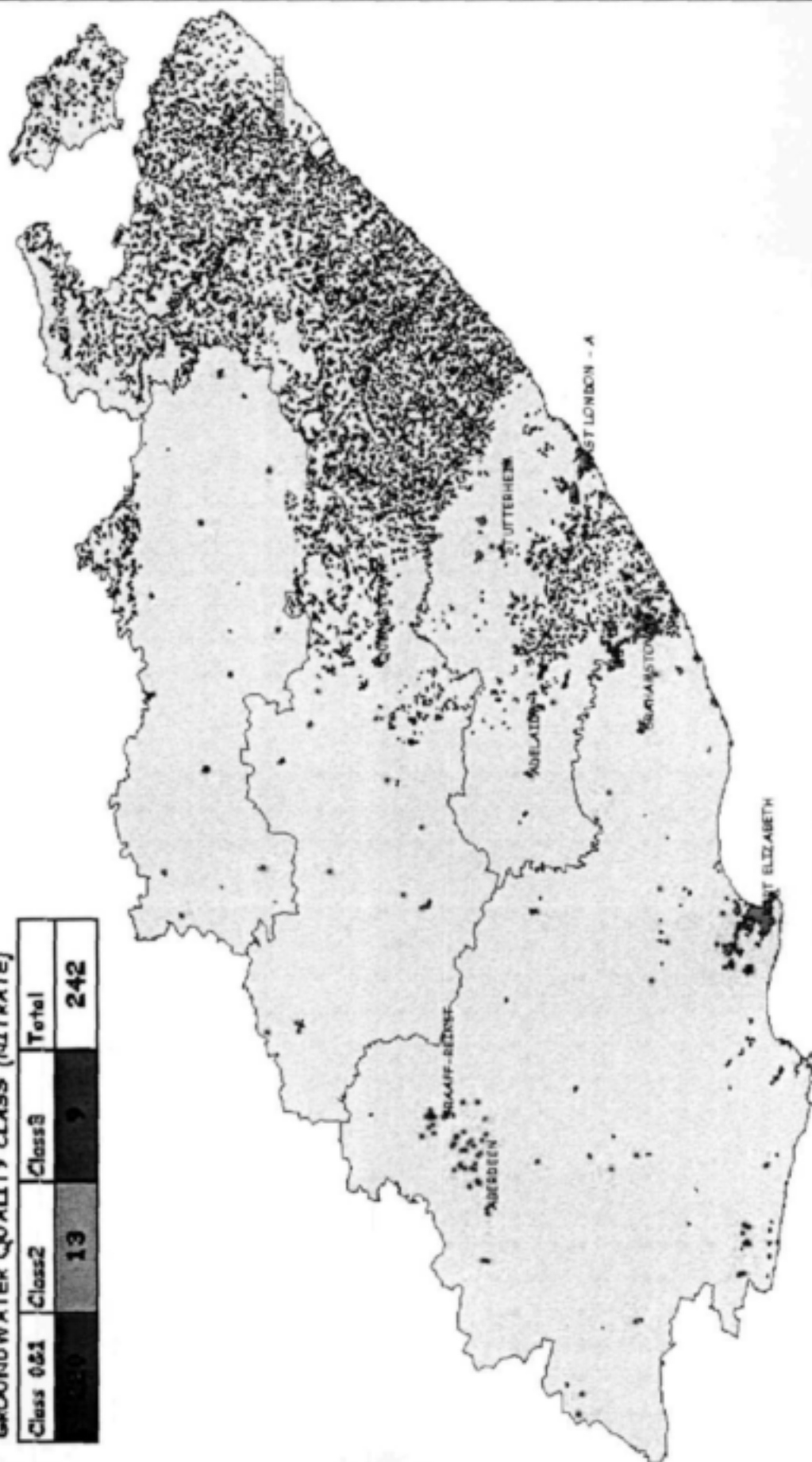
APPENDIX 2

Boreholes with nitrate classification

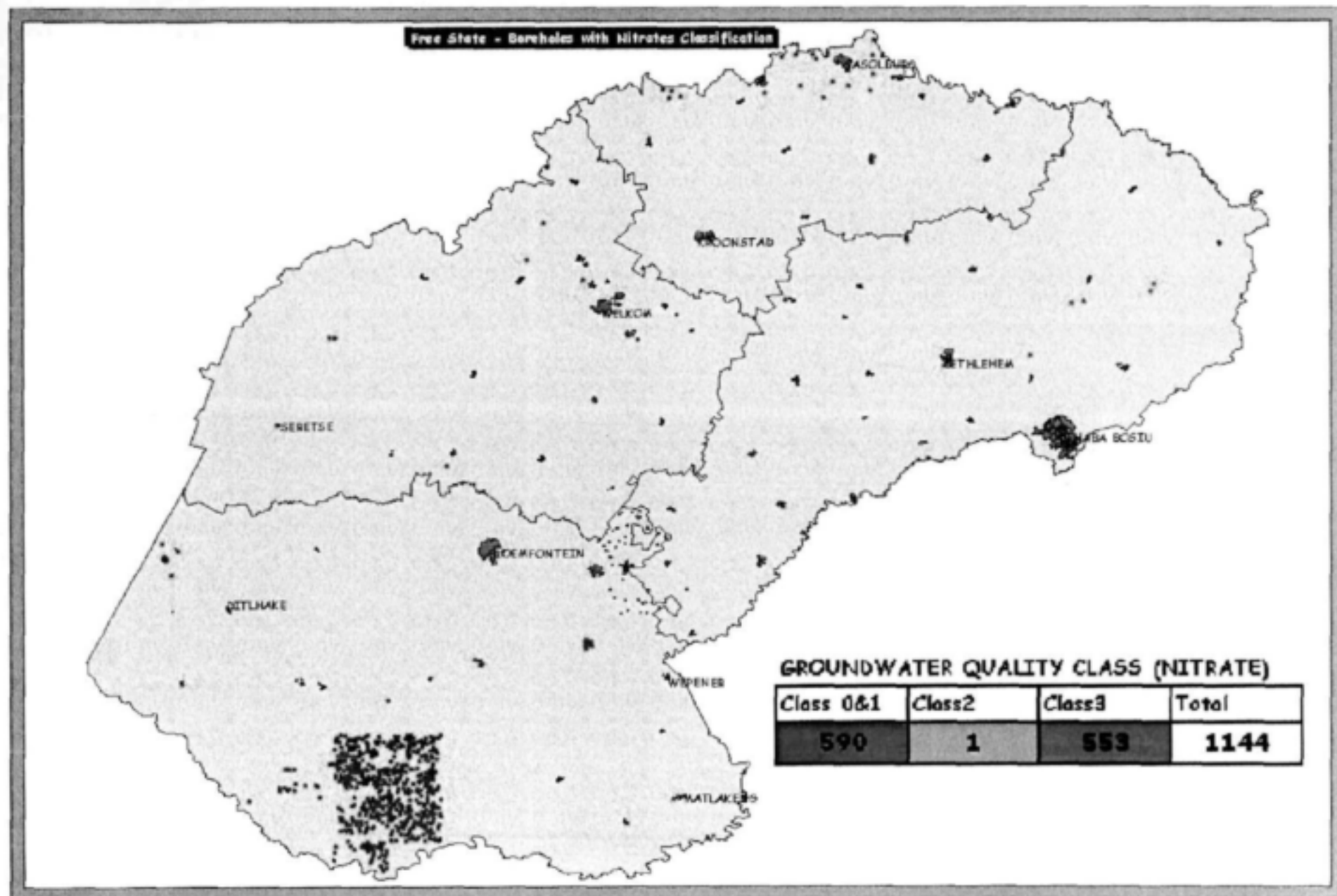
Eastern Cape - Boreholes with Nitrate Classification

GROUNDWATER QUALITY CLASS (NITRATE)

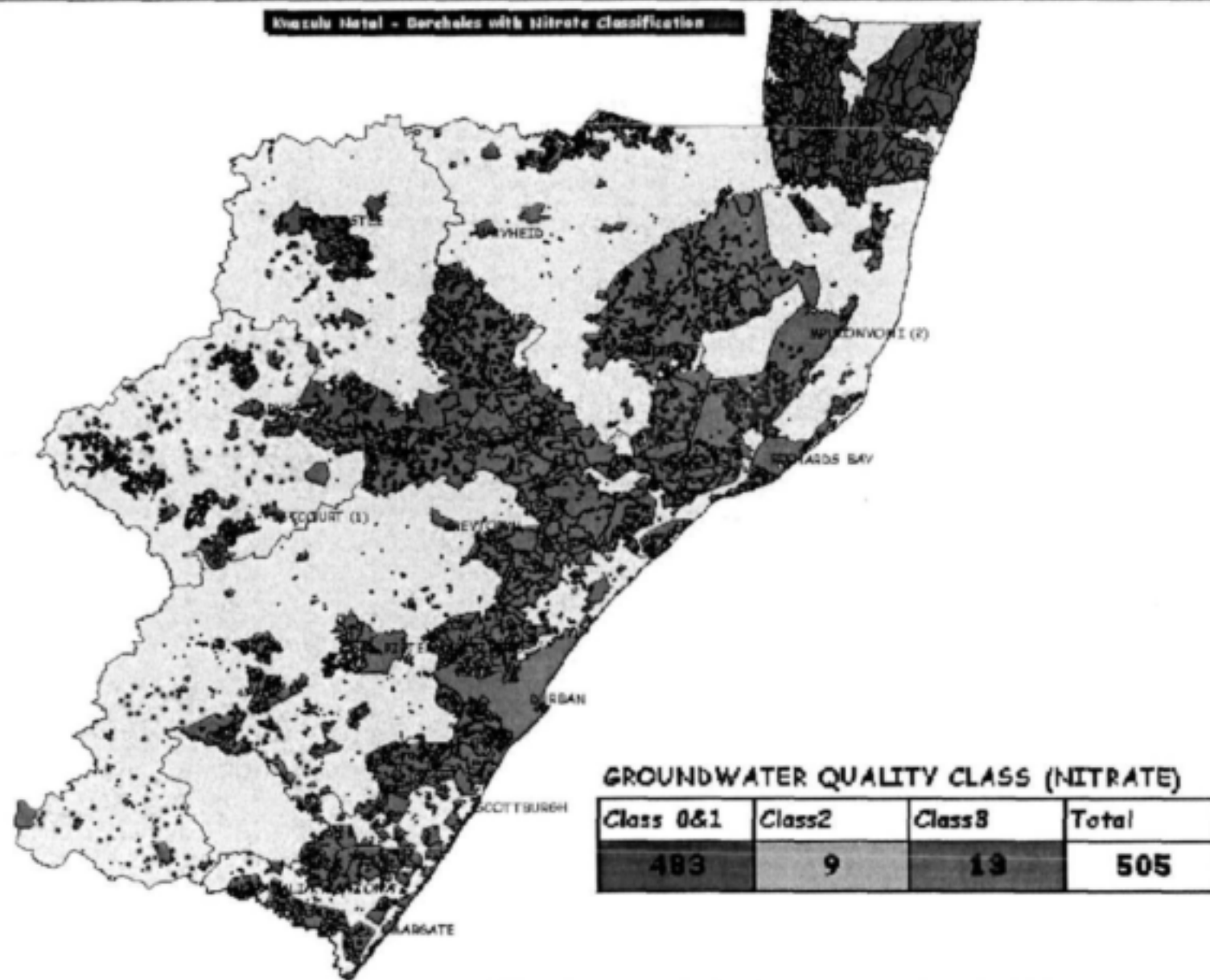
Class 0&1	Class2	Class3	Total
220	13	9	242



Boreholes with nitrate classification



Boreholes with nitrate classification

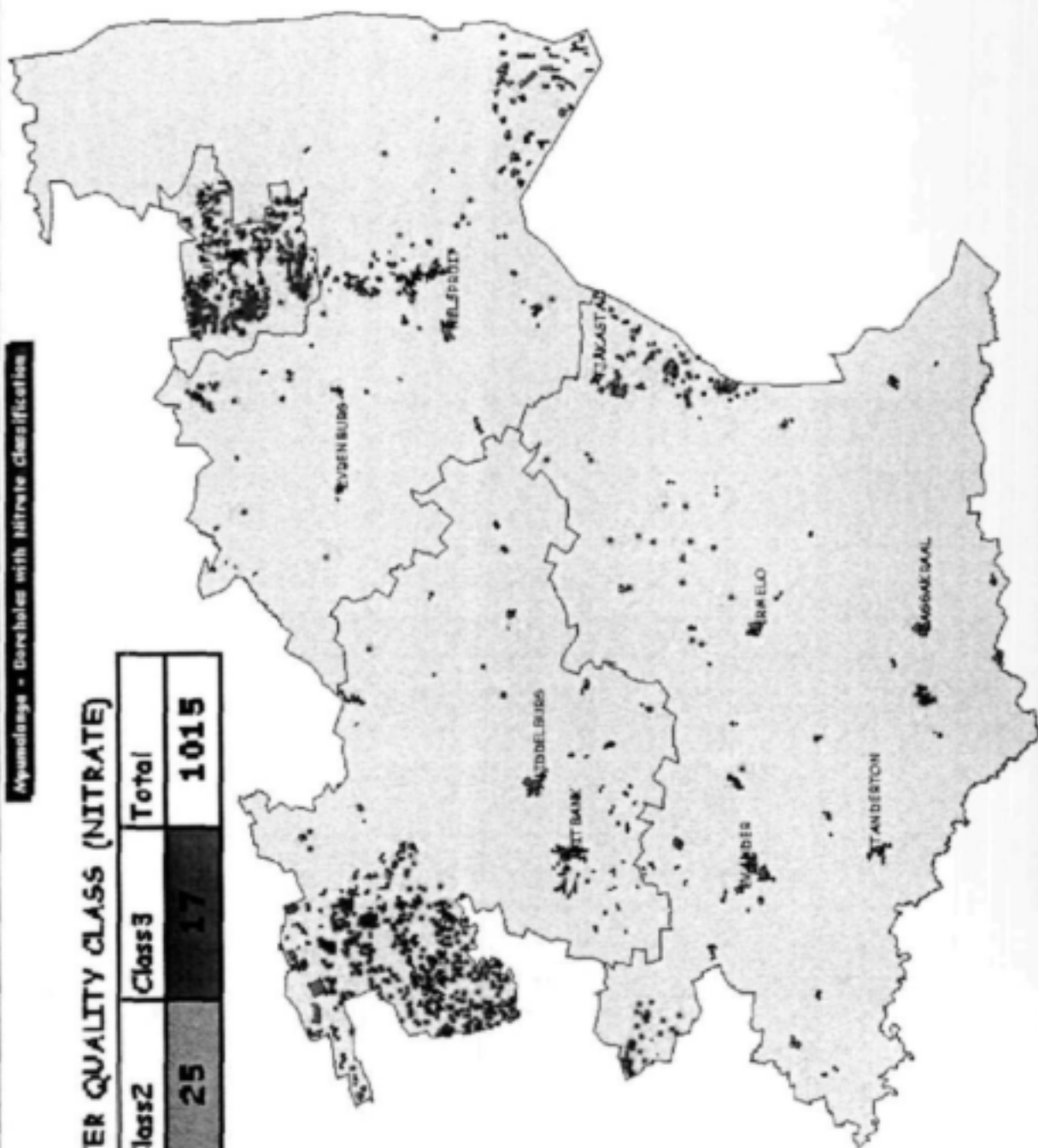


Boreholes with nitrate classification

Apudisaga - Boreholes with nitrate classification

GROUNDWATER QUALITY CLASS (NITRATE)

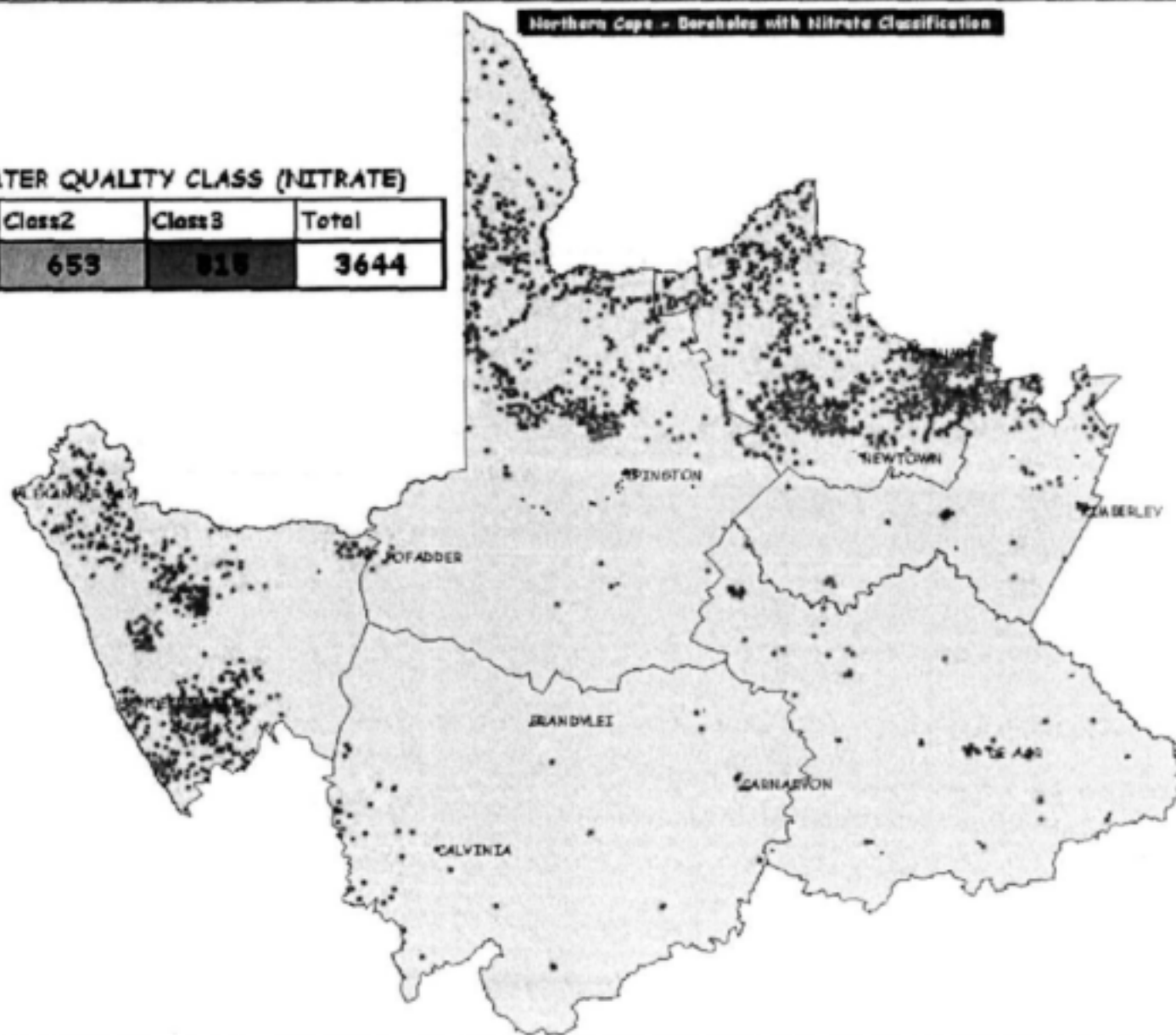
Class 0&1	Class2	Class3	Total
973	25	17	1015



Boreholes with nitrate classification

GROUNDWATER QUALITY CLASS (NITRATE)

Class 0&1	Class2	Class3	Total
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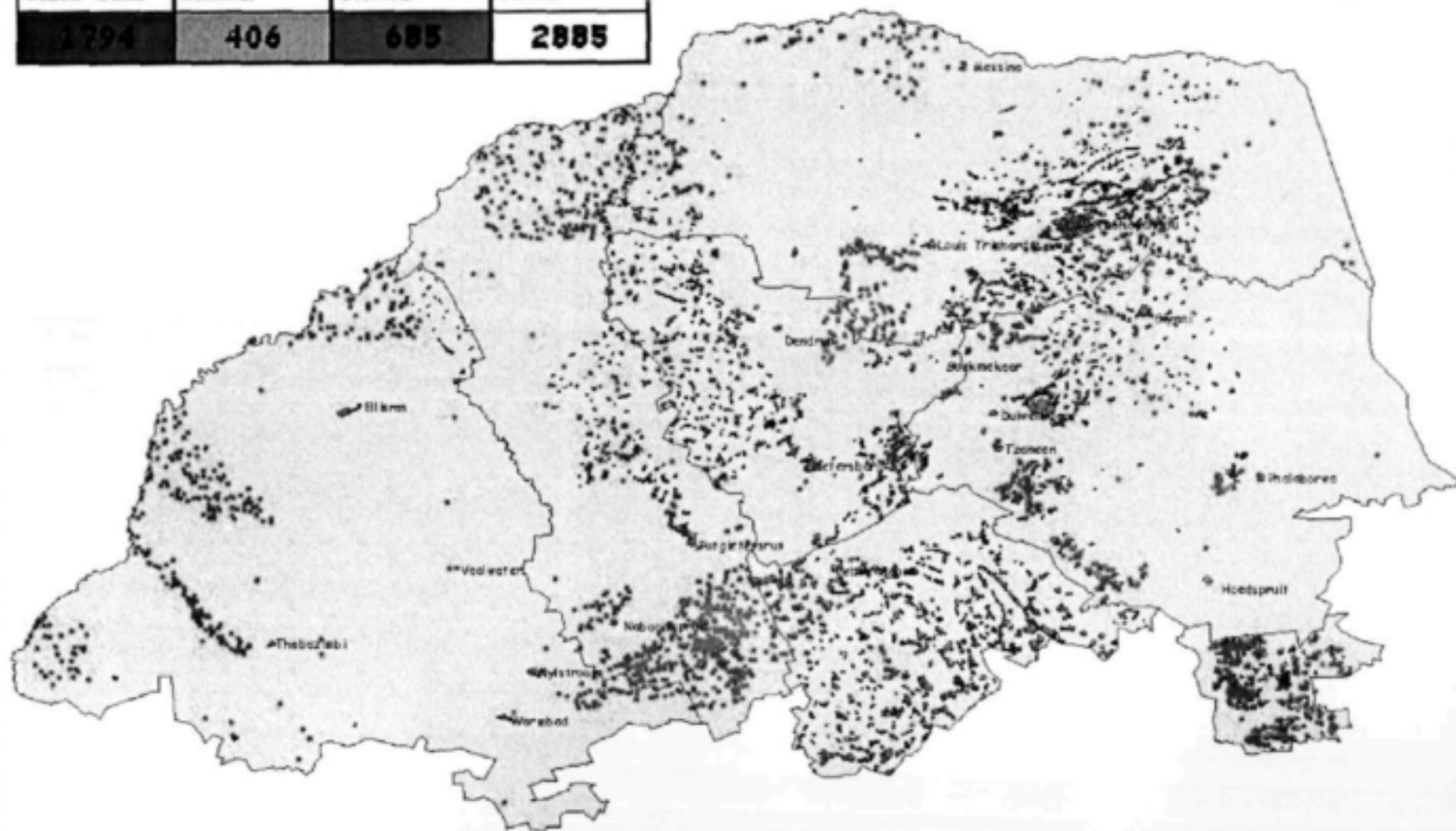


Boreholes with nitrate classification

Northern Province - Boreholes with Nitrate Classification

GROUNDWATER QUALITY CLASS (NITRATE)

Class 0&1	Class 2	Class 3	Total
1794	406	685	2885



Boreholes with nitrate classification

North West Province - Boreholes with Nitrate Classification

GROUNDWATER QUALITY CLASS (NITRATE)

Class 0&1	Class2	Class3	Total
6284	648	532	7464

