THE INFLUENCE OF ANTHROPOGENIC NITRATE ON GROUNDWATER QUALITY IN THE THABA NCHU AREA

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Submitted in fulfilment of the degree

Magister Scientiae in Geohydrology

in the

Faculty of Natural and Agricultural Sciences

Institute for Groundwater Studies (IGS)

at the

University of the Free State

Bloemfontein

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NOVEMBER 2012

DECLARATION

I declare that the dissertation hereby handed in for the qualification of a Magister of Science degree at the University of the Free State, is my own independent work and that I have not previously submitted the same work for a qualification at/in another University/faculty. I further more cede copyright of the dissertation in favour of the University of the Free State.

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Mbinze Akwensioge

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AKNOWLEDGEMENT

I could not have accomplished this without the help of many, all of whom cannot be listed here.

I would like to thank in particular my supervisor, Prof. Gideon Steyl, for his advice, guidance and support throughout this research.

I gratefully express appreciation to all the staff members at the Institute for Groundwater Studies for assistance, technical expertise, administration, laboratory analyses, fieldwork and encouragement. Thanks are due to:

o Mr. Eelco Lukas for first-hand assistance with WISH.
o Ms. Lore-Marie Cruywagen and other workers for laboratory analyses.
o Mrs. Lorinda Rust and Mrs. Dora du Plessis for all administrative arrangements.
o Mr. Fanie de Lang for helping me comprehend my study area.
o Mr. Gerrit van Tonder for proofreading.

To Mr. Teboho Shakhane of the Institute for Groundwater Studies, Mr. Titsteso Nchebe, Mr. Isaacs Grant and Mr. John Jones of Bloemwater, I am grateful for your permission and field assistance in gathering groundwater samples.

I would also like to acknowledge the South African Weather Service for their immediate response for requested data.

To my wonderful family who has always been there for me, I extend my special thank you for your love, patience, words of encouragement and for always believing in me no matter what.

Above all, I wish to thank God for the grace, love, and patience He has shown me in my life. I could never have scaled this wall without Him and the people He put in my life.

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1. INTRODUCTION

1.1 Background

Groundwater, due to its relative purity, enjoys a privileged place as a potable water source worldwide (Dwivedi, *et al.*, 2007). The presence of nitrates in groundwater is mainly perceived as a pollution problem, and in general this has been shown to be valid. Among the selected chemical threats to groundwater in the world, nitrate (NO_3^-) is listed as second most common pollutant of groundwater next to pesticides (Spalding and Exner, 1993; Bachmat, 1994, cited in Dwivedi, *et al.*, 2007). Groundwater is of particular importance in South Africa. Groundwater supplies approximately 65 % of South Africa's rural drinking water with at least 300 towns in South Africa dependent on groundwater as the sole source of potable water (Woodford, *et al.*, 2009).

The occurrence of high nitrate concentrations in groundwater presents a serious threat to certain water users. Particularly infants and livestock are vulnerable to the health impact of nitrate. However, the alleged carcinogenic properties of nitrate have not yet been substantiated (Tredoux, 2004). The health threat is related to the reduction of nitrate to nitrite in the digestive tract and the subsequent formation of methaemoglobin which prevents the blood from conveying oxygen to the cells in the body. In view of the risks involved, Tredoux (2004) stated that the World Health Organization (WHO, 1985; 1998) set the limit for nitrate in drinking water at 10 mg/L (expressed as nitrogen, N), with a recommended level of 6 mg/L (as N). In South Africa the nitrate criterion for drinking water is also set at 10 mg/L, though according to the Department of Water Affairs (DWA) and CSIR it is 6 mg/L (Tredoux, *et al.*, 2009; Maherry, 2010). According to the South African National Standard (SANS) 241:2006 and 2011 for drinking water, the "acute heath" limit for nitrate is 11 mg/L (as N). Anecdotal information indicates that the ingestion of water with a NO_3-N level exceeding 50 mg/L is fatal for infants. The presence of pathogens in the drinking water generally increases the morbidity at low nitrate levels (WHO, 2004 in Appendix B as cited in Tredoux, 2004) and this is one reason why the water quality criteria for nitrate are set at very low levels. Weyer (2001) believed it is also possible that spontaneous abortion of foetuses may be linked to the ingestion of high nitrate water, as cited in Tredoux (2004).

Nitrate in groundwater is a feature found in large parts of the world and a significant population uses water with nitrate levels in excess of the WHO maximum drinking water standard (Spalding and Exner, 1993 cited in Tredoux, 2004). Evidence is accumulating that nitrate levels in many aquifers are rising and that the problem of increased exposure of the

world population to high nitrate inputs, particularly in the developing nations, will become more pressing (WHO, 1985; Spalding and Exner, 1993; mentioned in Tredoux, 2004). This was recently demonstrated by a hydrogeological study at Ramotswa near Gaborone in Botswana (Staudt, 2003 referred in Tredoux, 2004).

Tredoux (2004) cited however that nitrate deposits as well as high nitrate concentrations in groundwater are found in many arid and semi-arid zones around the world. In most of these areas, recent anthropogenic impacts can be ruled out. Whereas nitrate pollution, which by definition is derived from anthropogenic sources, can be managed and be reduced, natural nitrate sources generally cannot be controlled and other means will have to be adopted for managing the nitrate content of the groundwater in such areas (Tredoux, 2004).

Tredoux and Talma (2006) and Tredoux, *et al.* 2004 (cited in Maherry *et al.*, 2010) proved that the study of nitrate concentrations in South and southern Africa is not a new subject, with the publication of a nitrate distribution map in 2001. However, these studies were constrained by the amount of data obtained, GIS software and computer processing power, making it difficult to determine the levels of, and extent to which nitrate occurs, as referenced in Maherry, *et al.* (2010 cited in Tredoux, *et al.*, 2004).

Nitrate is soluble and thus has a high mobility and potential for loss from the unsaturated zone by leaching (DeSimone and Howes, 1998; Chowdary, *et al.*, 2005; cited in Almasri, 2006). In its nitrate (NO_3) and other forms, nitrogen can move through soil into groundwater. Nitrogen can also contribute to surface water quality problems. Nitrate concentration in groundwater is of concern due to potential effects on human health as well as on livestock, crops and industrial processes at high concentrations. A condition called methamoglobinaemia, also known as "blue baby syndrome" results from the ingestion of nitrate in its inorganic form. Infants as well as children and adults from illnesses or treatments that lower the levels of stomach acid, are vulnerable to methaemoglobinaemia.

Nitrate in groundwater is a feature found in many regions and a significant part of the world population uses water with nitrate levels in excess of the WHO maximum drinking water standard. Above 300 mg/L as N, nitrate poisoning may result in the death of livestock consuming water. At lower concentrations, other adverse effects occur in animals which include increased incidence of still borne calves, abortions, retained placenta, cystic ovaries, lower milk production, reduced weight gains and vitamin A deficiency (Tredoux, 2004).

In highly-developed countries, with their intensive agriculture, fertiliser and manure application to land were identified over the past few decades as the main source of

anthropogenic nitrate entering the groundwater resources (Bouchard, *et al*., 1992 cited in Tredoux, 2004). Accordingly, a vast amount of research has been conducted into the impacts of agriculture on groundwater quality. Particularly in Europe, the land application of surplus nitrogenous wastes from intensive animal husbandry and dairy farms are being closely managed. These countries mostly have a humid climate and it remains to be seen how far the approaches used in such countries can be applied locally. Walton, 1951, O'Riordan and Bentham (1993 cited in Tredoux, 2004) argued, on the other hand, that most of the methaemoglobinaemia mortalities in the USA and Europe have been associated with inadequate on-site sanitation systems affecting the local (private) drinking water supplies.

In South Africa, high nitrate concentrations in groundwater occur mainly in a wide band stretching northeasterly from the Northern Cape, through the Northwest Province into the Northern Province (Tredoux, 1993 stated in Tredoux, *et al*., 2000). These areas are linked to similar areas in Namibia and Botswana which stretch over many hundreds of kilometres. In these areas, excessive nitrate and, to a lesser extent, fluoride concentrations are the main reason for groundwater to be unfit for rural water supply (Marais, 1999 cited in Tredoux, *et al*., 2000).

1.2 Aim and objectives

The main aim of this study is an analysis of groundwater quality in Thaba Nchu in the vicinity of contamination sites. The influence of human activities on groundwater quality will be analysed by identifying the source of nitrate contamination and determining its extent, degree and distribution in groundwater. This will also help the hydrogeologist in

- explaining the impact of the existing and potential contamination sources on groundwater;
- presenting results of the inventory on maps; and
- using results of the inventory to suggest alternative strategies to protect groundwater.

1.3 Methodology

The project methodology allowed for data compilation and assessment, and fieldwork. A desktop study and limited fieldwork was undertaken in order to collate sufficient information to compile the groundwater impact assessment and the candidate site assessment report. These will be used to

- determine the geology and geohydrology of Thaba Nchu;
- carry out a hydrocensus and sample boreholes for chemical and isotopic analyses;
- interpret high nitrate occurrence in the context of local hydrogeology and land use change using mainly environmental isotopes (^{18}O, ^{2}H) and nitrate isotopes (^{15}N and ^{18}O) as tools for tracing sources of waters, solutes, and associated processes in the groundwater system; and to
- propose management options for remediation of nitrate contamination in the aquifers.

1.3.1 Data sources

The following data sources were used during the study:

- Council for Geosciences.
- Department of Water Affairs.
- Bloemwater.
- South African Weather Service.
- Google Earth as source of identifying possible target areas as well as layout plans.
- Previous documents on the internet.

1.3.2 Field work

The fieldwork conducted during the study included a site visit to the study area to discuss water related issues and possible existing environmental problems.

Mapping of geological outcrops, hydrocensus of groundwater use and users on the site, and groundwater sampling (to determine ambient groundwater qualities) were undertaken as part of the field work.

A large proportion of information was also gained from field work conducted in this research which included an extensive network of abstraction boreholes across the area. Parameters such as groundwater quality (EC) and pH where measured, and water samples collected. Also, land-use activities that affect groundwater quality were taken note of.

1.4 Limitations to this research

- Lack of borehole logs which would have given detailed local geology of the sites sampled.
- Water levels could not be taken for all boreholes.

- Some boreholes were not sampled at certain times due to automatic on and off pumping periods.
- No access to some boreholes in all sampling periods.
- Rainfall data not available for each village.

1.5   Thesis outline

This chapter introduces the subject of nitrate in groundwater, giving a brief motivation, and outlining the objectives and methodology of the study.

Chapter 2 presents the distribution of nitrate in groundwater as discussed in the literature with an overview of the nitrogen cycle in the environment, and discusses case studies on this pollution type drawing conclusions which are relevant to this research design. The hazards of nitrate in groundwater to human health and livestock are also described.

Chapter 3 gives a detailed insight into the specific features of the study area, including climate, topography and drainage and water supply. It as well provides information on the geological setting and the geohydrology of the investigated aquifer.

Chapter 4 summarizes the methods applied for the investigation of geochemistry, hydrochemistry and isotope hydrology, and their application to the nitrogen cycle and nitrate source identification. In addition, it explains the hydro-geochemical setting of the study. The results of nitrogen analyses of groundwater samples are presented. The origin of the groundwater types occurring in the Thaba Nchu groundwater system is discussed.

Chapter 5 gives an overview of some of the options for managing groundwater pollution risks derived from sanitation for on-site methods. These include planning, design and construction of facilities, as well as monitoring their safe operation.

Conclusions and recommendations are presented in Chapter 6.

2. LITERATURE REVIEW

This chapter explores the sources of nitrates in groundwater, health and environmental impacts, remediation options and methods for nitrate pollution estimation. While Thaba Nchu is the main study area in this research, the scope is also expanded to include research from case studies that examine nitrate-occurring problems and approaches put forward to fix them.

2.1   Nitrate in groundwater

Nitrate (NO_3^-) is a plant nutrient that, in excess concentration, has caused health problems in infants and animals and has led to eutrophication of natural water bodies throughout the world (Fennessy and Cronk, 1997 as cited in ITRC, 2000). WHO (1996) specifies a maximum concentration of nitrate-nitrogen in drinking water of 10 mg/L.

Nitrogen (N) is one of the main biogeochemical elements and along with carbon, oxygen, sulphur and phosphorus these elements in their biogeochemical cycles constitute the main life supporting system for our planet. The most important reactions involving nitrogen are of a biochemical nature and are either driven by microorganisms or enzymes. For this reason the impact of nitrates on groundwater needs to be viewed in terms of the nitrogen biogeochemical cycle (Figure 2-1). Whereas nitrogen compounds in most environments play a beneficial role the presence of such compounds in water is generally detrimental (Tredoux, *et al.,* 2009).

Nitrogen inputs, whether due to natural fixation of nitrogen, fertiliser application, or pollution, all contribute to the pool of soil organic nitrogen. A series of (bacterially mediated) transformations are needed to convert the organic nitrogen to nitrate which could potentially be leached to the groundwater. Anthropogenic inputs increase the soil nitrogen pool to such an extent that leaching of nitrate is enhanced. This is also true for fertiliser application to land as well as the tilling of the soil which enhances the nitrification of soil organic nitrogen. Depending on the conditions in the unsaturated zone and in the aquifer, denitrification, that is, reduction of the nitrate to nitrogen is also possible. This is an important natural process which assists in maintaining the balance with respect to the nitrate in the groundwater (Tredoux, *et al.,* 2009).

The fate of nitrate is complex and includes several physical and biological processes of which denitrification plays a major role. There are four major forms of nitrogen in the soil and vadose zone:

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- nitrogen gas.
- organic nitrogen.
- ammonia nitrogen bound on clays and in aqueous form in pore water.
- nitrate.

Denitrification results in the reduction of nitrate to nitrogen gas.
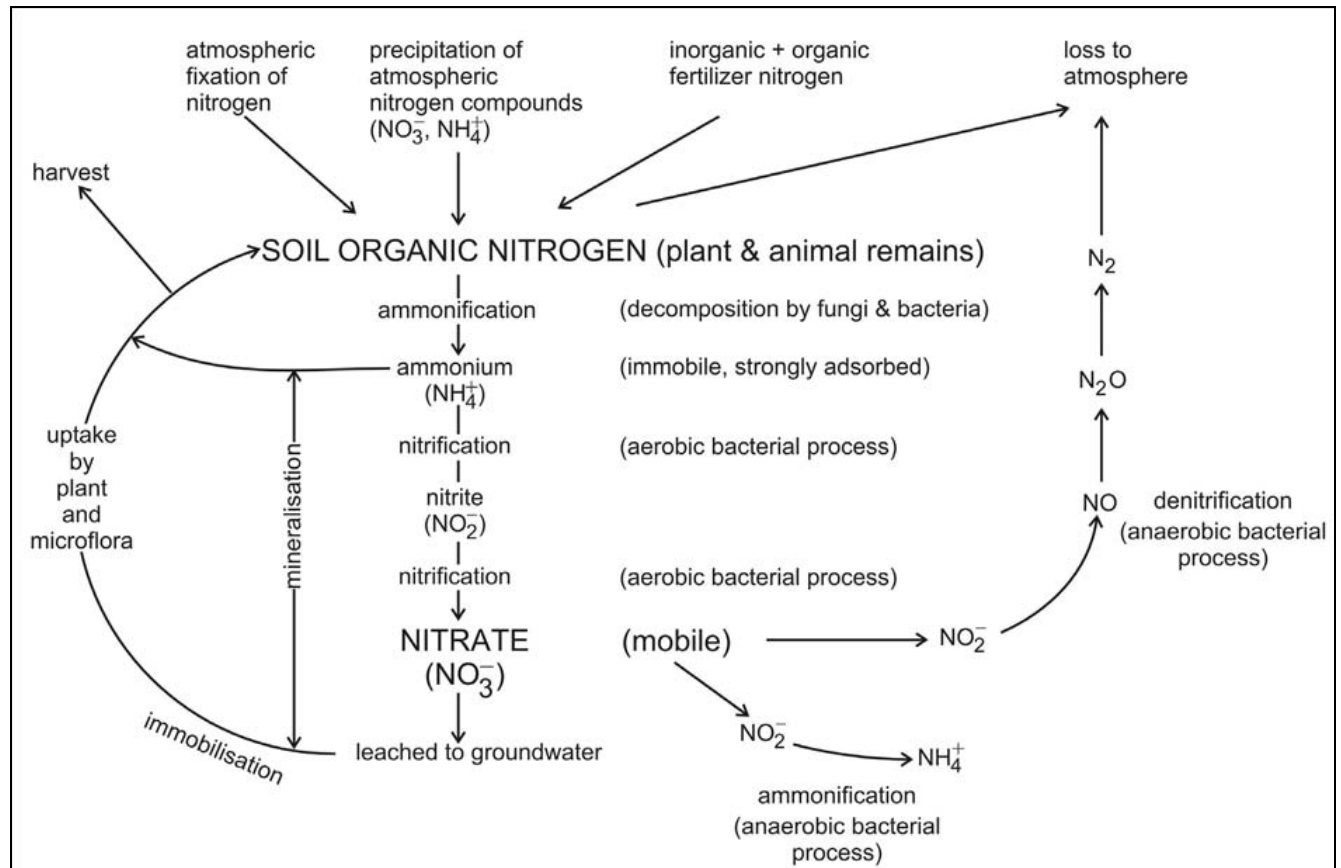
Figure 2-1: The biogeochemical nitrogen cycle (Source: Hiscock, *et al.,* 1991 cited in Tredoux, *et al.,* 2009)

Nitrogen may be added to the soil through fertilizer, rain, animal and human waste, organic matter, and anthropogenic influences such as explosives and chemical wastes (ITRC, 2000). Nitrogen may undergo chemical transformations before it is transported into groundwater. The major divisions of the nitrogen cycle are mineralisation, immobilisation, nitrogen fixation, ammonification, nitrification and denitrification (Fahrner, 2002).

The conversion of nitrogen species to various organic forms is through immobilisation or microbial or plant assimilation. Mineralisation is the conversion of complex organic nitrogen to more simplified inorganic forms (eqn. 2.1). Nitrogen may be present in the soil in the form of ammonium (NH_4^+). Ammonium may be metabolised by organisms, assimilated by plants, adsorbed by clay minerals and/or organic matter, and oxidised to nitrate (NO_3^-). Nitrification

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is the biochemical oxidation of ammonium to nitrate. In the presence of specific bacteria and oxygen, ammonium is enzymatically oxidised in a stepwise process to nitrite (NO_2^-) followed by nitrate (NO_3^-) (eqn. 2.2 and 2.3).

$$RNH_2 + H_2 \longrightarrow NH_4^+ + energy \qquad (2.1)$$

$$2NH_4^+ + 3O_2 \longrightarrow 2NO_2^- + 2H_2O + 4H^+ + energy \qquad (2.2)$$

$$2NO_2^- + O_2 \longrightarrow 2NO_3^- + energy \qquad (2.3)$$

$$5CH_2O + 4NO_3^- + 4H^+ \longrightarrow 2N_2 + 5CO_2 + 7H_2O \qquad (2.4)$$
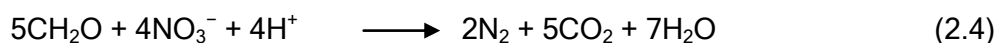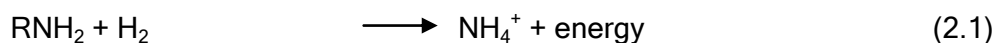
* where R signifies an organic compound

Nitrification will only occur in oxidising environments. Secondary parameters affecting nitrification include temperature, moisture content, population of nitrifiers and pH. Denitrification is the biochemical reduction of NO_3-N to nitrogen gas in the absence of oxygen (eqn. 2.4) (ITRC, 2000).

Nitrate occurs extensively in groundwater in southern Africa. The map based on data for 50,000 groundwater sources (Figure 2-2) shows that elevated nitrate concentrations occur both locally at isolated points as well as in vast areas regionally extending over hundreds of kilometres. In the semi-arid to arid regions of the Northern Cape Province and Namibia significant groundwater nitrate occurrences are found in large areas where anthropogenic influences can be excluded. In these areas, the (human and animal) population density is very low but even confined groundwater with an apparent age of several thousands of years may have significant nitrate levels. Therefore, under natural conditions significant loss of nitrogen from the soil zone may occur in such climatic regions, causing enrichment of groundwater with high levels of nitrate (Tredoux, *et al.*, 2009).
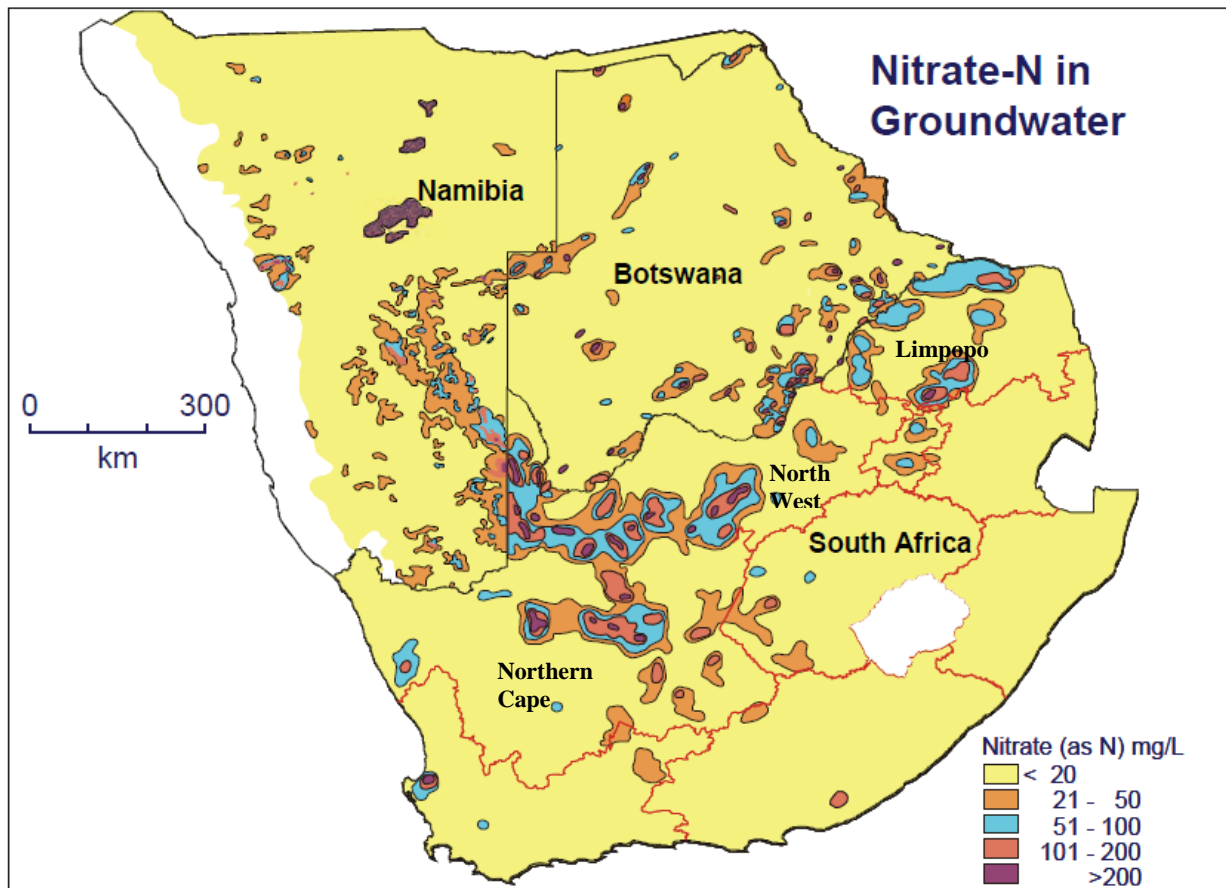
Figure 2-2: Map of southern Africa showing groundwater nitrate distribution (Source: Tredoux, *et al.,* 2009)

2.2   Sources of nitrate

Nitrogen losses due to denitrification help to maintain relatively low nitrate concentrations in groundwater and surface waters (ITRC, 2000). In most naturally occurring environments, nitrate concentrations in groundwater are < 3 mg/L (Smith, *et al*., 1987 mentioned in Fahrner, 2002). Nitrogen losses due to denitrification help to maintain relatively low nitrate concentrations in groundwater and surface waters. National standards, as stated by the WHO (1996) have been established for drinking water at 10 mg/L NO_3-N. This standard applies to all public supply systems. To provide a higher margin of health safety, Germany has lowered their NO_3-N drinking water standards to 4.4 mg/L (Kross, 1995 cited in Fahrner, 2002). Thailand has established a bottled drinking water standard for nitrate at 4.0 mg/L (Ministry of Public Health, 1981 referred in Fahrner, 2002).

2.2.1 Natural occurrence of nitrate in groundwater

It is unusual for pristine groundwater systems to accumulate more than 3 mg/L nitrate (Madison and Brunnet, 1985 cited in Fahrner, 2002). However, some naturally occurring processes may occasionally cause nitrate contamination in groundwater.

2.2.1.1 Lightning storms

During lightning storms, atmospheric nitrogen is converted to nitrate and deposited to the soil through rain. In arid conditions, high nitrate concentrations may be caused by evapotranspiration of infiltrating rainwater in the shallow subsurface aquifer. During storm events, this high nitrate concentration may be transported to the shallow aquifer where nitrate concentrations can be up to 60 mg/L (McQuillan, 1995 cited in Fahrner, 2002).

2.2.1.2 Geological origin

Nitrogen-bearing rocks are globally distributed. Although often neglected in nutrient cycling in the past, geologic sources have been reported in recent studies to comprise a large potential pool of nitrogen (Holloway and Dahlgren, 2002; Lowe and Wallace, 2001; Holloway, *et al.*, 1998; cited in Stadler, 2005). This pool is estimated to contain about 20 % of the global nitrogen inventory (Schlesinger, 1997 referred in Stadler, 2005). The main source of nitrogen in rocks is organic matter that is deposited in sediments (Figure 2-3). Alternatively nitrogen can stem from thermal waters as a mixture of sedimentary, mantle and meteoric origin. Nitrogen can be incorporated into rocks as organic matter (for example, in carbonaceous shale), or as ammonium (NH_4^+) fixed in silicate minerals (Holloway and Dahlgren, 2002 referred in Stadler, 2005). The nitrogen that is contained in organic matter is converted to ammonium during diagenesis, which in turn can substitute for potassium (K^+) in silicate minerals. Ammonium end-member silicate minerals include buddingtonite, tobelite, ammonium muscovite and ammonium biotite (Lowe and Wallace, 2001 cited in Stadler, 2005).

These processes may be more pronounced in surface waters than in deeper groundwaters as the weathering rate of rocks and thus the release of nitrogen is higher under surface conditions, for example, natural geogenic nitrogen in stream water in Utah. However, in some cases distinguishing between anthropogenic and geogenic origin of nitrate in groundwater is challenging and needs to be looked at on a case-by-case basis (Holloway and Dahlgren, 2002 mentioned in Stadler, 2005).

Studies conducted in early nineties in semi-arid regions of North America suggested that it was not unusual for relatively large amounts of plant-available nitrogen to be present beneath root zones of native prairie vegetation. Concentrations of NO_3-N were as great as 36 µg/g soil 150 cm beneath native range in eastern Montana, at a time when very little of that land was cultivated (Buckman, 1910 cited in Dwivedi, *et al.*, 2007). These results suggest that, in regions where relatively unweathered sedimentary deposits exist beneath the root zone, there is potential for the presence of residual exchangeable ammonium, which is readily oxidized to NO_3-N when exposed to proper conditions.

An additional source of sub-soil NO_3-N accumulations may result from sub-surface seepage through perched water tables. Water and nitrates could leach through fallow sandy soils until they reached a permeable aquifer (Dwivedi, *et al.*, 2007). Nitrates would then flow essentially horizontally through the shallow aquifer and exit the soil by a hillside seep exemplified in the Republic of Malta (Figure 2-4). A concentration range of 50 - 100 mg/L NO_3-N of seep water is very common (Dwivedi, *et al.*, 2007; Stuart, 2012).
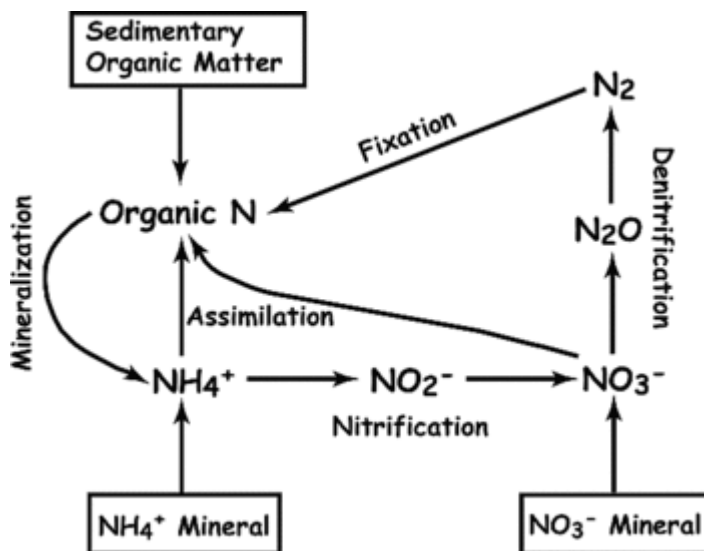
Figure 2-3: Geologic nitrogen cycle in sedimentary rocks (Source: Holloway and Dahlgren, 2002)
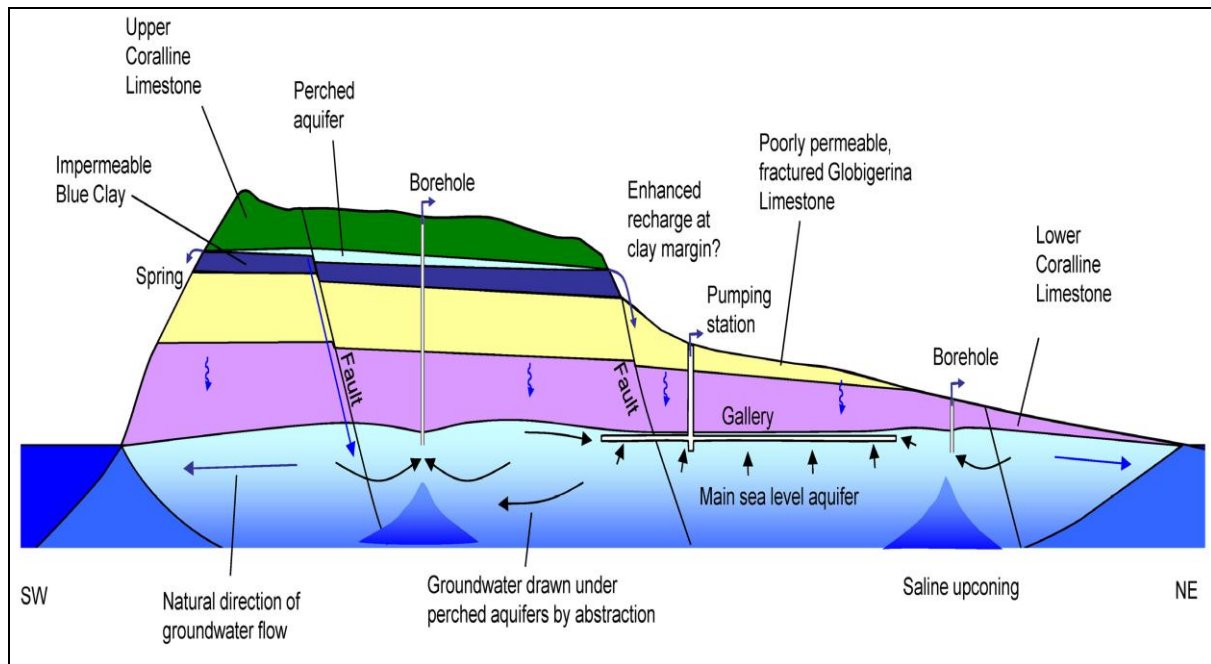
Figure 2-4: Impacts of nitrate on the water resources of Malta (Source: Stuart, 2012)

2.2.1.3 Precipitation

An appreciable quantity of N is added to most soils annually through precipitation. This N is often in nitrate and ammonium forms, both of which are commonly washed out of the atmosphere by precipitation. Much of the NO_3-N in the atmosphere originates from combustion, so values are often greatest downwind from power plants or major industrial areas. Major agricultural sources of atmospheric ammonium are ammonia volatilization from soils, fertilizers, animal wastes and vegetation. Demead, *et al*. (1978 cited in Dwivedi, *et al*., 2007) showed that appreciable quantities of ammonia may escape through stomata of plant leaves in the transpiration stream. This process is particularly important during senescence of well-fertilised vegetation. Some of the ammonia escaping the soil and plant surfaces may be reabsorbed and utilized by other plant leaves, with the balance escaping to the atmosphere. Harper, *et al*. (1983 referred in Dwivedi, *et al*., 2007) showed that atmospheric ammonia concentrations above the plant canopy are often near $\sim$10 g/m^3, but that these values can temporarily increase to well over $\sim$100 g/m^3 after fertilization with urea.

Total quantity of N added to the soil through precipitation is highly variable and depends on surrounding agricultural and industrial activities. In temperate regions and natural ecosystems where precipitation is the major source of nitrogen, the nitrogen quantity ranges between 10 - 14 kg/ha/yr (Dwivedi, *et al*., 2007).

Figure 2-5 shows an extreme example from Botswana where above average rainfall was experienced in the 1999 / 2000 rainy season and groundwater that was perfectly usable for stock watering became toxic to the livestock by September / October 2000. Some four years later the nitrate concentration returned to "normal" (Tredoux, *et al.,* 2009).

Groundwater recharge conditions differed totally from an average rainy season and caused the transport of nitrate from the unsaturated zone into the groundwater (Tredoux, *et al.,* 2009).
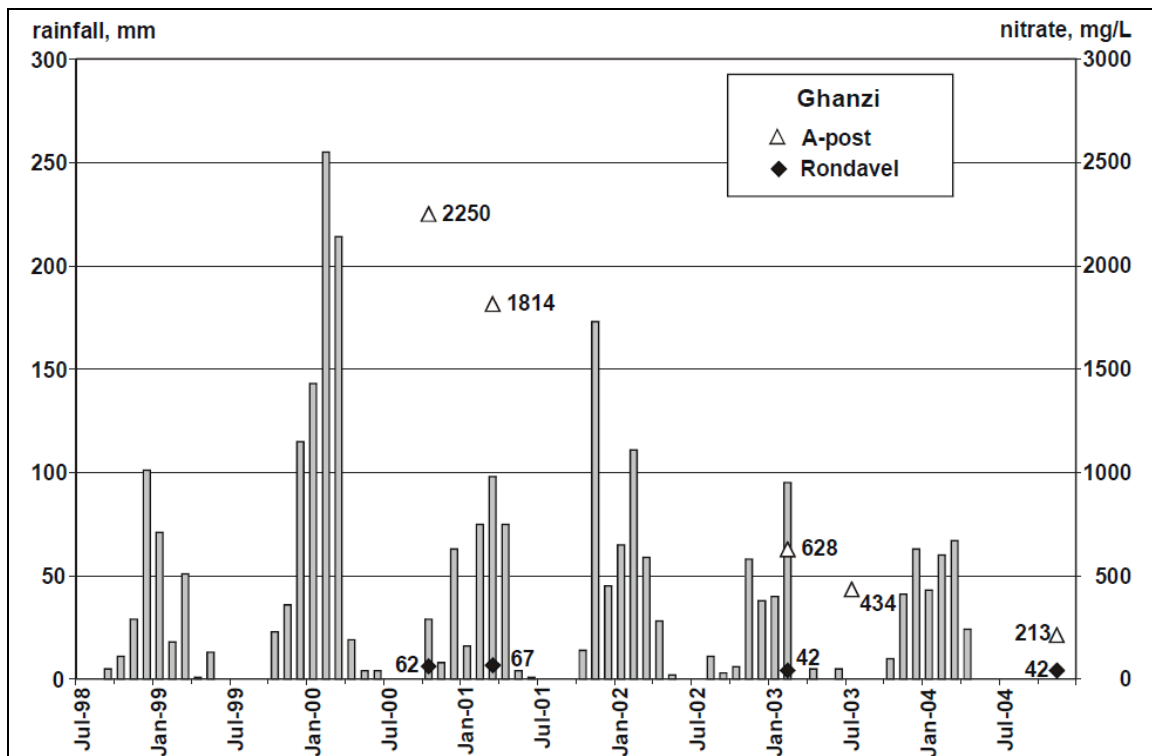
Figure 2-5: Rainfall and associated variation in nitrate concentrations (as NO_3) in groundwater. (Source: Tredoux *et al.*, 2009)

2.2.1.4 Other factors

Various factors are involved, which may include the nature and thickness of surface deposits, rainfall quantity, and distribution, depth to the groundwater level, distribution of vegetation types and presence of nitrogen-fixing vegetation.

High levels of "natural" nitrate only occur in groundwater, when most or all of the above factors are acting in unison. Natural disturbances of the plant cover, for example droughts (and possibly also bush fires) affect the nitrogen cycle, leading to nitrate leaching beyond the root zone, particularly during subsequent heavy rainfall events.

In the Australian arid zone nitrate occurrences were initially ascribed to biological nitrogen fixation, or a combination of nitrogen fixation and termite activity, and finally mainly to nitrate accumulation in termite mounds. Similarly, naturally high groundwater nitrate concentrations in the Sahel have been ascribed to leguminous vegetation and leaching of nitrate due to varying climatic cycles (Tredoux, *et al.*, 2009).

2.2.2   Anthropogenic sources of nitrate in groundwater

Apart from the natural sources of nitrate discussed above, most groundwater nitrates are derived from a wide range of anthropogenic sources. Anthropogenic generation of nitrate is well known and includes on-site sanitation, application of nitrogenous material to land (fertilisers), tilling of the soil, irrigation, industrial, and other activities. Whereas agriculture is the main source of nitrate in the highly-developed countries such as Europe and the USA, on-site sanitation is seen as the main anthropogenic source of nitrate in Southern Africa. Groundwater pollution problems related to on-site sanitation have been known for decades in the southern African subcontinent and several studies have been carried out. These features can be seen in the nitrate map above in Figure 2-2 as high nitrate levels around urban areas and also in the high-density rural settlements of the Northern Cape, Northwest, and Limpopo Provinces, South Africa, and in south-eastern Botswana (Tredoux, *et al.*, 2009).

In contrast, most other rural incidences are related to pollution point sources such as on-site sanitation, kraals, and other places where livestock congregate, especially at stock watering points, and feedlots. Non-point sources include manure and fertilizer application to land, and tilling of the soil, while deforestation and land clearing also provide significant nitrate addition to groundwater (Tredoux, *et al.*, 2009).

In the urban and peri-urban context sewage sludge drying beds at sewage farms and sludge "application" to land pose the greatest threat to groundwater, in addition to areas with inappropriate on-site sanitation (Tredoux, *et al.*, 2009).

2.2.2.1 Human and animal wastes

Waste produced by humans and animals are major sources of nitrate in any area characterised by significant human or animal populations. Nitrates from such waste can exhibit the characteristics of either point or non-point source pollution. Point sources occur at or near the actual waste facility involved and typically exhibit high levels of nitrate or ammonia in a limited area. Diffuse sources are spread over large areas (for example, in

agricultural fertilisation), and impacted aquifers are often characterised by lower (but ≥10 mg/L) levels of NO_3-N.

Nitrate from human waste originates mostly from individual septic systems or municipal wastewater treatment facilities and pit latrines in rural areas. Typically, effluent from such septic systems is in the order of 30 - 60 mg/L total nitrogen, with ammonia making up the majority of the nitrogen. The nitrogen content of this effluent varies widely depending upon the condition of the individual system and the type of waste being introduced (ITRC, 2000).

The majority of the population is served by municipal wastewater treatment systems. Nitrogen content of effluent from municipal systems will vary according to the nature of the incoming waste stream and the type and condition of the system. However, after primary treatment with activated sludge, the effluent typically still contains about 15 - 35 mg/L of total nitrogen. More advanced systems can reduce this to about 2 - 10 mg/L (ITRC, 2000). In Western Australia, effluent from wastewater treatment plants is currently disposed of via ocean outfalls although there are moves to utilise the effluent in land-based applications, which has implications for groundwater quality (ITRC, 2000).

Waste from dairies, open feedlots, confined feeding operations, stockyards and other facilities for raising and holding animals is also a potential source of nitrate and other forms of nitrogen. While public concern over animal waste includes such issues as odour, flies and surface water impacts, these facilities represent a massive source of nitrogen and other nutrient inputs to groundwater. For example, the University of Nebraska Cooperative Extension (1998 cited in ITRC, 2000) estimated that waste from animal stock typically contained from about 0.1 - 0.4 kg of nitrogen per kilogram of animal weight. Typically, total nitrogen concentrations of dairy wastewater ranged from 150 - 500 mg/L (ITRC, 2000).

2.2.2.2 Fertilisers

Nitrogen is the major component of fertiliser for agricultural, turf and garden use. Nitrogen fertiliser normally takes one of two forms: inorganic fertiliser and animal waste.

Inorganic fertiliser usage has become commonplace in the last half of the twentieth century with the advent of anhydrous ammonia, liquid nitrogen, urea and similar formulations that have greatly increased crop yields, for example, in Australia. In some cases, fertiliser has been over-applied, either from a lack of understanding of its impacts or crop nutrient requirements, or as a relatively inexpensive "insurance policy" against unpredictable conditions that may leave crops short of nutrients (ITRC, 2000).

Animal waste has been applied to cropland for generations, both as a means of fertilisation and waste disposal. Nitrate's high solubility and low sorptivity allows infiltration beyond the root zone when over-applied or over-watered. Thus, infiltration via precipitation or irrigation water easily transports nitrate, which is not taken up by plants, downward to groundwater. As a result of this process, elevated groundwater nitrate levels have occurred in heavily farmed areas. Recent attempts to reduce non-point nitrate contamination in groundwater have focused on proper timing of application and reduced amounts of fertiliser and irrigation water (ITRC, 2000).

2.2.2.3 Industrial uses of nitrate

Nitrogen compounds are used extensively in industrial settings. Some of the predominant nitrogen compounds used in industry are:

- anhydrous ammonia;
- nitric acid;
- ammonium nitrate;
- urea.

A few of the industrial uses for nitrate include:

- manufacturing of plastic;
- metal processing;
- raw material in the textile industry;
- pulp, paper and rubber production; and
- household cleaners.

Nitrate contamination may result from improper handling, disposal and use of these compounds, and levels of contamination will depend on the source (Potash Corp. Web site, 1999 cited in ITRC, 2000).

2.2.2.4 Cultivation

Cultivation also contributed to groundwater nitrate pollution by leaching of nitrate beneath the root zones. Evidence of nitrate movement below the root zone for cultivated soils receiving essentially no manure or fertiliser N inputs has been presented by a number of investigators (Buckman, 1910; Stewart, *et al.*, 1967; Boyce, *et al.*, 1976; Brown, *et al.*, 1982; mentioned in Dwivedi, *et al.*, 2007). This N may amount to several hundred kilograms per hectare and can contribute significantly to groundwater contamination with nitrates. In European countries, conversion of permanent grasslands to arable land causes strongly enhanced leaching for a limited time period (Dwivedi, *et al.*, 2007). Mean NO_3-N concentration of the annual

groundwater recharge show rather high concentration for sandy soil with arable crops, intensively managed grazed grasslands and field cropping of vegetables. The NO_3-N concentration exceeded drinking water limit of 11.3 mg/L by a factor of between 2 and > 4 (Landreau and Roux, 1984; Overgaard, 1984; Rohmann and Southeiner, 1985; De Smedt and Loy, 1985; Foster, *et al.*, 1986; Linn and Doran, 1984; referenced in Dwivedi, *et al.*, 2007) showed that rates of mineralization and nitrification of organic sources of N in the soil increase as water-filled pore space increases to near 60 % of total pore volume (approximate water content at field capacity). At higher water-filled pore space values, mineralisation and other aerobic processes decline sharply, and anaerobic processes, such as denitrification, begin. Doran (1987 cited in Dwivedi, *et al.*, 2007) found that compared with native sod, water-filled pore space in ploughed soil often favoured rapid mineralisation and nitrification for several days or weeks after ploughing. This resulted in a rapid accumulation of NO_3-N in the surface of ploughing soil, which could have leached below the root zone with sufficient precipitation.

Crop residues produced each year contain 3 - 4 million metric tons of N, most of which is recycled annually (Power and Papendick, 1985 cited by Dwivedi, *et al.*, 2007). Types of crop residue (legume versus non-legume) and crop residue management system used to determine to a large extent the fate of this N. Residues from a legume, such as soybean, decompose relatively rapidly, and much of the N in legume residues is mineralized and utilized by the next crop grown (Power, *et al.*, 1986 cited by Dwivedi, *et al.*, 2007). Residues from non-legumes, such as cornstalks and wheat straw, decompose much slower and often initially result in immobilization of inorganic N in the microbial biomass associated with the decomposition process. The subsequent mineralization of this N is a relatively slow process. Consequently, seldom do appreciable quantities of soil nitrates accumulate in the soil after addition of non-legume residues. Method of cultivation can also have a major effect on cycling of N and the accumulation of nitrates. Disturbing the soil with tillage (ploughing, disking) increases aeration and mixes crop residues with readily available carbon sources intimately with soil organisms. With access to ample supplies of both oxygen and energy from the carbon source, microbiological activity is usually greatly enhanced after tillage until the soil becomes too dry (Doran and Power, 1983 cited by Dwivedi, *et al.*, 2007).

2.2.2.5 Irrigation

A special mention is made of irrigated agriculture because nitrate contamination of groundwater is especially prevalent in irrigated areas. For sustained irrigation, some leaching must occur periodically to remove soluble salts brought in with the irrigation water. Unlike

rain-fed agriculture, a significant quantity of salt is introduced with all irrigation waters, and these must be flushed out of the root zone every year or two. If the leaching occurs at a time when appreciable nitrates are present in the root zone, these nitrates are then leached into the vadose zone and, eventually, into the watertable (Power and Schepers, 1989 cited by Dwivedi, *et al.*, 2007). In irrigated regions of the Great Plains in US, much of the leaching occurs during the winter and spring months, when actively growing crops are absent (Schepers, *et al.*, 1985; Hergert, 1986; cited by Dwivedi, *et al.*, 2007). Ideally, for both reduced cost of operation and maintenance of groundwater quality, a farmer would like to use management practices that minimize the amount of residual nitrate in the soil during this non-crop periods.

2.2.2.6 Explosives

Nitrogen is a major element in the manufacture of explosives, which primarily utilises ammonium nitrate and diesel fuel. Without proper management and treatment, waste streams that contain high concentrations of ammonium nitrate and diesel fuel can cause groundwater quality degradation. In some instances, this waste stream, along with improper handling of the ammonium nitrate, has created nitrate contamination. Presently, most explosive manufacturers have taken pollution prevention steps to reduce or eliminate this waste (due to regulations or economical savings). Waste streams from explosives manufacture contain nitrogen concentrations ranging from 200 mg/L to over 1,000 mg/L (ITRC, 2000).

2.3 Methods for estimating nitrate pollution

In order to find out the extent of nitrate pollution, it is essential to have methods for estimating nitrate contamination of the sites. A number of approaches have been used. Thus, traditionally NO_3-N leaching has been determined using lysimeteres where the drainage water is collected and NO_3-N content measured (Chapman, *et al.*, 1949; Owens, 1960; Pratt and Chapman, 1961; cited in Dwivedi, *et al.*, 2007), however, it is expensive method.

Pratt, *et al.* (1978 cited in Dwivedi, *et al.*, 2007) described a cheaper method where the ratio of chloride in the irrigation water, corrected for plant uptake, the chloride below the root zone is used to estimate leaching fraction (LF). The LF, seasonal evapotranspiration and NO_3-N concentrations below the root zone are combined to estimate the NO_3-N leaching. Difficulties associated with solute leaching model are said to be calibration and their boundary

conditions which could not be easily satisfied in complex land use systems and non-uniform strata (Addiscott and Wagenet, 1985; McLay, *et al.*, 2001; cited in Dwivedi, *et al.*, 2007).

Another approach is looking for the correlation between the dominant land use in an area and the actual nitrate concentration measured in the underlying aquifers (Barringer, *et al.*, 1990; Burkart and Kolpin, 1993; Eckhardt and Stackelberg, 1995; Levallois, *et al.*, 1998; Ahn and Chon, 1999; McLay, *et al.,* 2001; cited in Dwivedi, *et al.*, 2007). This approach is based on the assumption that land use influences the nitrogen flow in the surface soil and its consequent leaching out into the groundwater system. Among all these studies, agriculture stands as the most commonly correlated land use with nitrate contamination of groundwater. Severe nitrate contamination is found to be mainly associated with vegetable cultivation, orchards, and floriculture, due to the high rate of application of chemical and organic fertilizers (Salameh Al-Jamal, *et al.*, 1997; McLay, *et al.*, 2001; cited in Dwivedi, *et al.*, 2007).

Geographical Information System (GIS) is recently being recognized as a powerful tool in environmental studies and modelling (Goodchild, *et al.*, 1996 referred Dwivedi, *et al.*, 2007). However, it is also subjected to error and uncertainty introduced at almost every step of the spatial information generation and processing, from the data collection to the interpretation of the results (Aronoff, 1993 mentioned in Dwivedi, *et al.*, 2007). Furthermore, the high value of GIS products in the evaluation, communication, and management of environmental problems is unambiguous. The GIS technology was employed to investigate nitrate contamination of groundwater by chemical fertilizers in the Kakamigahara Heights and Central Japan (Dwivedi, *et al.*, 2007). Data was analysed to study the extent and variation of nitrate contamination and to establish spatial relationship with responsible land use types. Ninety percent of the water samples showed nitrate concentration above the human affected value (3 mg/L NO_3^-), while more than 30 % had exceeded the maximum acceptable level (44 mg/L NO_3^-) according to Japan regulation. The study indicated the association of pollution levels specifically with vegetable fields, which were significantly higher than the under urban land or paddy fields (Babiker, *et al.*, 2004 referenced in Dwivedi, *et al.*, 2007).

For isolated sample analysis for nitrate contamination in soil or water bodies, easy and quick methods have been developed. Many commercial nitrate test kits are available which use the heavy metal cadmium to reduce nitrate in the process of nitrate testing. In order to assess the nitrate pollution problem, Nitrate Test Kits (NTK), based on nitrate reductase, which are environment and user friendly have recently been developed by a company called Nitrate Elimination Company, Inc (NECi). Nitrate reductase used in the kit is very stable making enzyme-based nitrate testing easier than ever (Campbell, *et al.*, 2002; 2004; Patton, *et al.*, 2004; cited in Dwivedi, *et al.*, 2007).

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2.4   Effects of nitrate

2.4.1   Human health hazards

2.4.1.1 Methemoglobinemia

Nitrate-contaminated water is a well-documented cause of the medical condition methaemoglobinaemia, commonly known as "blue baby syndrome" (Knobeloch, *et al.*, 2000 cited in Mohr, 2009). Methaemoglobinaemia is a disease generally resulting from the ingestion of high concentrations of nitrate in its inorganic form (Burt, *et al.*, 1993). In the stomach and small intestine of individuals with very low stomach acidity, indigenous bacteria chemically reduce the nitrate (NO_3^-) to nitrite (NO_2^-), a more reactive form of the compound. Nitrite is absorbed through the walls of the small intestine into the blood stream where it combines with haemoglobin to form methaemoglobin. This process blocks the oxygen-carrying capability of the blood. When the concentration of methaemoglobin becomes too high, the victim becomes cyanotic and can die of asphyxiation. The body does not have the capability to naturally change the methaemoglobin back to effective haemoglobin (ITRC, 2000).

The cause of Blue Baby Syndrome is generally the mixing of infant formula with water containing greater than 10 mg/L nitrate as nitrogen. Infants are not the only susceptible population, however. Children and adults suffering from maladies or treatments that lower the levels of stomach acid are also vulnerable to methaemoglobinaemia. Nitrate poisoning certainly contributes to national infant death rate statistics. For example, in one 30-month period alone in Minnesota, there were at least 144 cases of infant methaemoglobinaemia, including 14 deaths (Rosenfield and Huston, 1950 cited in Johnson and Kross, 1990).

2.4.1.2 Other associated effects

Although methaemoglobinaemia is the only disease that is currently directly attributable to elevated nitrate concentrations, there are other suspected health effects. Important amongst these is the possibility of spontaneous abortions in women of child-bearing age. A small study of these occurrences was carried out in Indiana, USA in 1993 (Centres for Disease Control and Prevention, 1996 cited in ITRC, 2000). Four women, living in residences served by private wells contaminated with nitrate ranging from 19 - 29 mg/L nitrate as nitrogen, experienced a total of eight spontaneous abortions. Three of the women lived within two kilometres of a point source of nitrate contamination. One of the women had four spontaneous abortions within the first 8 - 11 weeks of her pregnancies. At least one of these

women had previously carried a child to term. The fourth woman resided approximately 16 kilometres from the first three. She had previously carried four babies to healthy births but had two spontaneous abortions in 1994. The home's water supply contained an average nitrate concentration of 29 mg/L. After switching to nitrate-free drinking water, all four women carried babies to term (Centres for Disease Control and Prevention, 1996 cited in ITRC, 2000).

Nitrate is identified as a possible cancer risk due to its transformations in the body. Approximately 5 % of ingested nitrate is converted to nitrite, which can then combine with organic compounds to form N-nitroso compounds, which have been shown to be potent animal and human carcinogens (Blair, *et al.*, 1997 referred in ITRC, 2000). An ecological study in China was also cited as showing a possible link between nitrate and leukemia mortality rates (Wu, *et al.*, 1993 stated in ITRC, 2000). Another study in Nebraska (Ward, *et al.*, 1996; Weyer, *et al.*, 2001; mentioned in Ward, *et al.*, 2005) showed a slightly positive correlation between high nitrate concentrations in water supplies and non-Hodgkin's lymphoma.

2.4.2   Animal health effects

Nitrate-contaminated water consumed by livestock has resulted in nitrate poisoning. At high enough nitrate concentrations (> 300 mg/L), nitrate poisoning may result in animal death. At lower concentrations, nitrate poisoning can increase the incidences of still born calves, abortions, retained placenta, cystic ovaries, lower milk production, reduced weight gains, and vitamin A deficiency (ITRC, 2000).

Livestock may be harmed at nitrate-nitrogen concentrations between 100 - 300 mg/L, and nitrate poisoning in cattle, sheep, and horses may occur at concentrations > 300 mg/L NO_3-N (ITRC, 2000). Recommended limits of nitrate in drinking water for livestock and poultry should not exceed 100 mg/L. Accurate assessment of the source of nitrate poisoning in stock is difficult because of the potential of nitrate accumulation in crops which may further cause nitrate accumulation in the animal (Kvasnicka and Krysl, 1990; Faries, *et al.*, 1991; cited in ITRC, 2000).

In several instances nitrate poisoning has been identified as the cause of stock losses. This generally happened after periods of very heavy rainfall when some months after the event groundwater that was perfectly suitable for potable use becomes laden with nitrate and other

salts, and often also harmful bacteria. Examples in Tredoux *et al.,* (2009) of recorded losses confirmed as nitrate poisoning are:

- 1969: Namibia: Tens of livestock;
- 1969: Texas: 2 herds of cattle;
- 1974: Namibia: Hundreds of livestock;
- 1989: South Africa: 147 heads of cattle;
- 2000: Botswana: > 356 heads of cattle;
- 2001: South Africa: > 60 heads of cattle;
- 2002: Botswana: 48 heads of cattle.

Not all instances where livestock are lost due to nitrate poisoning are recorded as the cause of death may not be recognised and in addition livestock losses are a very sensitive issue. It is therefore important for the public at large to be aware of the problem in order to improve environmental management, particularly to reduce groundwater pollution, and to prevent methaemoglobinaemia and stock losses (Tredoux, *et al.,* 2009).

Nitrate poisoning is characterised by a brown colouration of the blood of the affected animal and the colour change can also be seen on mucous membranes and other body parts. At sub-lethal levels of nitrate (but often above 110 parts per million as nitrogen) abortion and poor milk production have been recorded for lactating cows (Tredoux, *et al.,* 2009).

2.4.3   Environmental effects

Nitrogen concentrations exceeding background levels (~ 3 mg/L) in surface waters reflect pollution from domestic, industrial or agricultural sources (Smith, *et al.,* 1987). Since the early 1970s, trends show an increase in nitrate concentrations in rivers and streams. Nitrogen is one of the most important nutrients that regularly limit primary productivity. Excess input of nitrogen to the environment results in eutrophication in fresh and marine waters (Cole, 1983 cited in ITRC, 2000).

Kimmel (1981 cited in ITRC, 2000) stated that the effects of nutrient loading on water quality and productivity are particularly important for natural water bodies, which are often sources for municipal water supplies and water-based recreation. Cole (1983, cited by ITRC, 2000) noted that levels of nitrate much lower than the maximum contaminant level for drinking water contribute to increased rates of eutrophication in surface waters.

Runoff from cropped agricultural fields and feedlots is significantly higher than from pasture land (Beaulac and Reckhow, 1982 mentioned in ITRC, 2000). In a study by Smith, *et al.* (1987 cited in ITRC, 2000), increased nitrogen loading to runoff from cropped lands was associated with increased nitrogen fertilisation rates, which amounted to a 68 % increase on cultivated lands from 1970 – 1981. Runoff from animal feedlots provides high concentrations of nitrate and ammonium (Beaulac and Reckhow, 1982 cited in ITRC, 2000).

Wetlands and forested areas are our prime defences for trapping and purifying nutrients in runoff before they enter streams (Fennessy and Cronk, 1997 cited in ITRC, 2000). When there is nitrate loading to coastal streams and rivers, it generally stimulates algal blooms in salt-water estuaries and bays. In the Gulf of Mexico, nitrate runoff from the Mississippi River has resulted in up to 7,032 square miles of hypoxia (Rabalais, *et al.*, 2001 cited in Fahrner, 2002). In Chesapeake Bay rivers, animal waste nitrogen is believed to be the cause of a deadly *Pfisteria* bloom in the summer of 1998 (Burkholder and Glasgow Jr., 1997 cited in ITRC, 2000).

2.5   Nitrate remediation options and their requirements

2.5.1   Traditional options

Groundwater remediation of nitrate contamination has not received as much attention as known carcinogenic contaminants. Remediation of nitrate plumes has not been as common or extensive as other contaminants of concern. However, when a groundwater nitrate plume has been identified, certain corrective remediation activities have been employed. Site-specific information has determined which remediation option to employ. Note that most remediation options involve pumping of contaminated groundwater (cited in ITRC, 2000).

2.5.1.1 No action

For various reasons, no remediation action for nitrate-contaminated groundwater has been a common approach and perhaps the option most often chosen. Some reasons for no action are public awareness, extent of contamination, inconsistent regulatory enforcement, economic issues, and responsible parties who are unable to pay for remediation. When a supply well is impacted with nitrate contamination, certain institutional actions are taken to provide clean water without addressing the contamination. Examples of this are deepening the supply well to find clean water, blending the contaminated water with clean water to meet standards, or finding an alternate water supply. If no action is taken, groundwater nitrate

plumes remain and may continue to increase in concentration and size, posing a continued or greater threat (cited in ITRC, 2000).

2.5.1.2 Pump with beneficial use

Pumping and using nitrate-contaminated groundwater has been the most common remediation technique employed after no action. This remediation usually entails pumping large volumes of contaminated water and directly applying it onto croplands. Crops remove nitrates from the root zone for growth. The crops are then harvested, and the nitrates are removed from the environment. There are numerous disadvantages to this remediation technique: (mentioned in ITRC, 2000)

- Large costs.
- Considerable engineering and planning to extract and deliver the contaminated water.
- Possibility of further nitrate contamination.
- Securing water rights.
- Developing appropriate land use for crop application.
- Regulatory permitting.

In addition, the pump and use of nitrate-contaminated groundwater may be employed in other industries, such as the construction industry. The contaminated water may also be used as a mixer with fertilisers for application on crops (ITRC, 2000).

2.5.1.3 Pump and treat

Pumping and treating nitrate-contaminated groundwater is another remediation technique often employed. This option is usually employed at public supply well heads and may not address the nitrate plume. The treatment of the nitrate-contaminated groundwater may be through wastewater treatment plants, construction of a treatment plant, reverse osmosis, ion exchange, or electrodialysis. Nitrate-contaminated ground water is pumped and discharged to existing wastewater treatment plants for nitrate removal, or specific treatment plants are constructed to address the nitrate contamination. This treatment may be expensive, and existing treatment plans may not be able to handle the increased volume. Ion exchange involves pumping nitrate-contaminated water through a resin bed containing a strong base anion exchange resin, whereby nitrate is exchanged for chloride or bicarbonate. In reverse osmosis, nitrate is removed by forcing the water across a semi-permeable membrane and leaving nitrate and other ions behind. A reverse osmosis waste stream needs to be treated and disposed from this system. In electrodialysis, ions are transferred through membranes

from a less concentrated to a concentrated solution due to the passage of a direct electric current. This process is expensive and requires close monitoring (Kappor, 1997 referred in ITRC, 2000).

2.5.1.4 Pump to waste

Pumping nitrate-contaminated groundwater to waste has also been employed, although this is usually not encouraged. The nitrate-rich water may be discharged to a contained evaporation system or injected into a deep saline aquifer or geologic unit. Disposal of the evaporate may be a problem if improperly managed. It would not be prudent to move a contaminant source to a non-contaminated location. The injection of nitrate-contaminated groundwater into a deep geologic unit poses many uncertainties (ITRC, 2000).

2.5.1.5 Phytoremediation

Phytoremediation is a means of removing, transforming, or binding contaminants in soil and groundwater through the use of plants, both as active and passive remediation tools. Plants can remediate contaminants through one or more of four processes: phytotransformation, phytoextraction, phytostabilization, and rhizofiltration (Schnoor, 1997 referenced in ITRC, 2000). Of these, phytotransformation is the process most active in plant removal of nitrogen compounds of interest. In addition to their ability to transform nitrogen compounds, some plants transpire great quantities of water. Thus, not only can plants remove certain types of contaminants, they can also act as groundwater extraction and flow control structures. In addition, phytoremediation techniques generally meet with public acceptance due to the ease of understanding and a desire to see living things transform a contaminated site (ITRC, 2000).

While this technique is a highly effective means of dealing with fertilizer and other nitrogen compound contamination, there are limits to its application. High concentrations of nitrate and/or ammonia can result in plant toxicity, either overall or at certain developmental stages of the plant. Alkaline or saline soils may also prove toxic, as may the presence of other contaminants. Depth of contamination may exceed the rooting depth of plants, thus also limiting the application, though some sites show that nitrogen uptake and transpiration can dramatically alter contaminant patterns at depths up to 10 m below ground. Heavy, tight soils may limit rooting depth as well, even with species that are normally deep rooted, as can poorly drained soil conditions. Traffic patterns, property boundaries, right-of-ways, building proximity, and deed restrictions may also prove to be limiting issues, as can regulatory prejudice. Another potentially limiting factor in the decision to employ phytoremediation is the

length of time it takes plantings to mature sufficiently to become effective at significant nitrogen removal. Sites that demand immediate action to protect drinking water supplies may not be able to wait for maturation of a planting. While many of these issues can be overcome, there is still a good deal of research needed before we will see this technology used to its maximum potential (cited in ITRC, 2000).

2.5.2   New and emerging technologies

Remediation of nitrate contamination has recently received renewed interest. These new technologies can be divided into three broad categories. These are as follows:

- Permeable Reactive Barrier (PRB) methods.
- Biological methods.
- Electrochemical methods.

2.5.2.1 Permeable reactive barrier (PRB) methods

Permeable reactive barriers (PRBs) are currently being researched for their application to denitrify contaminated ground water. Los Alamos National Laboratory in cooperation with the University of New Mexico is studying the feasibility of denitrifying reactive barriers (ITRC, 2000). These methods entail the placement of a permeable physical or chemical barrier in the flow-path of the pollution plume. The configuration of the barrier varies depending on the type of pollution source and the aquifer properties. The chemically reactive part of the barrier also varies depending on the actual contaminant being treated. The main emphasis is placed on the various barriers that have been used for nitrate removal. Two types of barriers are discussed. The first type, treatment walls, involves the construction of a physical barrier consisting of chemically reactive material. In the second type, In-Situ Redox Manipulation (ISRM), the aquifer material is chemically modified to serve as a chemical redox barrier.

Schipper and Vojvodic-Vukovic (2000 cited in Clarke, *et al.*, 2004) stated the factors that may affect the performance of the wall (denitrification/nitrification rates) including competing biological reactions such as dissimilatory nitrate reduction to ammonium and nitrogen immobilisation. Permeable reactive barriers could be described as the most versatile treatment method around, as it treats a variety of contaminants with various wall materials. Table 2-1 shows contaminants and wall materials that are able to remediate these contaminants.

Table 2-1: Contaminants that can be treated using permeable reactive barrier technologies (Source: Clarke, *et al.*, 2004)

Contaminant	Reactive Wall Material
Nitrate	Organic carbon or mixed organics (bacteria is used in addition to this in certain countries)
Metals	Fe(0), organic carbon
Acid mine drainage	Organic carbon
Gasoline/petrol derivatives	Oxygen releasing compounds
Halogenated Organics (CCl4, HCB, DCE, TCE, etc.)	Fe(0), bimetallic materials, Al, Fe, Zn, Mg, Sn.
Phosphorous	Metal oxides, limestone
Cr(VI), Cr	Fe(II) in aquifer material, Fe(0)

The following factors may affect the effectiveness of operation of permeable reactive barriers:

- Treatment walls or barriers may lose their reactive capacity over time, hence requiring replacement of the reactive medium.
- Biofilm formation or chemical precipitation of mineral salts may decrease the permeability of the treatment wall or surrounding aquifer.
- The depth and width of the barrier may be a limiting factor in its treatment capability.
- PRB treatment is limited to a subsurface lithology that overlies either impermeable bedrock or a continuous aquitard, at a depth within the vertical limits of trenching equipment.

2.5.2.2 In-Situ redox manipulation (ISRM)

ISRM creates a permeable treatment zone by injection of chemical reagents into the subsurface hydraulically, down gradient of the contaminant source. The type of reagent is selected according to its ability to alter the oxidation/reduction state of the aquifer materials, mainly iron in the subsurface, and groundwater to such an extent that it will allow the destruction or immobilization of specific contaminants. The method is based on creating a permeable reactive barrier, placing optimum treatment capacity in the most permeable part of the subsurface (Clarke, *et al.*, 2004).

The following aquifer characteristics are essential for the successful application of ISRM:

- High permeability, porous primary aquifers.
- Appreciable natural iron hydroxides, preferably iron-coated sands.
- A simple, well characterised subsurface flow system.
- Impermeable bedrock.

- Injection borehole(s) between contaminant source and abstraction borehole.

Requirements for PRB are similar to that of ISRM. It is intended for shallow aquifers in which a physical barrier can be constructed. This method can be used to treat a multitude of contaminants (Clarke, *et al*., 2004).

2.5.2.3 Biological treatment

Although long applied in slow sand filtration, bacterial microorganism, capable of reducing nitrates have been harnessed only recently for a specific treatment application. Biological denitrification as applied to drinking water comprises fixing the bacteria on a substrate to increase the population of active flora, while keeping them inside the biological reactor, which makes possible an increase in the efficiency of the biological reaction. These processes use autotrophic or heterotrophic bacteria which convert nitrates into gaseous nitrogen provided they have an oxidisable substrate which may be a solid as sulphur, a liquid such as a carbon compound or a gas such as hydrogen (Clarke, *et al*., 2004).

2.5.2.4 Aboveground denitrification

Due to the pervasiveness of nitrate-contaminated ground water and its impact on public supply wells, research has been conducted to biochemically denitrify water aboveground. This process takes advantage of biodenitrification and is accomplished by pumping nitrate-contaminated ground water into packed tower biofilm columns. Denitrifying bacteria and a carbon source are added to the columns to stimulate the denitrification process. This process has recently become commercially available (Silverstein, 1997 cited in Clarke, *et al*., 2004).

2.5.2.5 Denitrification in combination with other contaminants

As described in the nitrogen cycle, denitrification occurs naturally, however, usually at very low rates unless an abundant carbon source is present. One example is a grain silo facility contaminated with carbon tetrachloride (CT) and nitrate. A gasoline plume commingled with the CT and nitrate. The carbon-containing gasoline compounds created anaerobic conditions whereby nitrate was the electron acceptor, and the compounds in the gasoline were the electron donors. The CT was subsequently mineralized with the residual nitrate continuing to serve as an electron donor (McQuillan, *et al*., 1998 referred in ITRC, 2000). For many documented gasoline plumes in the presence of a nitrate plume, denitrification occurs along with bioremediation of the gasoline. The introduction of nitrate into gasoline plumes has been proposed to encourage anaerobic bioremediation of the gasoline.

2.5.2.6 Electrokinetic methods

These methods have been developed with a focus on remediating spills or leaks of organic chemical products. Much of the emphasis is on mobilising contaminated pore water and there is an expectation that the abstracted water would require additional ex situ treatment. Chew and Zhang (1998 cited in Clarke, *et al.*, 2004) showed that nitrate removal was improved over that which could be obtained by electrokinetics alone by combining it with an iron wall. Their experiment showed that using electrokinetics at various constant voltages without the iron wall, only 25 - 37 % of the nitrate was transformed to other forms of nitrogen. This was improved to up to 88 % removal when the iron wall was in place, suggesting that the PRB is an important component of such a system.

2.5.2.7 Ion Exchange

In the ion exchange process special resins are used to substitute chloride ions (Cl^-) for the nitrate radical. This method of removal requires several steps for successful decontamination. Laboratory experiments have shown that ion exchange resin can reduce nitrate concentration from as high as 250 - 2.5 mg/L (Jain and Sharma, 2011). Essentially, the process relies on the fact that water solutions must be electronically neutral, and therefore by inserting a negative ion, another negative ion can be removed from the water (George, 1989; Frazer and Chilvers, 1981; cited in Mathur, *et al.*, 2012). Besides the negative nitrate radical (NO_3^-), common anions include sulphate radical, chloride ion, bisulphate ion, bicarbonate ion and carbonate ion. Some of the common cations or positive ions are calcium, magnesium and sodium.

The first part of the process is the selection of an appropriate resin for the removal of the specific problematic ion, which in this case is nitrate. However, resins are not completely nitrate selective, and often remove other anions before removing the nitrogenous compound. Guter (1981 referred in Mathur, *et al.*, 2012) stated that resin beds are made up of millions of tiny spherical beads, which usually are about the size of medium sand grains. As the solution passes through these beds, the chloride anions are released into the water, removing first the sulphate ion, then the nitrate radical. The entire process is composed of four major steps to remove the selected ions from solution:

- Resin recharge.
- Anion exchange.
- Resin becomes "exhausted".
- Resin regeneration.

In the first step of the process, the bed is recharged, reaching its maximum exchange capacity. The resin at this time has enough chloride ions to carry out the exchange as the solution passes through the complex. The ion exchange is the next part of the process. The resin bed begins to remove the sulphate radicals (SO_4^{2-}) first, and when the majority of SO_4^{2-} has been removed from the water the exchange of nitrate and chloride begins. The completion of this phase is the third step as the resin becomes "exhausted" of the ion used for exchange. At this point no more anions leave the solution. Finally, in the fourth component of the process, the bed is regenerated by passing a strong solution over the resin displacing the removed ions with the chloride (Cl^-) ion. Ion exchange appears to be simple in use and offers good reproducibility though the nitrates will be concentrated in brine and pose a disposal problem (Jain and Sharma, 2011). This method of nitrate removal does not completely eliminate the contaminant from solution (Mathur, *et al.*, 2012).

2.5.2.8 In-situ treatment in the ground

This technique involves transforming the nitrates in the aquifer into gaseous nitrogen and is achieved by injecting suitable reducing agent through wells or boreholes. In principle, the reaction could go through from nitrate to nitrate and to nitrogen and eventually to ammonia. The problem is thus to control the reaction to produce maximum nitrogen which can evolve from the water. Otherwise, either nitrate or ammonia will have to be retransformed to nitrate when water is abstracted before its distribution (Jain and Sharma, 2011).

2.5.2.9 Reverse osmosis

In this process water pressure is used to force water through a thin-film composite or cellulose triacetate membrane (Harries *et al.*, 1991; Kunz, 1997; cited in Hunter, 2008). In the process water moves from the more concentrated solute side of the membrane to the less concentrated solute side of the membrane. The pressure used to drive the process must be sufficient to overcome the osmotic pressure; thus, the higher the concentration of salts in the supply and reject waters, the higher the water pressure must be to operate the system. Under pressure, molecules of water dissolve into the membrane and pass through the membrane to the permeate side by the process of diffusion. Dissolved ions, such as salts, that are charged are likely to be rejected by the membrane. Contaminants such as nitrate, nitrite, ammonia, and other salts cannot dissolve into the membrane and remain on the concentrate side of the membrane. Uncharged molecules, such as organic contaminants are more likely to pass through the membrane. Thus reverse osmosis produces a permeate water with very low inorganic mineral content, and a brackish reject concentrate with high inorganic mineral content (Harries *et al.*, 1991; Kunz, 1997; cited in Hunter, 2008).

The limitations of reverse osmosis relate to: (i) retention of the species is non-specific and alters the initial composition of water considerable (ii) pre-treatment is absolute requirement in order to avoid fouling of membranes: and (iii) disposal of concentrate waste require treatment (Jain and Sharma, 2011).

2.5.2.10 Electrodialysis

This technique which employs the principle of electrolysis combined with the use of selective membranes is applied for the removal of nitrates. The principle characteristics of the treatment are average specificity and limited efficiencies, need for pre-treatment and generation of a fairly concentrated waste (Jain and Sharma, 2011).

2.6   Case studies

2.6.1   Mountain View community, New Mexico

Groundwater in Mountain View has been highly contaminated with nitrate; over 200 nitrates plumes exist in New Mexico alone, but the Mountain View plume is the largest in the state, covering about 700 acres and contaminating over 1.6 billion gallons of water (Faris, 2007a; McQuillan, *et al.*, 1999; cited in Mohr, 2009). It is believed that the source of the groundwater nitrate contamination is the result of a vegetable "truck farmer" who over-fertilised between ~1946 and 1962, thus polluting the groundwater with nitrate and other dissolved solids (McQuillan, *et al.*, 1999 cited in Mohr, 2009). It is possible that up to 350 pounds per acre per year of nitrogen fertilisers were over-applied to the farm acreage (Faris, 2007a cited in Mohr, 2009). In addition to the incremental application of fertiliser throughout the farm, it was rumoured that the farm contained an unlined fertiliser mixing pit where high concentrations of contaminants leached directly to groundwater (Faris, 2007a referred in Mohr, 2009).

In some worst-case areas, water is polluted with total dissolved solids (TDS) to such an extent that with or without the nitrate the water would still be unfit for human consumption (McQuillan, *et al.*, 1999 referenced in Mohr, 2009). Worst plume examples include TDS of 4,776 mg/L and nitrate (NO_3 as N) concentrations of 525.5 mg/L; this is over 52 times the allowable concentration of nitrate in drinking water, which is 10 mg/L (McQuillan, *et al.*, 1999 cited in Mohr 2009).

The documented case of "blue baby syndrome" occurred on June 10, 1980, after a 4-month old Hispanic male infant ingested oatmeal prepared with well water that contained 207 mg/L of nitrates (Castle, 1981 cited in Mohr, 2009). The child had a blood methaemoglobin level of

14.9 % at the time of admission to the University of New Mexico Medical Center; normal levels range from 0.4 - 1.5 % (McQuillan, *et al.*, 1999 cited in Mohr, 2009). After being hospitalised twice, the child recovered (Castle, 1981 cited in Mohr, 2009). The 1980 case of methaemoglobinaemia was documented as having occurred outside the "area of suspected contamination"; however, the water at that residence was thoroughly contaminated. As is clearly depicted in Figure 2-6, the child who was hospitalized consumed water from a zone believed to be outside the suspected area of contamination and surrounded by neighbours with no known legal hook-up to municipal county water, according to the Albuquerque Bernalillo County Water Utility Authority and Bernalillo County Public Works Division, as of January 2008 (Albuquerque Bernalillo County Water Utility Authority and Bernalillo County Public Works Division, 2008 cited in Mohr, 2009).
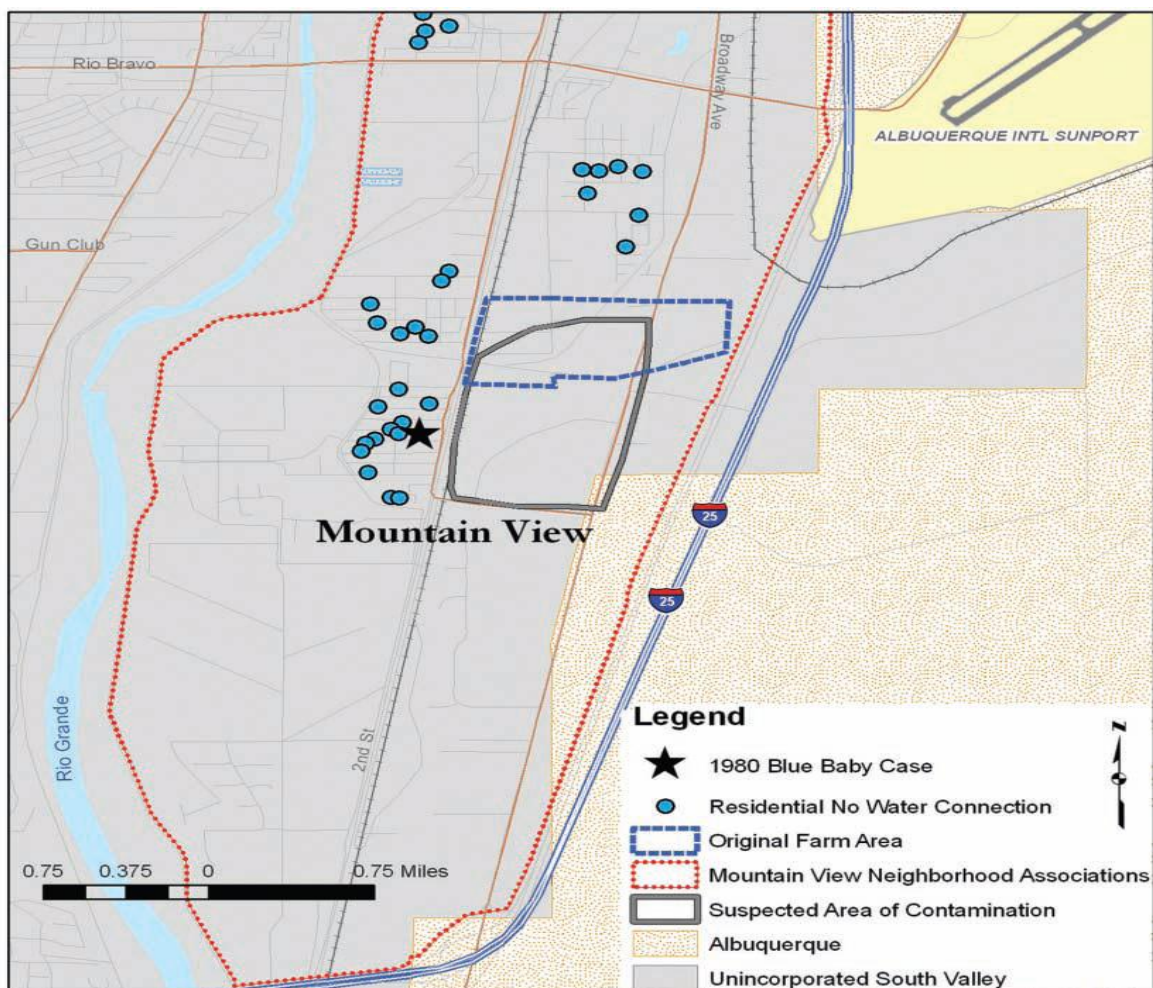
Figure 2-6: Mountain View residents without water and the 1980 blue baby case (Source: Penman, 2007 cited in Mohr, 2009)

Residents claim that there were several other cases of methaemoglobinaemia, including one alleged death, but all of these claims are unverifiable because methaemoglobinaemia is not a reportable disease in New Mexico. At least one of these unverifiable cases appears to have credence, however; in 1984 a case of methaemoglobinaemia allegedly occurred, and in 1985 an emergency State of New Mexico appropriation placed most of the areas' hardest hit residents onto the neighbouring City of Albuquerque municipal water sources, which would not normally have served residents of the unincorporated Bernalillo County. If there had been no additional methaemoglobinaemia cases between 1980–1985, it seems unlikely that the provision of municipal water would have occurred as an emergency state legislative appropriation. Despite the fact that most residents were hooked up to municipal water in 1985, at least eight polluted Mountain View supply wells remained in use, with no hope of city water service "due to engineering constraints" as of 1999 (McQuillan, *et al.*, 1999 cited in Mohr, 2009).

Several successful tests of in-situ biodenitrification processes were conducted on-site in the Mountain View nitrate plume by the New Mexico Office of Natural Resources Trustee (ONRT) (Faris, personal communication cited in Mohr, 2009). During one successful test, a circular zone of 3,000 feet was selected, with centre well values of 275 mg/L of nitrate (Nuttall and Dutta, 2004 cited in Mohr, 2009). The nutrient mixture composed of molasses, yeast extract, and trimetaphosphate was diluted and injected into wells specifically drilled to facilitate the development of a biobarrier. An incubation period of two weeks was allowed, after which the biofilm, essentially a wall of natural bacteria having been fed the molasses mixture, had grown in place in the circular region.

Nitrate at the centre well test area was reduced from 275 - 64 mg/L in the first 57 days (Nuttall and Dutta, 2004 referenced in Morh, 2009). On the injection of additional nutrients, the centre well nitrates dropped to 3.6 mg/L, well under the drinking water standard of 10 mg/L; the entire process of denitrification occurred within the test period of 286 days (Nuttall and Dutta, 2004 cited in Mohr, 2009). It was anticipated that if a biodenitrification barrier could be constructed within and down the gradient of the Mountain View contamination site, natural groundwater gradient flow through the barrier would stimulate denitrification (Faris, 2007a cited in Morh, 2009).

2.6.2   The Limpopo Province, South Africa

The Limpopo Village under discussion is a typical South African rural traditional village, where people make a living from subsistence farming. The reason for the monitoring

exercise was that a number of complaints had been received from villagers that related to fatigue, stomach cramps, nausea, and they were concerned about their water supplies (Bosman, 2009).

The geology of the area is quite complex, as it forms part of the Bushveld Igneous complex, with numerous dolerite dyke intrusions and fractures. Aquifers are highly heterogeneous, and the faults and dykes display varying water-bearing characteristics (Tredoux, *et al.*, 2001). Fracture systems are predominantly vertical in nature, with some poorly developed horizontal fractures. Both shallow and deep aquifers have been identified, with the shallow aquifer occurring at between 20 - 30 m below natural ground level. The mine abstracts water from this shallow aquifer for use in the metallurgical plant, at a yield of up to 11 L/s from an unknown location (Bosman, 2009).

To determine if the complaints of villagers, namely that their water supplies was the cause for their ailments, were valid, samples were taken from the various sources of water supply for the village according to Bosman, 2009, (Figure 2-7), namely:

- the village dam, used primarily for livestock watering; and
- drinking water supply boreholes at the primary and secondary schools, and a community tap.

At the time when the samples were taken, nitrate was not yet identified as a possible cause for concern, and hence these samples were analysed for all macro-chemicals, microbiological contaminants, and heavy metals at a SANAS accredited laboratory (Bosman, 2009).
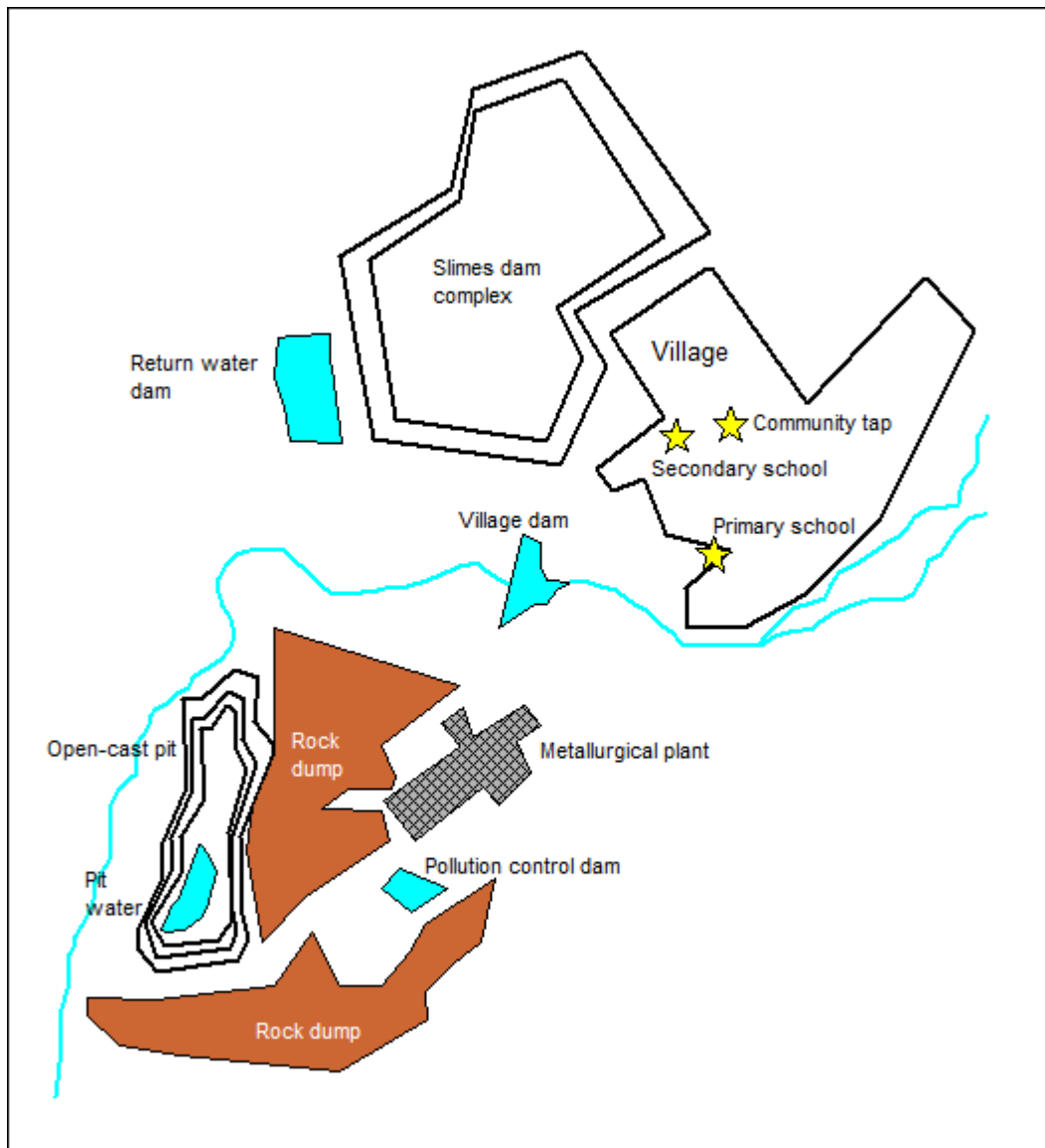
Figure 2-7: Schematic outline of village and surroundings (Source: Reproduced from Bosman 2009)

The quality of water from the village dam was quite good, although it was not used for drinking purposes, and this sample was used as background indicator (Bosman, 2009). All samples of village drinking water supplies exceeded the South African Drinking Water Standard of 6 mg/L NO_3-N. The concentration of nitrate (57.6 mg/L NO_3-N) in the sample taken from the borehole used by the primary school exceeded this standard almost tenfold. Subsequent analysis by another party found similar results in the primary school borehole – extremely high nitrate values, and no faecal microbial contamination. This is of particular concern, as such high nitrate levels could lead to serious health effects, especially to children in their developmental years, who were using this water at the time of sampling. It was hence critically important to determine the cause of these elevated levels of nitrate (Bosman, 2009).

Based on the initial sampling results, a process of elimination was followed to determine the cause for the elevated nitrate levels in the village drinking water supplies as follows (Bosman, 2009):

As none of the samples had elevated phosphate levels, it was concluded that the overuse of fertiliser in agricultural activities was not a possible cause for the elevated levels of nitrate in any of the samples.

The high levels of total coliforms in the sample taken at the community tap indicated that the most probable cause for the high levels of nitrate at the community tap could be related to sewage contamination. Although total coliforms was not measured at the secondary school, the similarities between the chemical compositions of the community tap and the secondary school, and the close proximity of these two sampling locations, indicated that the most probable cause for the high levels of nitrate at the secondary school could also be related to sewage contamination.

The samples at the community tap and the secondary school had levels of both sulphate and chloride that were elevated from the background levels as observed in the village dam. Since the mobility of especially chloride in groundwater is quite high, the elevation of both these constituents above background levels could indicate a potential influence as a result of mining activities.

The primary school sample, in which the highest concentration of nitrate were determined, did not have any total coliforms or detectable phosphate present, and also showed sulphate and chloride levels elevated above background, and at higher levels than at the community tap and the secondary school. The sulphate in this sample (114 mg/L), while still within the SANS Standard, showed an increase of more than tenfold above the background values of 9.9 mg/L in the village dam.

The absence of phosphate and total coliforms indicted that neither agricultural over-use of fertiliser, nor sewage contamination from humans or livestock concentration, could be the cause of the high levels of nitrate in the primary school sample. The absence of phosphate and total coliforms in the primary school sample, combined with the elevated levels of sulphate and chloride, indicated that mining-related activities had a definite influence on the high nitrate concentration in the primary school borehole.

A number of potential sources of nitrogen exist in an opencast mine, particularly the nitrate and ammonia species in the nitrogen-cycle, depending on the specific circumstances at a

particular source. Through the processes of nitrification and de-nitrification, nitrates could reach the surrounding aquifers via various pathways, and potentially cause nitrate pollution of drinking water resources (Bosman, 2009). These sources and pathways include the following:

- Bedrock disturbance through blasting, and rock dumps
- Pit water
- Pollution control dam
- Metallurgical process plant
- Tailings dam
- Exposure pathways

□ *Management measures*

If mining occurs in an environment that contains high levels of geological nitrogen, precautionary management measures should be implemented to prevent the release of species in the nitrogen cycle such as ammonia and nitrate into the environment. These measures can include the following (Bosman, 2009):

There is the implementation of appropriate storm water management around the excavation to prevent the ingress of run-off into the excavation. This will reduce the volume of pit water that is contaminated with nitrate, which would reduce the costs associated with the management of this water (Bosman, 2009).

Implementation of appropriate storm water management around rock dumps through the establishment of a clean and dirty water system, which would reduce the volume of run-off contaminated with nitrate from the rock dumps (Bosman, 2009).

Implementation of appropriate containment measures for all impoundments used to store contaminated water, such as pollution control dams, return water dams and tailings dams, such as clay and plastic linings (Bosman, 2009).

□ *Monitoring measures*

The following recommendations made by Bosman (2009) are of note in this respect:

Groundwater pollution detection monitoring programmes around mines, in addition to the generally accepted variables of pH, electrical conductivity, sulphates, chlorides, cyanide,

selected heavy metals and nitrates, should also include ammonia, total coliforms or E. coli, and phosphate.

Great care should be taken in the interpretation of monitoring data, especially as it relate to the presence or absence of the species in the nitrogen cycle.

Elevated levels of nitrate or ammonia in combination with higher than background sulphate levels should be identified as an early warning of a possible pollution plume, and further investigation should be initiated in order to act pro-actively to prevent such pollution plumes from reaching water supplies of users outside the mine boundaries.

3. BACKGROUND INFORMATION

This chapter reviews of all available data concerning the study area such as topography, climate, land use, catchment and water supply. It also provides an understanding of the study area based on its characteristic geology and geohydrology features.

3.1 Location

Thaba Nchu is found in the eastern part of Free State Province about 60 km east of Bloemfontein. It consists of both an urban area with private land ownership and a rural area of both private and communal land with people living in 31 scattered villages in the area of 70,364 hectares. Some of these villages are spread across the area, north and south of Thaba Nchu town (Figure 3-1). This settlement also lies at the foot of the well-known Thaba Nchu Mountain, also known in the local Sesotho language as 'Black Mountain' (Mangaung Metropolitan Municipality, 2011).

Land is divided into three niches; residential, arable and grazing. Residential land accounts for 2.1 %, arable land for 12.7 % and grazing land for 85.2 % of the total land area (Baiphethi, *et al.*, 2010).
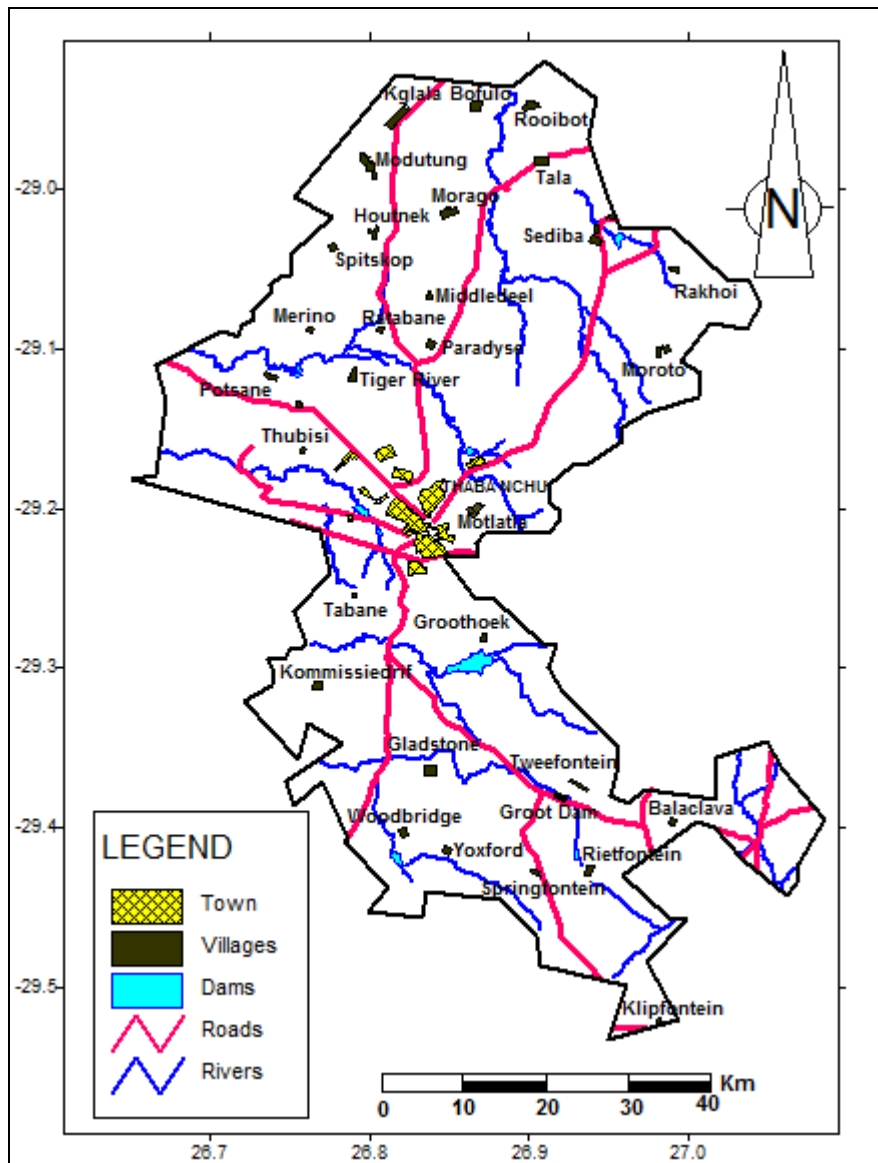
Figure 3-1: Map of Thaba Nchu including neighbouring villages (Source: Modified from Baiphethi, *et al.*, 2010)

3.2   Climate

The climate in Thaba Nchu can be described as a typical Highveld climate, characterised by warm summers and cold, frosty winters. The long term annual rainfall in the area is 545 mm. The high evaporative demand and relatively low rainfall make this a semi-arid area (Hensley, *et al.*, 2000 cited in Baiphethi, *et al.,* 2003). The chart in Figure 3-2 shows the average rainfall values for Thaba Nchu per month. Much of the summer rainfalls, which occur between November and March, are high-intensity storms that promote runoff (Woyessa, *et al.*, 2006) and the lowest evaporative demand.
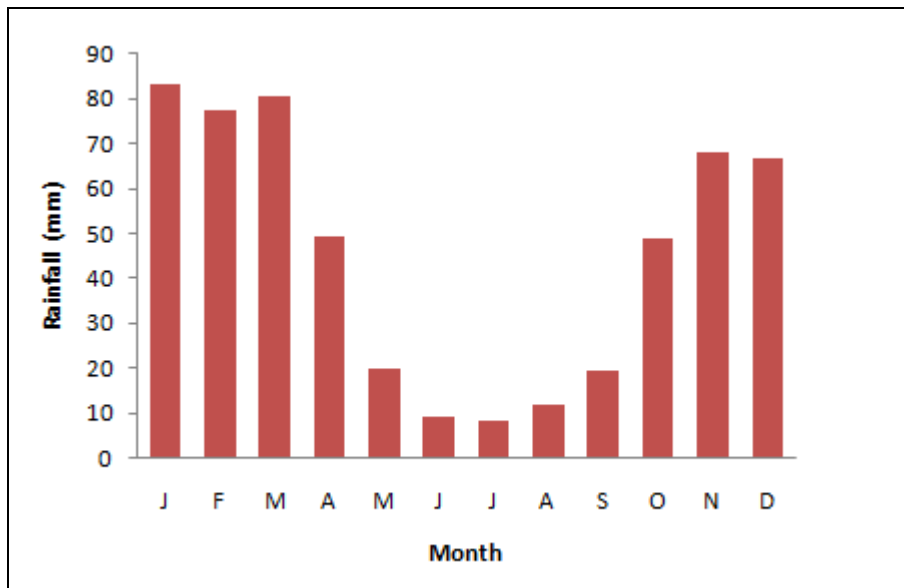
Figure 3-2: Average monthly rainfall in Thaba Nchu (Source: Land Type Survey Staff, 2000 modified from Woyessa, *et al.*, 2006)

3.3 Water supply

Due to the low availability of water in the study area it has become necessary to import water from other river systems as shown in Figure 3-3 (Caledon/Modder Transfer Scheme, 2011). The interbasin transfers are

- The Caledon-Modder (Novo) Transfer Scheme which was commissioned at the end of 1999. This is a direct transfer scheme which pumps untreated water from the Caledon River to Knellpoort Dam and from there to the upper reaches of the Modder River basin upstream of Rustfontein Dam near Thaba Nchu. This scheme is not operational at present but if the demand for water increases in the area it will be used.

- Transfer from the Groothoek and Seroalo dams that provide water to Thaba Nchu.

A new water purification plant at Rustfontein Dam is now used to supply Botshabelo and part of the Thaba Nchu demand. Groothoek Dam is a relatively small dam and is only used to supply Thaba Nchu with water (Maré and Seago, 2010).
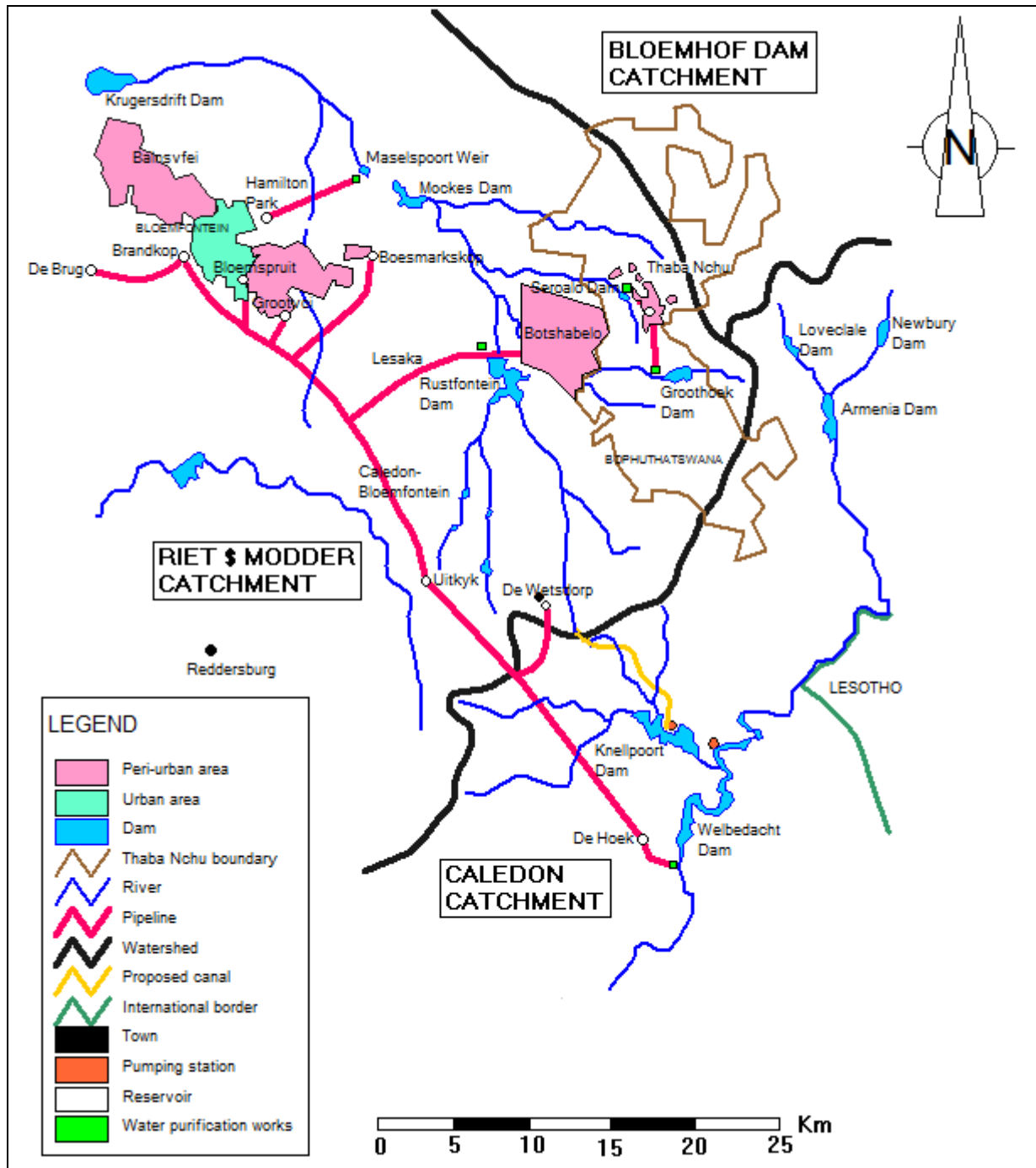
Figure 3-3: Water supply to Bloemfontein and Thaba Nchu augmented from water transfer schemes (Source: Modified from the Caledon/Modder Transfer Scheme, 2011)

A maximum of 4.4 mL/d (1.61 million m³/a) is supplied from Groothoek Dam to Thaba Nchu. The rest of the requirement for Thaba Nchu is supplied from Rustfontein Dam by Bloemwater (Maré and Seago, 2010). Water for domestic purposes is also supplied in the villages by Bloemwater using boreholes (**Error! Not a valid bookmark self-reference.**).

Table 3-1: Summary of sub-catchments and towns with adequate water resources (Source: ISP's Upper Orange WMA Strategies, 2004)

Name of Town	Quaternary Catchment	Key Notes
Krugersdrift sub-catchment		
Thaba Nchu	C52B	Caledon/Modder system Bloemwater and Groothoek Dam
Welbedacht RSA sub-catchment		
Thaba Patchoa (including Balaclava, Rietfontein and Klipfontein)	D23D	Armenia Dam and Boreholes. Sufficient supply from Armenia Dam

3.4   Topography and drainage

The topography of the study area is shown in Figure 3-4. Surface elevations across the area vary between 1400 mamsl and 1900 mamsl. Most of the drainage patterns are in the East-West direction. The Sepane Spruit and Kgabanyane River are ephemeral. The main man-made infrastructure elements within the study area that affect the groundwater environment are the Groothoek Dam and Seroalo Dam. There also exist much smaller reservoirs in the study area.
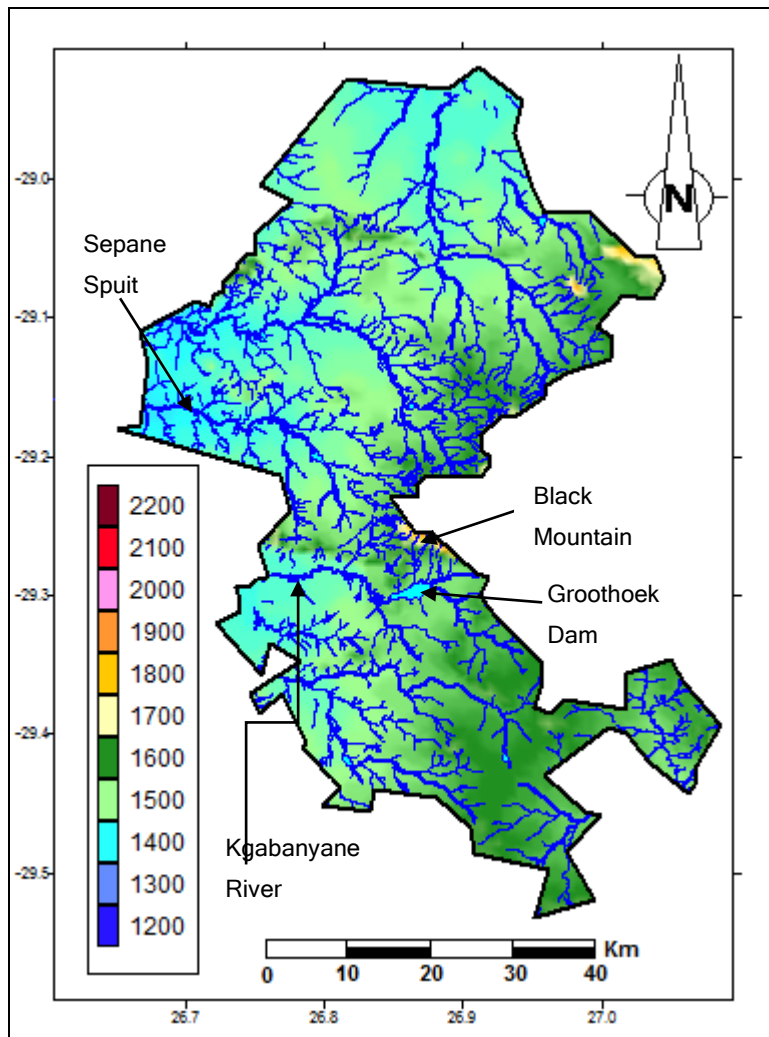
Figure 3-4: Topographic surface contours showing the rivers and dam

The study area is located in the upper reaches of the Modder River catchment (Figure 3-5) in parts of quaternary catchments C52B and C52C of the Upper Orange Water Management Area. C41D (top) and D23D (bottom) are the green parts of the Thaba Nchu map located in the Middle Vaal, Lower Orange Catchment (Woyessa, *et al.,* 2006).
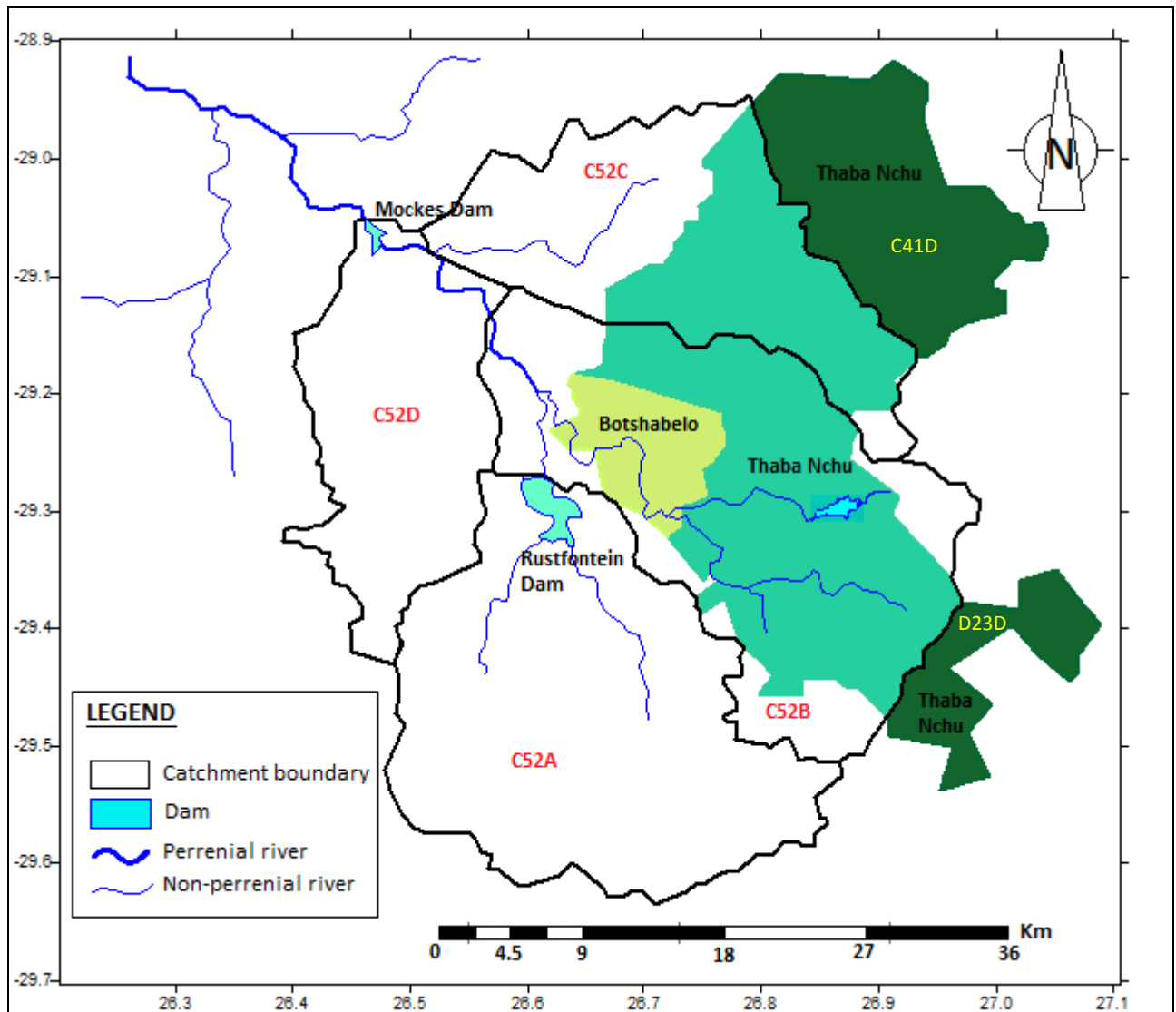
Figure 3-5: Upper Modder River Catchments including Thaba Nchu and Botshabelo. The green parts are out of the water management area (Source: Modified from Woyessa, *et al.,* 2006)

3.5   Geology

The Thaba Nchu region of the Free State Province is situated between the stratigraphic hinge line developed during Adelaide times and that of the later deposition of the Tarkastad Subgroup (Catuneanu, *et al.,* 1998 referred in Rutherford, 2009). The map in Figure 3-6 from the 1:250 000 Geological Map (1963) shows that the area comprises rocks from both the Adelaide and the Tarkastad Subgroups as well as from the Molteno, Elliot and Clarens formations of the Stormberg Group. The Adelaide Subgroup can be up to 400 m in thickness while the Tarkastad has been reported as up to 900 m thick (Rutherford, 2009).

Rocks of the Adelaide Subgroup exposed in the study area comprise yellow-green sandstone bodies alternating with blue-grey and dusky red mudrock and green grey siltstone units. The Tarkastad Subgroup is subdivided into the yellow sandstones and red and blue mudrocks of the Katberg Formation, and the maroon and red mudrocks of the Burgersdorp Formation. These sediments have been extensively intruded by dolerite sills and dykes of the Early Jurassic (182 Ma) Karoo Dolerite Suite (Le Roux, 1993 referenced in Rutherford, 2009). The sediments are underlain by Ecca Group and then by the Dwyka Group tillite (diamictite, not shown on map), which represents the basal unit of the Karoo Supergroup.
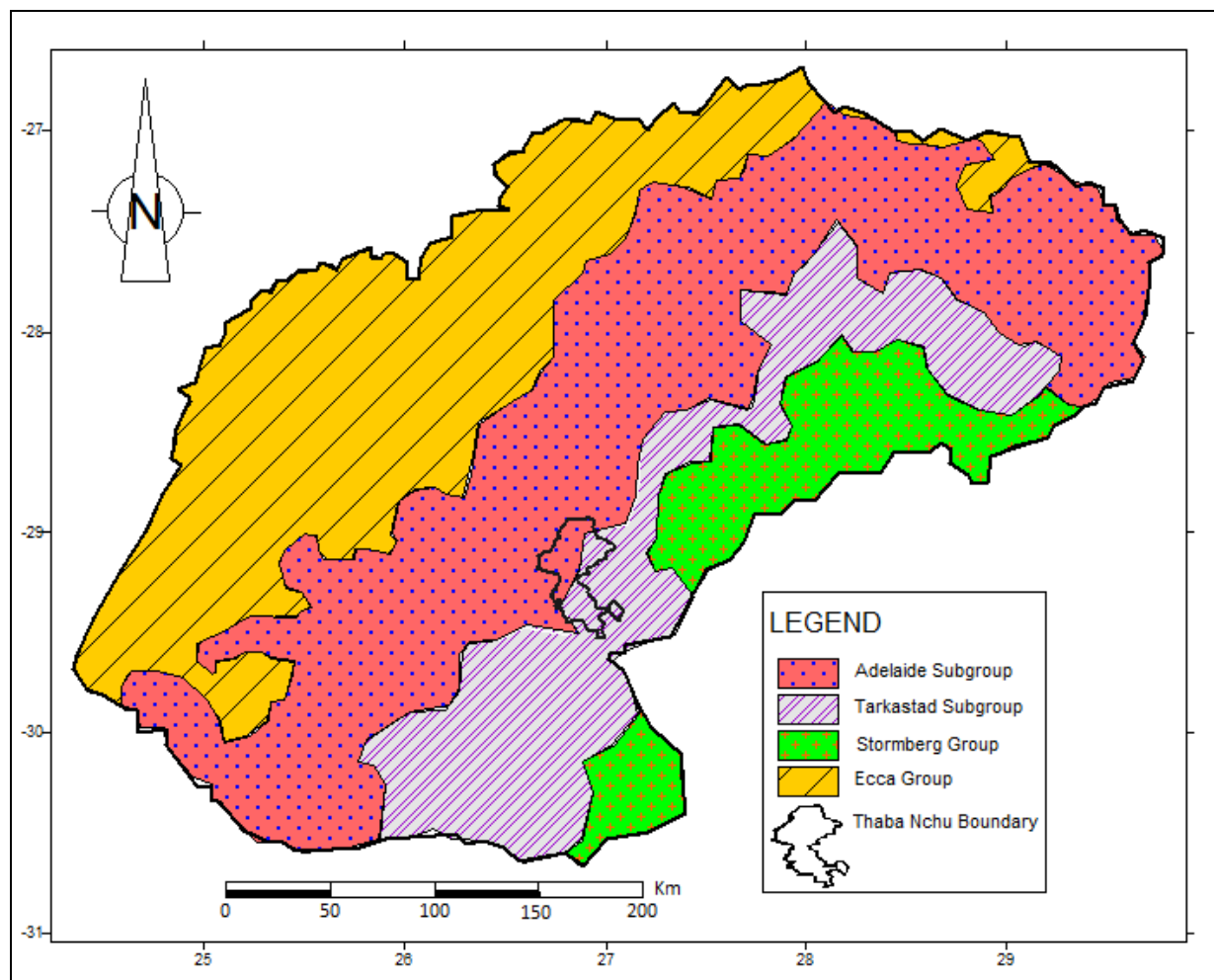
Figure 3-6: Geology map of the Free State Province; outline of the Thaba Nchu boundary shown (Source: Modified from Rutherford, 2009)

3.6   Geohydrological Setting

The geohydrological information available for the formations within the study area is predominantly argillaceous and arenaceous rocks and a small basic rock intrusion. The aquifers are intergranular and fractured with borehole yields ranging between 0.1 - 5.0 L/s

(Figure 3-7). The sandstones of the Beaufort Group can be massive and dense and have limited permeability and storage. Transmissivity values ranging between 0.25 m^2/d and a storativity range between 0.001 and 0.005 can be expected (Rantlhomela, 2010). It thus offers only moderate groundwater yield, especially in the absence of dolerite intrusions. 70 % of boreholes drilled into the sandstone have yields of < 3 L/s. Contacts between different rock lithologies and bedding planes within the sediments often yield groundwater.
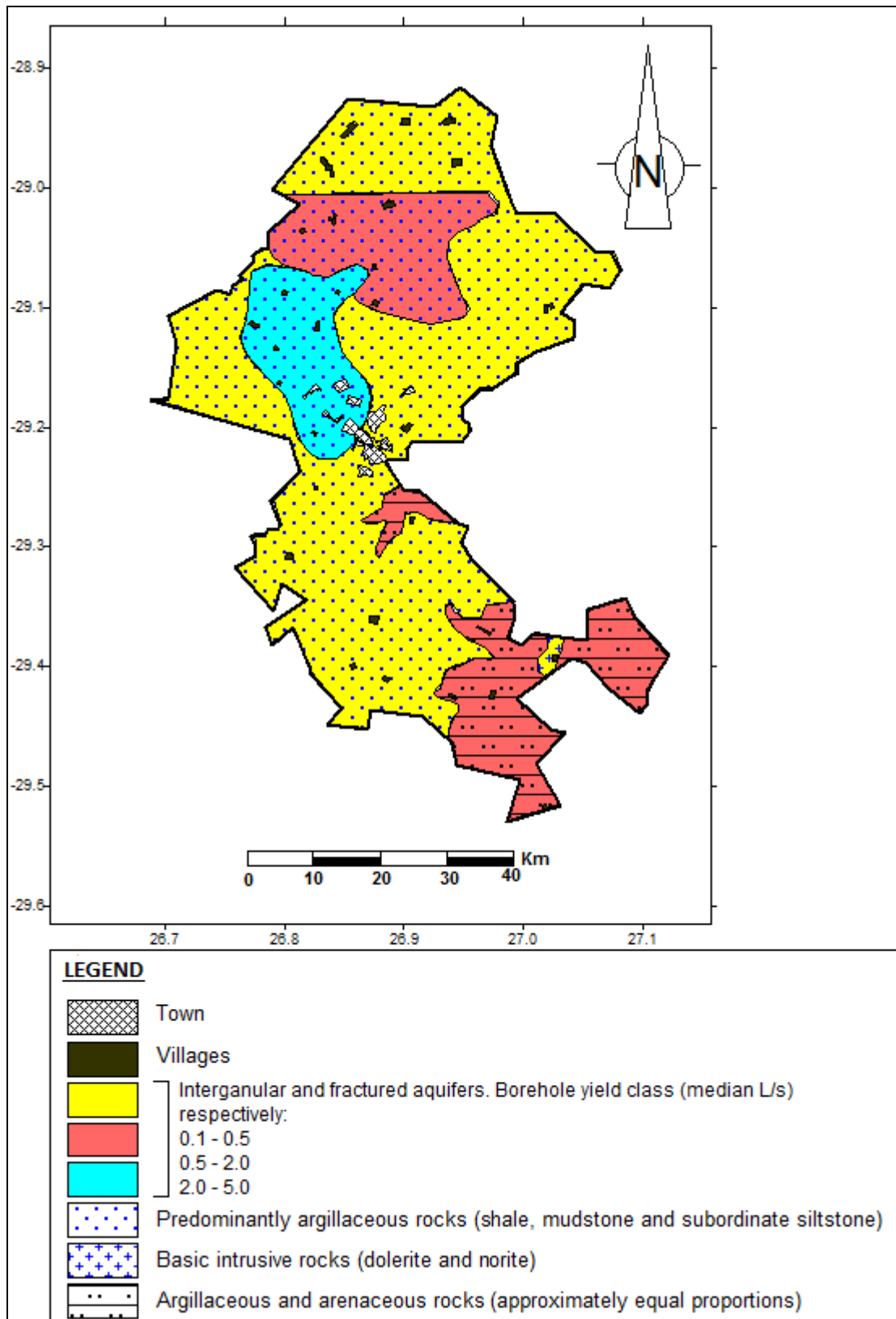
Figure 3-7: Geohydrological map of Bloemfontein and Thaba Nchu (Source: Modified from The Council for Geoscience, 2011 personal communication)

4. METHODOLOGY, RESULTS AND DISCUSSION

This chapter provides an overview of the extent of nitrate contamination in the southern Thaba Nchu aquifers and comparing their development with background natural values and also identifying nitrate-occurring sources. This is done by using analytical methods and interpretation of acquired data for hydrochemistry and isotope interpretations. This will help with creating management options for future groundwater remediation.

4.1 Materials and methods

4.1.1 Groundwater sampling and analytical methods

A total of 26 groundwater samples (11 from Bloemwater boreholes and 15 from hand pumps) were collected from Thaba Nchu for chemical and isotopic assessments. The sampling periods were in November 2011 and March 2012 which corresponded to the rainy season, and in May 2012 which corresponded to the dry winter month. All the boreholes were not sampled at all times. The sampling locations are shown in Figure 4-1 which represent the southern part of the study area. The sampling locations are found in Appendix A Table 1. All boreholes were not sampled at every sampling period due to inaccessibility, automatically turned off pumps and a dry borehole in one case (NP2).

To avoid contamination, clean new 100 mL and 500 mL plastic containers were used for collecting the water samples from the boreholes mostly by pumping groundwater through submersible pumps, and in one case, using a bailer. In cases of inaccessible privately owned boreholes, the samples were collected directly from public taps. The samples were stored in polyethylene containers, adequately labelled and preserved in a cooler box until they were taken to the laboratory for analysis. Other un-acidified water samples were collected, cooled, and conserved for stable isotope analyses. Samples for nitrate isotopes were collected in 100 mL polyethylene bottles that were filtered through a Millipore Filtration apparatus and refrigerated before shipping to the Northern Arizona University laboratory, USA, for analyses.
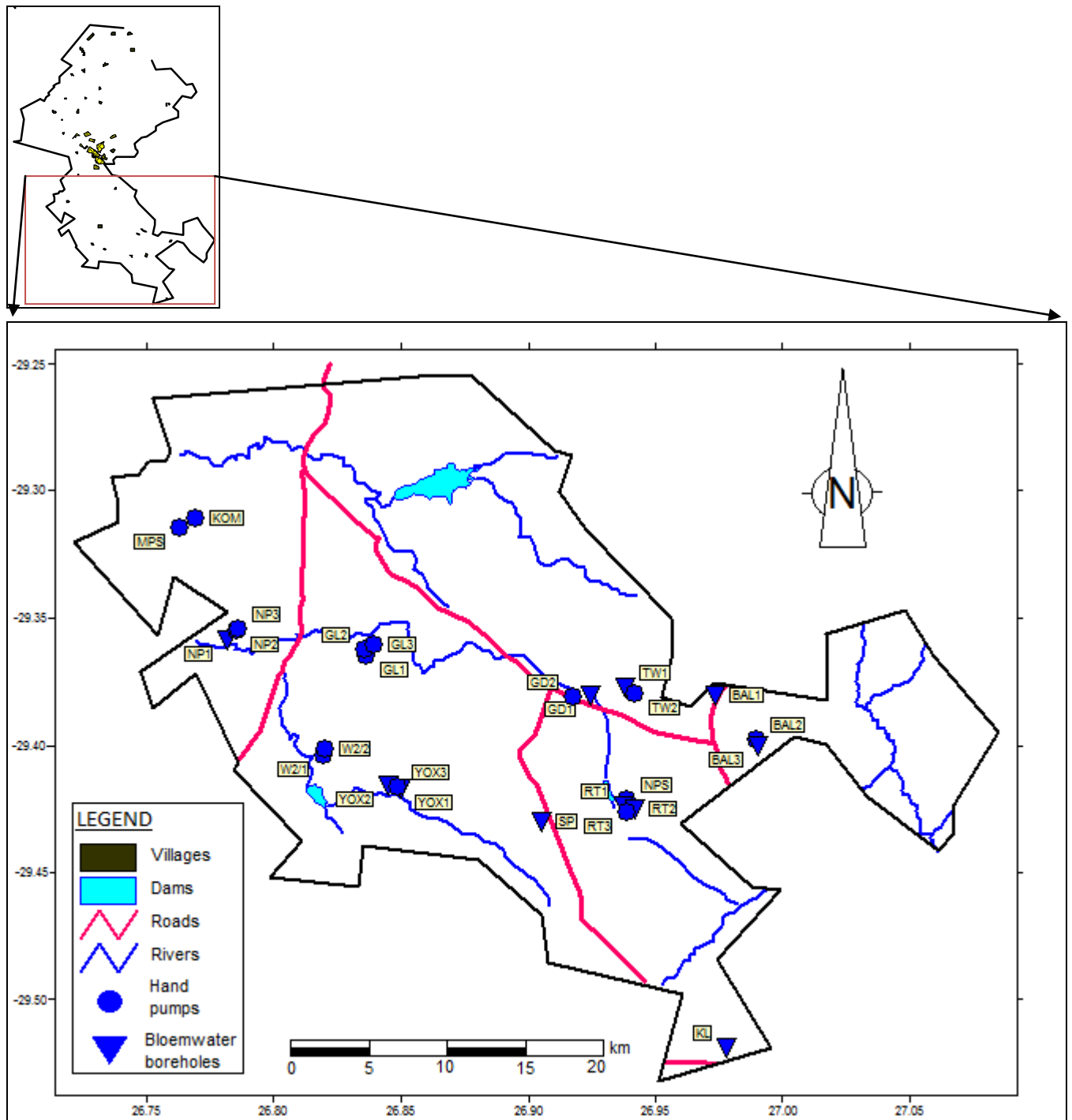
Figure 4-1: Boreholes found during hydrocensus and sampled in the southern villages of Thaba Nchu

4.1.2   General chemistry

In-situ measurements such as pH and electrical conductivity (EC) were measured at the well head in the field using pH and electrical conductivity meters. To understand or confirm the geochemistry of the sites, additional analyses were performed for the metals, alkalinity, and total dissolved solids. Samples for analysis of major inorganic constituents were filtered through 0.45 µm membrane filters and filled in an acid-washed polyethylene bottle, one aliquot being acidified to pH less than 2 by addition of high-purity HNO_3 for analysis of cations. Major ions for the samples were measured by ion chromatography coupled with inductively coupled plasma optical emission spectrometry (ICP-OES) on a Perkin Elmer 3000 DV system for cations and Dionex (DX-120) chromatograph with anion columns at the Institute for Groundwater Studies, University of the Free State. The results are presented in Appendix C.

4.1.3   Isotopes

Environmental isotopes were used to determine the origin of groundwater, to determine groundwater-surface water interaction and also to trace water pollution and water leakage. The environmental isotopes occur naturally and they are found in abundance in the environment. Oxygen-18 (^{18}O), Deuterium (^2H) and Tritium (^3H) are commonly used isotopes in isotope hydrology (Gürer, 2003 cited in Gurer, *et al.,* 2008). In this study, only ^{18}O and ^2H were used. Environmental isotope analyses were carried out in order to determine the existing groundwater isotopes in the aquifers.

^2H and ^{18}O isotopes analyses of 21 samples (20 from groundwater and one from surface water) collected in March 2012 were performed at the isotope laboratory in the University of Kwazulu-Natal, Pietermaritzburg, by respectively employing the Los Gatos Research (LGR) DT-100 Liquid Water Isotope Laser Analyser. The standards used were prepared by calibration against the following known standards: LGR2 (δ^2H -117.00, $\delta^{18}O$ -15.55), VSMOW2 (IAEA) (δ^2H 0.0, $\delta^{18}O$ 0.0) and IA-RO53 (IAD) (δ^2H -61.97, $\delta^{18}O$ -10.18). All hydrogen and oxygen isotopes analysis are expressed in the conventional δ -per mil (δ ‰) notation referenced to Vienna-Standard Mean Oceanic Water (V-SMOW). The LGR DT-100 analyser does not, however, report δ values on a V-SMOW scale, but as $^2H/H$ and $^{18}O/^{16}O$ ratios (Lorentz, 2012 personal communication).

Nitrogen isotope analyses of 19 groundwater samples collected within this study were conducted using bacteria described by Sigman, *et al.* (2001) at the Colorado Plateau Stable Isotope Laboratory, Northern Arizona University, USA. Nitrate (NO_3) in water samples is converted to nitrous oxide (N_2O) gas by bacteria that lack the enzyme to reduce it to N_2 gas.

N_2O can then be analysed with an isotope ratio mass spec (IRMS) to determine $\delta^{15}N$ and $\delta^{18}O$ values of nitrate. *P. aureofaciens* is used for most analyses, but *P. chlororaphis* may be substituted in some cases (for example, ^{15}N-enriched samples or salt extracts where only $\delta^{15}N$ is needed). The determined ^{15}N and ^{18}O were also reported in standard delta notation (δ ‰) with respect to atmospheric air for ^{15}N while ^{18}O is expressed relative to the standard of Vienna Ocean Water Standard Mean (VSMOW). Precision, reported as one standard deviation, is ≤ 0.30 ‰ for $\delta^{15}N$ and ≤ 0.60 ‰ for $\delta^{18}O$ (Moan, 2010). Nitrates isotopes for groundwater samples collected in March 2012 were also used in this study. These samples were analysed using Dionex (DX-120) chromatograph as mentioned in subtitle 4.1.2. There are many advantages to using the bacteria method. Some of the advantages include the need for a small sample size required for analysis, a short analysis time, the ability to analyse samples with concentrations as low as 1 μM (1 micromolar = $1*10^{-6}$ mol/dm^3 or $1*10^{-3}$ mol/m^3) of nitrate, and that oxygen, as well as nitrogen, can be analysed isotopically from one sample (Sigman, *et al.*, 2001; Casciotti, *et al.*, 2002; cited in Bratcher, 2007).

4.2   Results and discussion

4.2.1   Previous works

Past monitoring data (sourced from the Department of Water Affairs, DWA, database and Bloemwater, Rustfontein Dam) in Thaba Nchu were collected from 1997 - 1998 and from 2000 - 2010, respectively, and evaluated in terms of evolution trend. Piper and Durov diagrams of these data evidenced the deterioration of the water quality in some boreholes especially the SP borehole. Their data are presented in Appendix B.

From DWA (Figure 4-2), the boreholes had little or no nitrates and the groundwater was fresh, clean, and relatively young. The water quality at this time was considered as the natural or background condition of the aquifer without the influence of human activities, except the SP borehole. The Bloemwater boreholes followed the same anion/cation trend as those of DWA, except that the water started to deteriorate with time especially the SP borehole which had consistently higher nitrate concentrations (Figure 4-3), mixing with older or newer groundwater. The reason for this peculiarity is going to be seen later in this study.
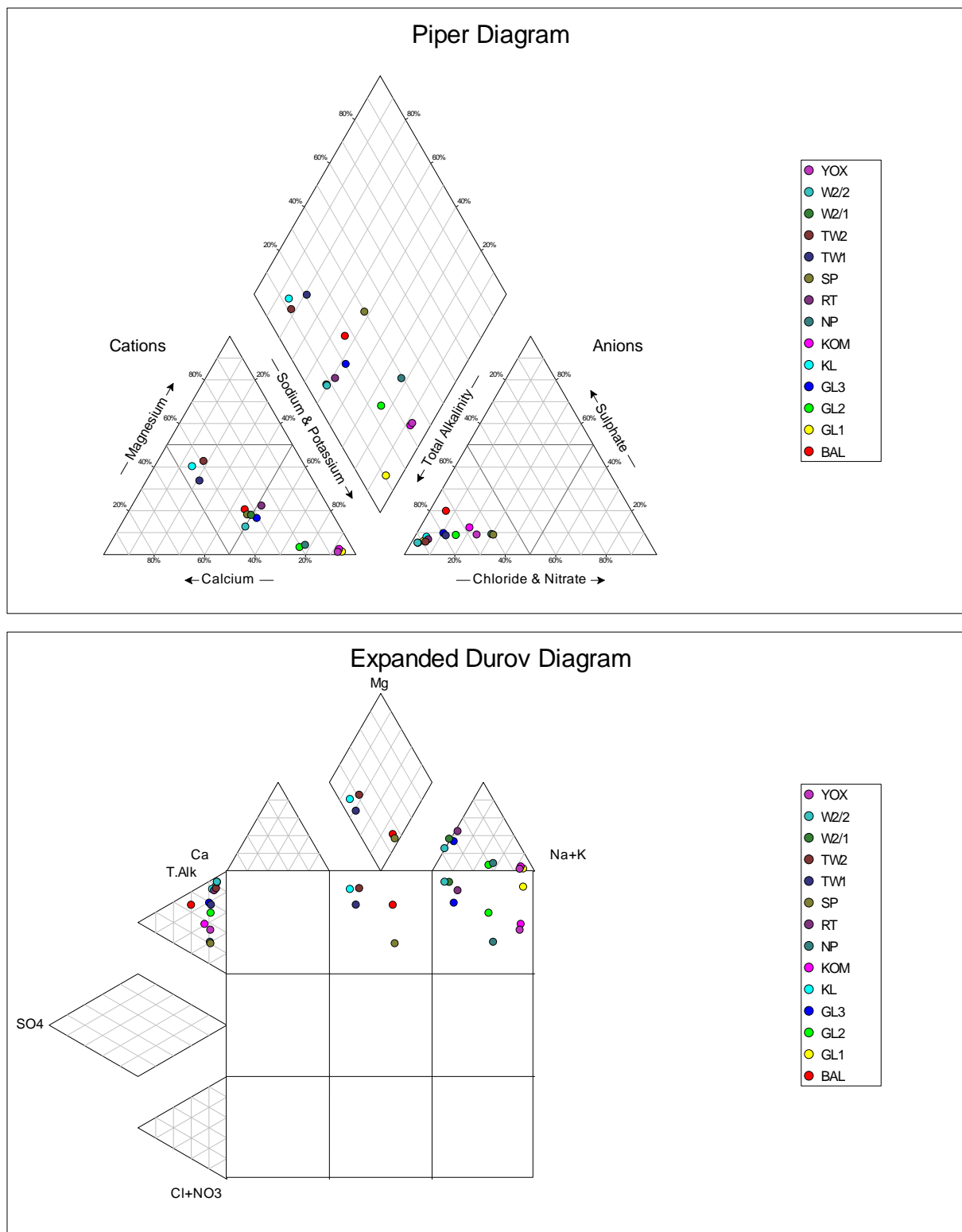
Figure 4-2: Piper and Durov diagrams for samples from DWA in 1997 and 1998
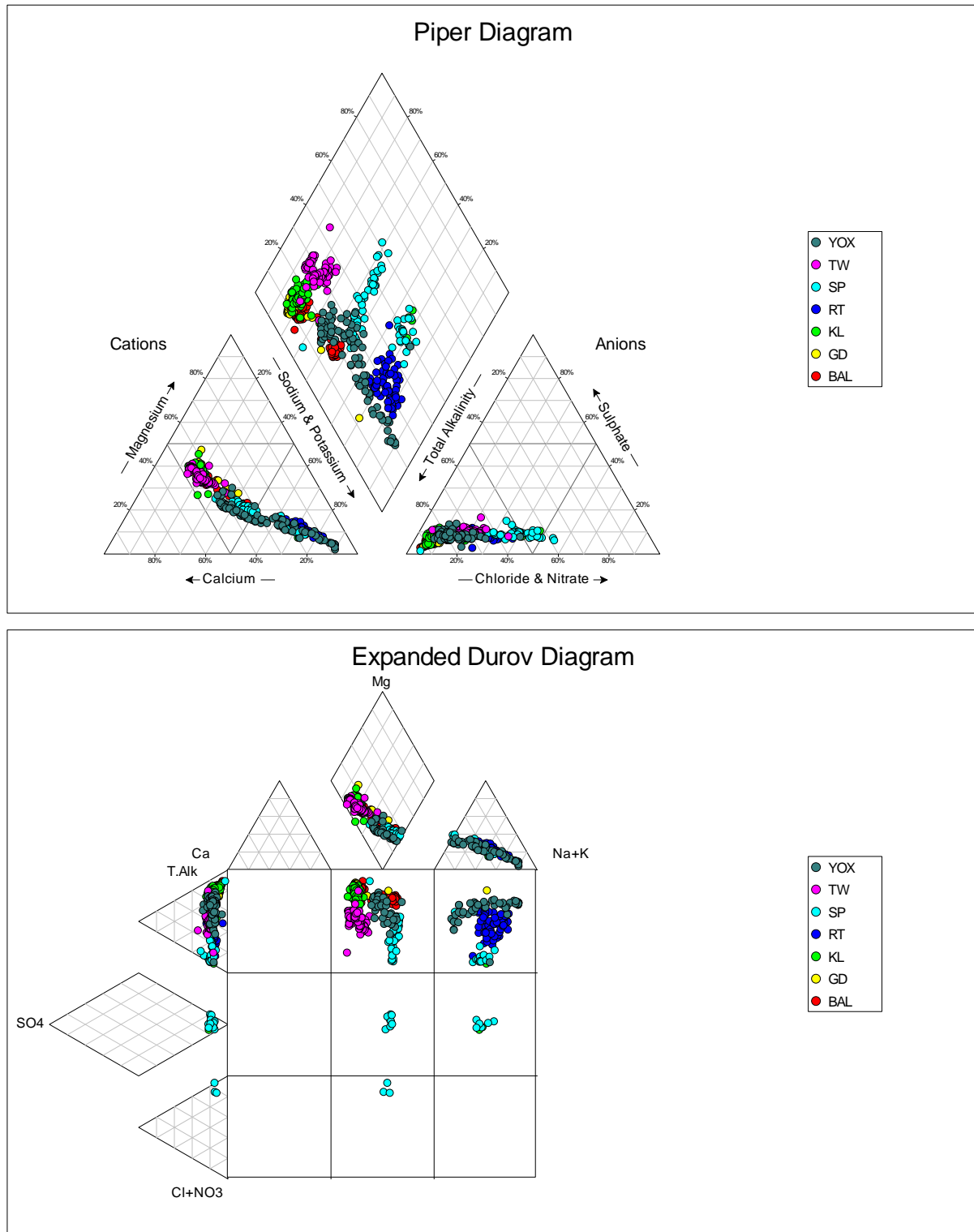
Figure 4-3: Piper and Durov diagrams for samples from Bloemwater from 2000 – 2010

4.2.2   Current nitrate pollution status of Thaba Nchu groundwater

Most residents in the Thaba Nchu villages rely on groundwater for potable supplies, although suitable water is available from Bloemwater boreholes. Local groundwater provides some domestic, farm and irrigation uses, however, and must be viewed as both a potential pathway for exposure to hazardous wastes and as a means for contaminant transport.

Nitrate concentrations in the well samples showed high spatial variations and ranged from 0.02 to 468.95 mg/L as N. In Figure 4-4, Figure 4-5 and Figure 4-6, some of the boreholes showed irregular spatial distribution of nitrate exhibiting very high concentrations like BAL2 (20.70 mg/L), NP2 (123.32 mg/L), NP3 (137.43 mg/L), GL1, GL2 and GL3 (46.34, 468.95 and 25.77 mg/L, respectively) and SP (23.43 mg/L) in March 2012 (Appendix C).

Current monitoring data were collected in November 2011, March and May 2012 and evaluated in terms of evolution trend relative to urban development. Statistical analysis of these data evidenced the progressive deterioration of the water quality in some boreholes (Figure 4-4, Figure 4-5 and Figure 4-6) induced mainly by human activities and probably associated natural cause(s) in the area. Values of nitrate evolved relative to these sources from a slightly high range in November 2011 (0.05 – 135.59 mg/L) to a wide range in March 2012 (0.04 – 468.95 mg/L), and then to a slightly lower range in May 2012 (0.06 – 444.64 mg/L) (Appendix C). It should be noted that these maps are representations of point concentrations per borehole in each village and therefore are not the ideal nitrate concentrations in the local aquifers.
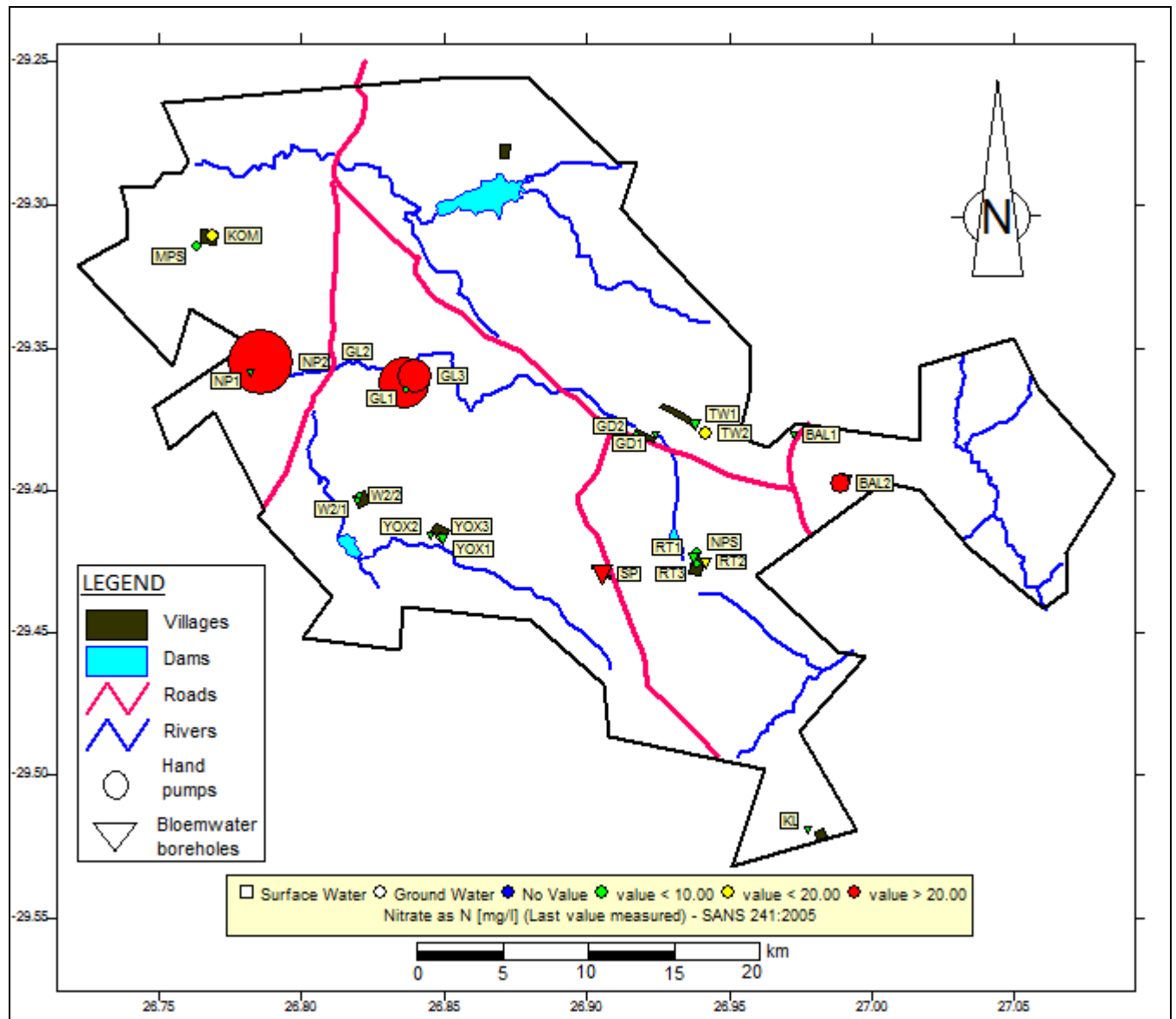
Figure 4-4: Current spatial distribution of NO$_3$-N concentrations in the south of Thaba Nchu in groundwater samples obtained in November 2011. Each circle shows the relative site name and concentration. All units are in mg/L nitrate as N
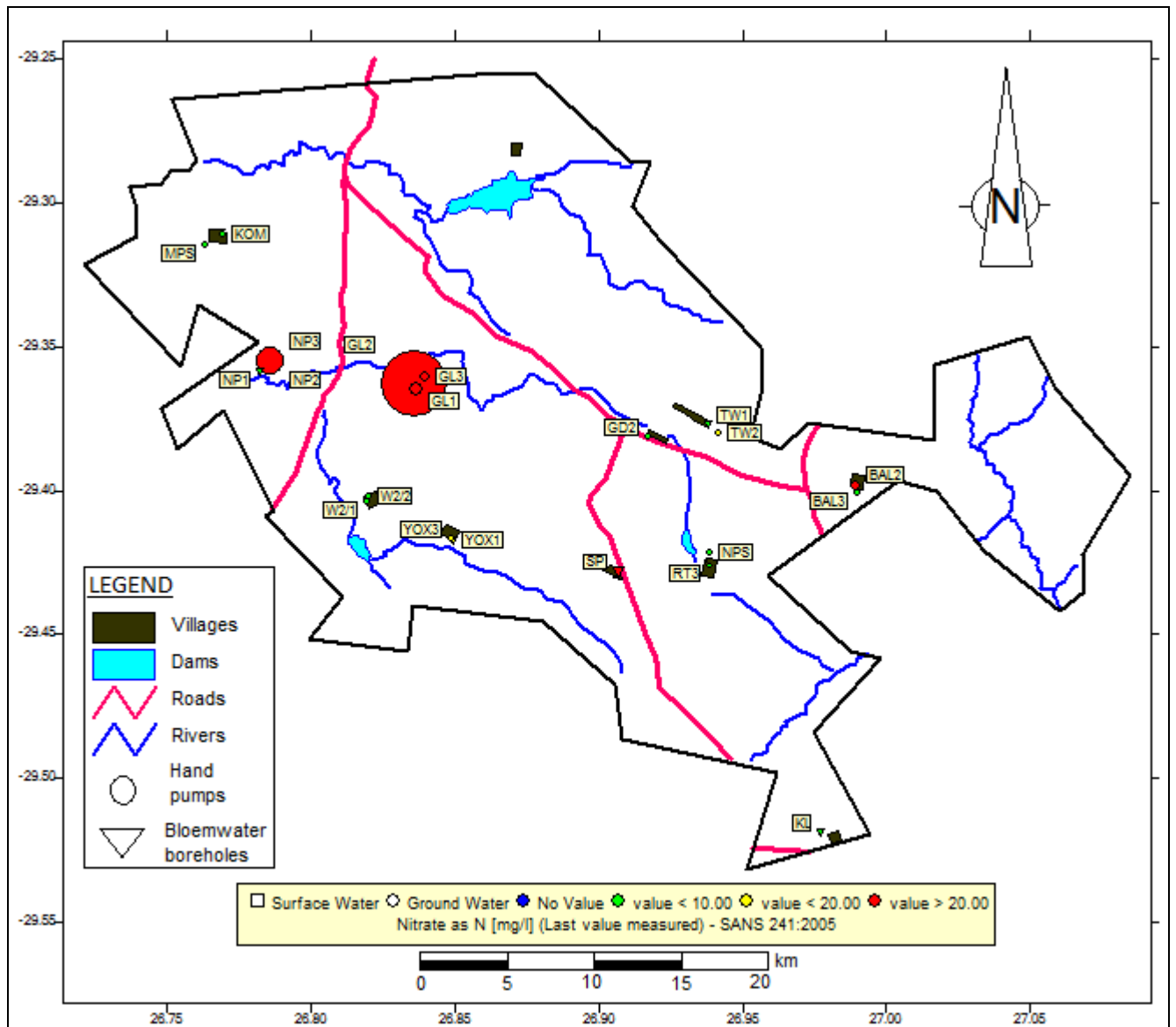
Figure 4-5: Current spatial distribution of NO$_3$-N concentrations in the south of Thaba Nchu in groundwater samples obtained in March 2012. Each circle shows the relative site name and concentration. All units are in mg/L nitrate as N
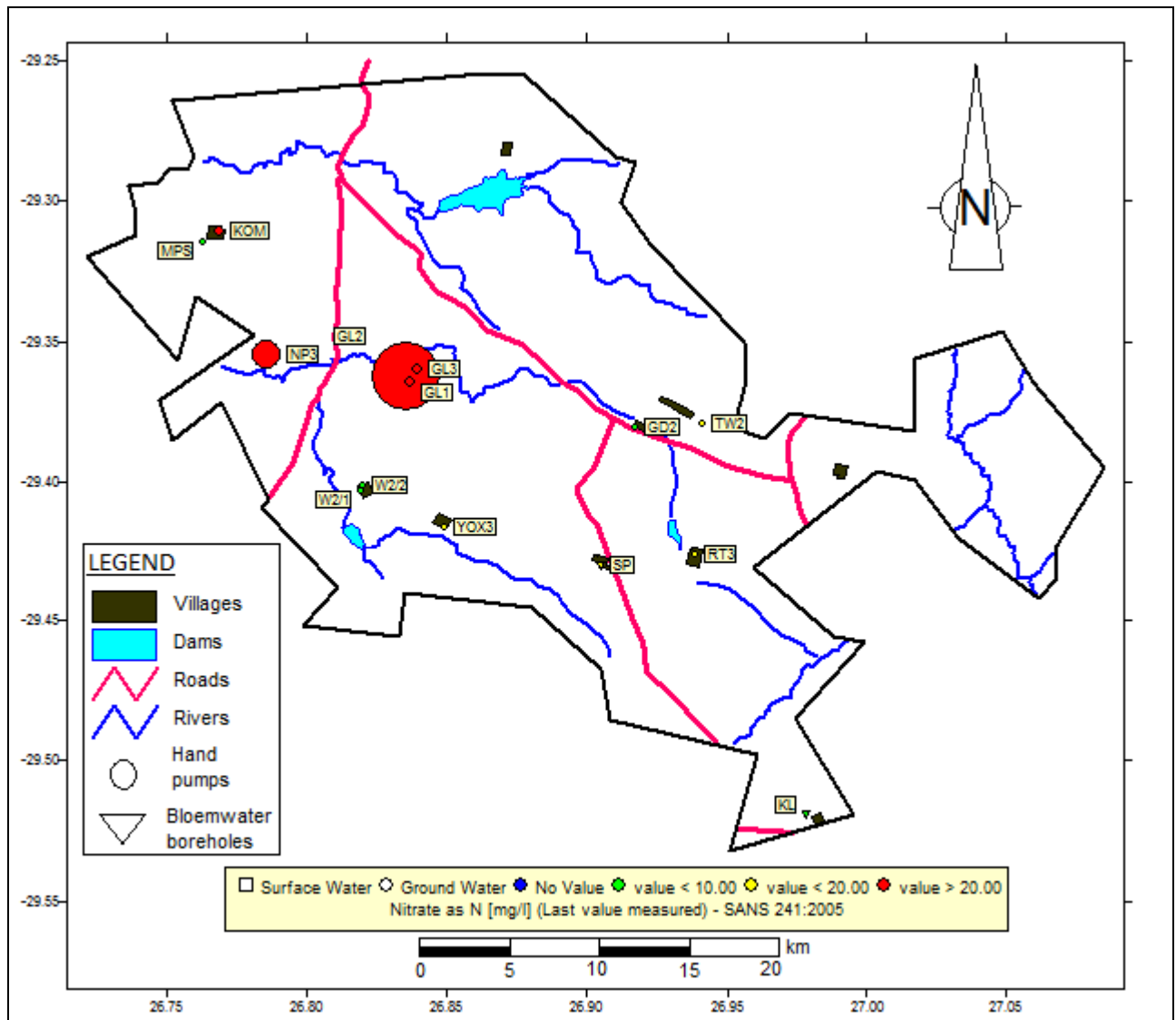
Figure 4-6: Current spatial distribution of NO₃-N concentrations in the south of Thaba Nchu in groundwater samples obtained in May 2012. Each circle shows the relative site name and concentration. All units are in mg/L nitrate as N

The frequency distribution of the entire sampled boreholes onto nitrate concentration classes (Figure 4-7) indicates that 17 boreholes (65 %) exceed the maximum recommended limit (<6 mg/L) in the Department of Water Affairs (DWA) drinking water standards. The distribution is made of five categories listed in Table 4-1. The asymmetric distribution of NO_3^- concentration is positively skewed (1.5). The skewed frequency distribution of NO_3^- concentration of groundwater suggests both point and non-point sources of pollution (Singh, *et al.*, 2005).
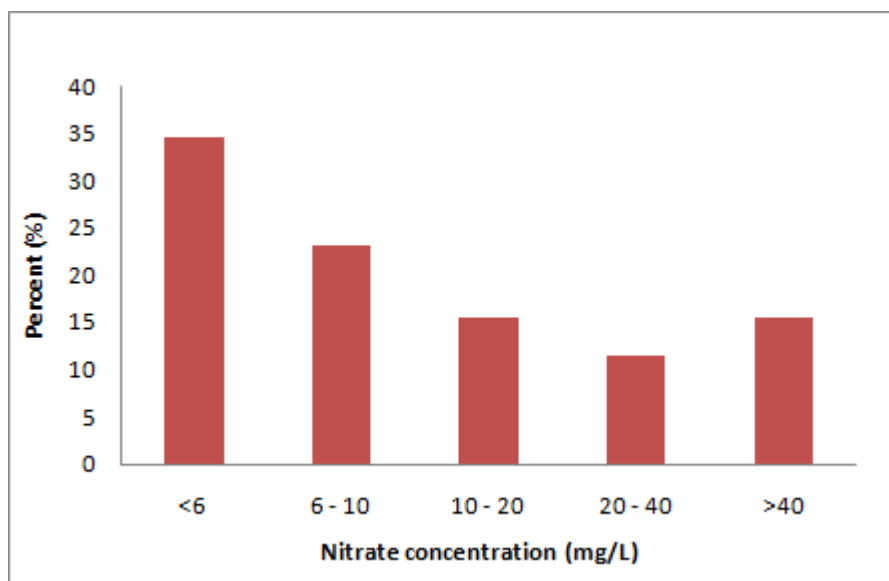
Figure 4-7: Frequency distribution of NO$_3$-N in groundwater

Table 4-1: Frequency distribution of nitrate-nitrogen specifications in Thaba Nchu according to DWA drinking water standards, borehole samples, percentages and potability class

Distribution (mg/L)	Number of boreholes	Percentage (%)	Potability class	Comments
<6	9	35	Ideal	Negligible health effects
6 – 10	6	23	Acceptable	Insignificant risk
10 – 20	4	15	Marginal	Slight chronic risk to some babies
20 – 40	3	12	Poor	Possible chronic risk to some babies
>40	4	15	Unacceptable	Increasing acute health risk to babies

4.2.3 Characterisation of contaminant sources

The main component of source characterisation is to quantitatively determine for each source the corresponding loading. The location of nitrate sources is displayed in Appendix D Table 1. The pie chart in Figure 4-8 depicts the breakdown of the percentages of on-ground nitrogen loadings from the different sources present in the Thaba Nchu aquifer system and suggests that pit latrines are the largest sources which account for 86 % of nitrate generated in the area. This indeed indicates that successful management options should target these sources. Although these sources are very likely to have a more distributed impact, other sources may not be overlooked since these have local impacts and thus could be responsible for the elevated nitrate concentrations at certain receptors (Erickson, 1992 cited in Almasri, 2006). This at least provides a preliminary understanding and early appreciation to the influential nitrate sources within the study area of concern and may indeed direct the

efforts into the data that need to be collected. Besides, one can easily expect what nitrate sources the management options should address when being developed and implemented.
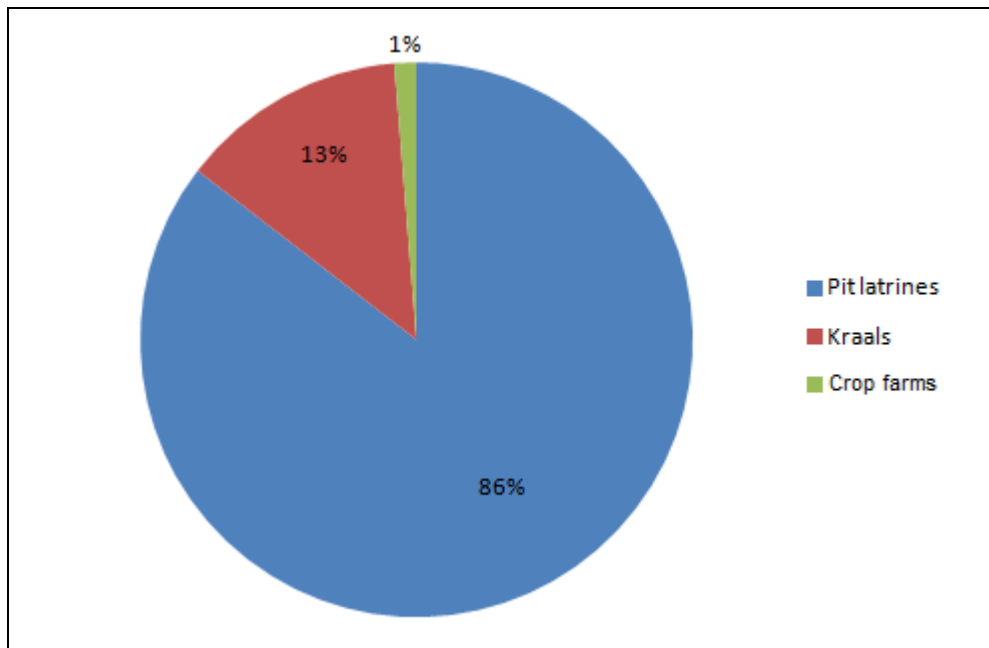
Figure 4-8: Percentages of on-ground nitrate loadings from different sources presented in the aquifer system

The boreholes and nitrate contamination sources are displayed in Figure 4-9. These sources appear in clusters in the respective villages. The distance between the closest contaminant sources and the boreholes were measured on Google Earth and listed in Appendix D Table 2. The boreholes that belong to Bloemwater are farthest from the villages and have low nitrate concentrations, except SP borehole which has had a consistent high nitrate concentration since 1997 (Appendix C). This is because there is a reservoir of surface water 73 m from the borehole littered with cow dung and this surface water recharges the SP borehole as it will be seen in the plot of δD and $δ^{18}O$ isotope concentrations (Figure 4-14, section 4.3.1).

Following the assumption by Toth (1963 cited in Haitjema and Mitchell-Bruker, 2005) for regional groundwater flow solution, shallow groundwater levels are a subdued replica of topography. Therefore, groundwater flow patterns are overlaid on the topographic map of Thaba Nchu (Figure 4-9).

The boreholes that are vulnerable to contamination have a distribution of high nitrate concentrations with calculated groundwater flow directions down-gradient of the contaminant sources (SP, NP2, NP3 GL1, GL2, GL3, and BAL2). It should be borne in mind that the movement of water or in this case migration of contaminants, in this assumption forgoes vertical flow through the aquifers.
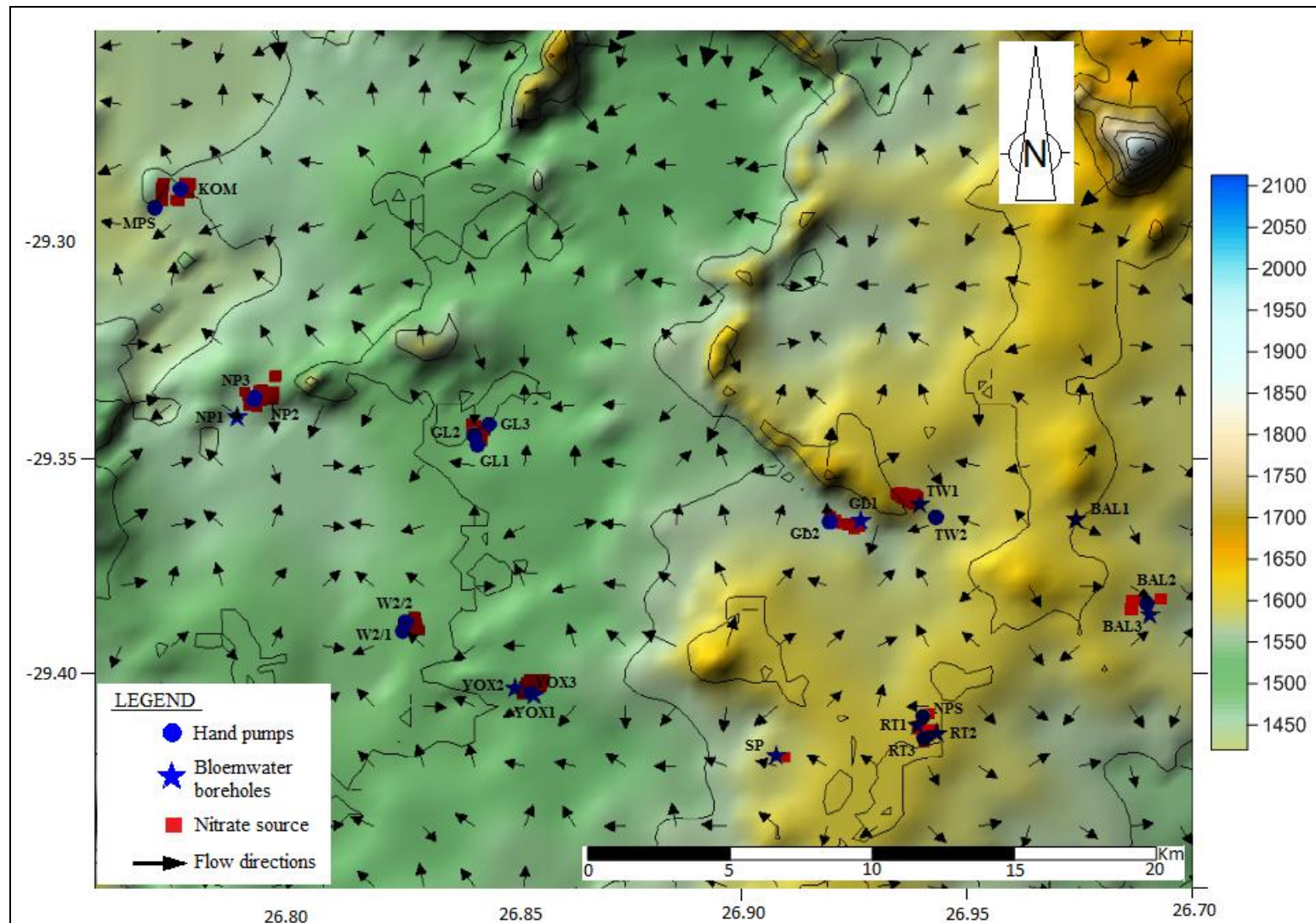
Figure 4-9: Boreholes and nitrate contamination sources in the respective villages including possible groundwater flow directions

The plot in Figure 4-10 relates rainfall intensity to the concentration of NO_3 in groundwater. Following the high rainfall in December 2011 and January 2012, GL2 experienced the highest increase in NO_3 followed by GL1. It can be argued that the groundwater levels in these boreholes are shallower than the other boreholes which allowed for a rapid leaching of nitrates from the overlying unsaturated zone and soil, hence their high NO_3 concentrations. Three months later with low rainfall events, the NO_3 concentrations reduced in these boreholes. Therefore, high nitrate concentrations were recharged under wetter conditions while lower nitrate concentrations appeared to be recharged under much drier conditions. Although other boreholes like NP2 and NP3 and GL3 experienced changes in the respective rainfall events in reverse order, it may be cancelled due to the slight rainfall in the following months. Boreholes even in the same area must not have the same reactions due to heterogeneity of the system.
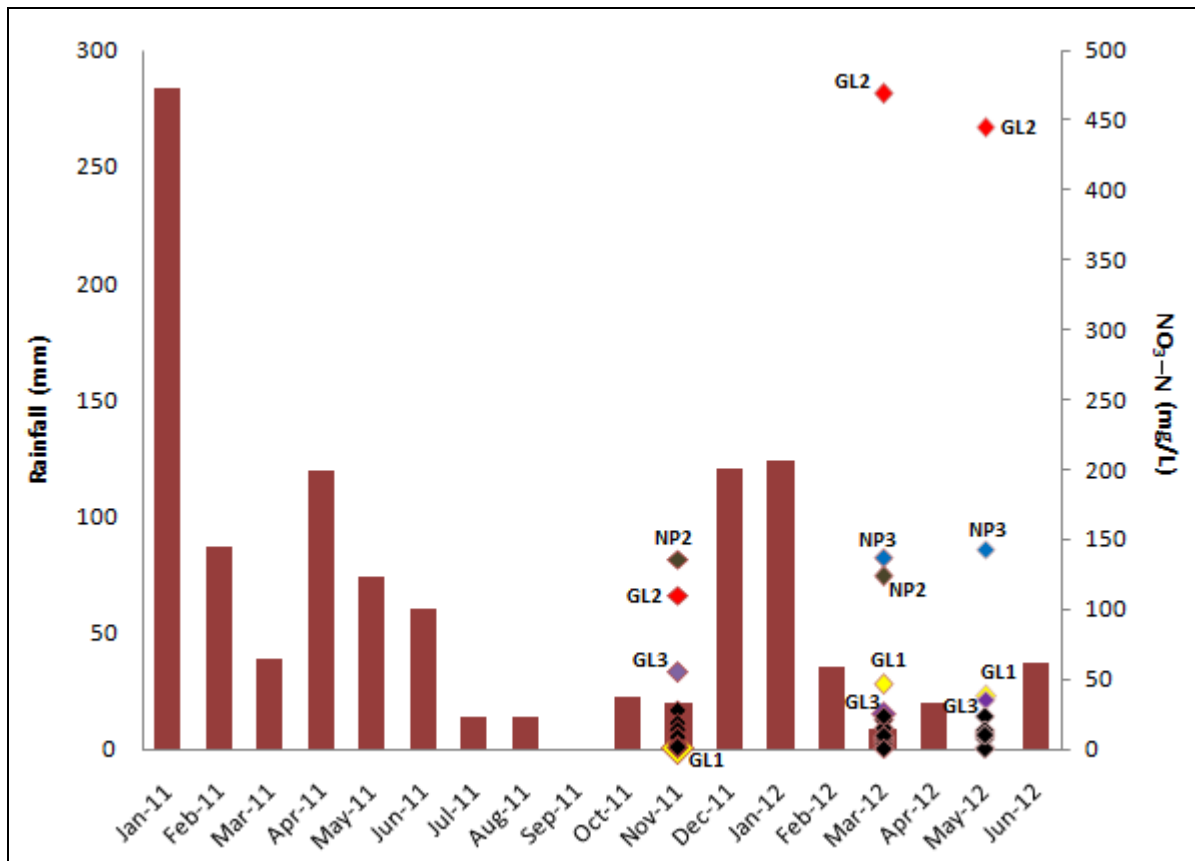
Figure 4-10: Associated variations in nitrate concentrations in groundwater associated with rainfall in Thaba Nchu

4.2.4   Groundwater geochemistry

The determination of the hydrochemical characteristics of the aquifer allows one to distinguish the principal geochemical facies and to recognize the occurrence of mixing phenomena between waters. The chemical composition of the groundwater samples are shown in Appendix C. The pH values ranged from approximately 7.2 - 10. The pH values in the groundwater samples in the aquifers were circumneutral to alkaline. Electrical conductivity values ranged between 23.2 mS/m and 979.0 mS/m. The highest EC values in a few wells located in rural areas had risen probably due to local pollution. This is evidenced by high NO_3^- and Cl^- contents which are probably associated with point sources from human and animal wastes at well heads.

Chemical composition of groundwater samples in the study area is characterised by significant spatial variability. The concentrations of major cations range from 19.4 - 739.3 mg/L Na^+, 0.8 - 49.15 mg/L K^+, 1.5 - 1025 mg/L Ca^{2+}, and 0.2 - 344.8 mg/L Mg^{2+}. For anions, concentrations of SO_4^-, total alkalinity (HCO_3^-) and Cl^- vary from 0.9 - 819.7 mg/L, 108 - 372.1 mg/L, and 7 - 1947.2 mg/L, respectively. The relative abundance of cations and anions in groundwater occur in the order Na > Ca > Mg > K, and HCO_3 > Cl > SO_4 > NO_3.

Piper and Expanded Durov plotting diagrams were used in the study of water chemistry and quality of groundwater samples collected in November 2011, March 2012 and May 2012 (Figure 4-11). The water types are designated according to the area in which they occur on the diagram segments (Appendix E Figures 1 and 2). These diagrams reveal the analogies, dissimilarities and different types of waters in the study areas, which are shown in Appendix E Tables 1 and 2.

In Figure 4-11, the Piper diagram shows the four most common water types encountered which are calcium/magnesium bicarbonate (red), calcium/sodium sulphate (blue), sodium bicarbonate/chloride (brown) and to a lesser extent calcium chloride/nitrate (green). In contrast with the other water types, the calcium chloride/nitrate water type showed significantly higher NO_3-N concentrations (NO_3-N > 100 mg/L). The cations show a trend from unpolluted to sodium/potassium enriched groundwater while the anions trend from unpolluted to chloride/nitrate-enriched groundwater.
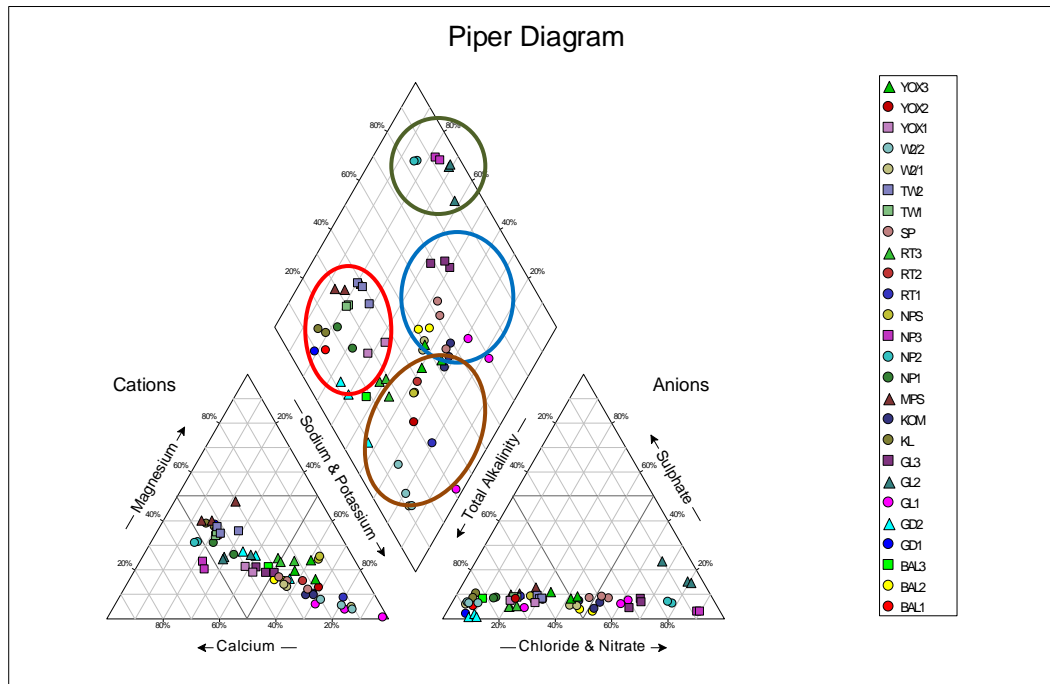
Figure 4-11: Piper diagram for groundwater samples collected in all sampling periods. Circles denote different water types

The concept of hydrochemical facies was presented by Walton (1970 cited in Tank and Chandel, 2009) to understand and identify the water composition in different classes based on the dominance of certain cations and anions in solutions in the Piper diagram (Appendix E Figure 1). It clearly explains the variation or domination of cation and anion concentrations. According to Appendix E Table 1 alkaline earth type of water (Ca^{2+} + Mg^{2+}) exceed the alkalis (Na^+ + K^+) where as in anion strong acids (Cl^- + SO_4^{2-}) exceed the weak acids (HCO_3^- + CO_3^{2-}) which show the hardness in all samples. 16 % samples (SP, BAL2, YOX3 and W2/1) show secondary alkalinity where chemical properties are dominated by alkaline earths and weak acids. Four samples (YOX1, RT3, BAL3 and GD2) show primary salinity where dominating ions are alkaline earth and strong acids. Three samples (GL1, KOM and RT2) show primary alkalinity (dominated ions, alkali and weak acids). Not a single sample falls in the secondary salinity (non-carbonate hardness).

The concept in Appendix E Figure 2 for the Expanded Durov (Figure 4-12) was also created based on the hydrochemical processes occurring within the aquifer. From Appendix E Table 2 it is seen that 40 % of the samples are fresh clean, relatively young groundwater that has started to undergo Mg ion-exchange. 28 % of the samples has undergone Na ion-exchange, or because of contamination effects from a source rich in Na. Two samples (KOM and BAL2) that have undergone SO_4 and NaCl mixing/contamination have been in contact with a source rich in Na. NP2 and NP3 waters indicate NO_3 or Cl enrichment, or dissolution, sample GL2 has

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undergone SO_4, but especially Cl mixing/contamination, and 3 samples (GL1, GL3 and SP) indicate very old, stagnant water, or water that has undergone significant ion exchange.
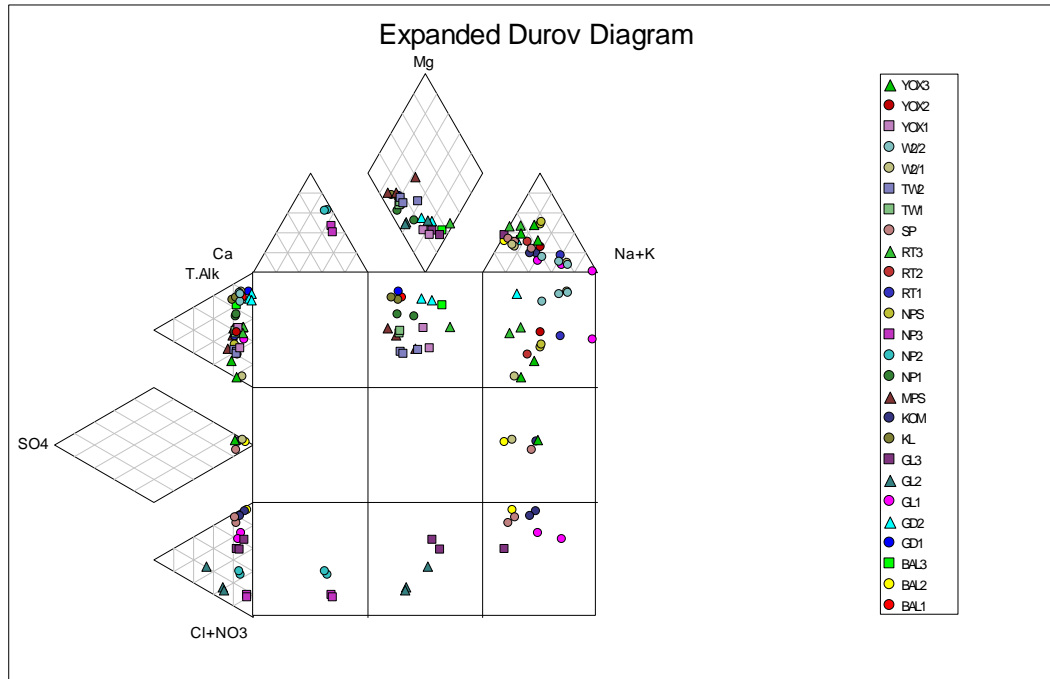
Figure 4-12: Expanded Durov diagram for groundwater samples collected in all sampling periods

4.2.5 Hydrochemical facies

The relationship between major chemical parameters of groundwater is presented in Appendix F Table 1. Correlation is the mutual relationship between two variables. Direct correlation exists when increase or decrease in the value of one parameter is associated with a corresponding increase or decrease in the value of the other parameter. The correlation coefficient (r-value) is said to be positive when increase in one parameter causes the increase in the other parameter and correlation is said to be negative when increase in one parameter causes the decrease in the other parameter. The strong to perfect correlation between the chemical parameters is an indication of common source.

NO_3 showed close affinities with Cl contents as the r-value is strongly correlated (0.99, p<0.00) suggesting a common source for these contaminants, such as animal wastes or fertiliser. A significant positive correlation between nitrates and chlorides, sodium and magnesium concentration in groundwater samples was found. Chlorides, as well as sodium in the groundwater, can be derived from domestic wastes (Sapek, 1996; Misztal and Sapek, 1997; Ostrowska and Plodzik, 1999 cited in Jaszczynski, 2008).

The significant negative correlation between NO_3 and HCO_3 was explained by the heterotrophic denitrification process, which is continuously removing nitrate from the Thaba Nchu groundwater aquifers rather than to the natural dissolution from soil or rock as believed by Mohamed, *et al.* (2003 cited in Babiker, *et al.,* 2004). The denitrifying bacteria use the oxygen of nitrate (electron acceptor) to generate energy from the organic carbon (electron donor) and release bicarbonate and nitrogen gas to the system as by-products.

In Figure 4-13, NO_3 and cation concentrations (Ca^{2+}) showed strong correlation ($R^2 = 0.99$) indicating that they originated from the same sources. Species such as Ca^{2+}, NO_3^-, and Mg^{2+} may be derived from chemical fertilisers and manure (NH_4NO_3, $(NH_4)_2SO_4$, $Ca(NO_3)_2$ and $(Ca, Mg)CO_3$) (Frapporti and Vriend, 1993; Puckett and Cowdery, 2002; Kaown, *et al.*, 2007; referred in Kaown, *et al.,* 2009). The plots of anions (Cl^- and SO_4^{2-}) and NO_3-N also show strong correlations. The strong positive correlation between NO_3 and SO_4 suggests a common source. Both ions would be introduced with the urea and ammonium-sulphate applied during fertilisation of the croplands. Another contributing source can be poor soil profile (semi-arid sandy or sandy clay) with high coarse texture that have high water filtration rate and possibly contributing in nitrate leaching to underground shallow waters (Suthar, *et al.*, 2009).These two ions are not adsorbed to the negatively charged sites on soil clay minerals and would rapidly migrate downward to the groundwater.

Similarly, SO_4 also exhibited a good correlation with Cl ($r = 0.95$), which suggested the contribution of animal and human excreta deposition on groundwater contamination. It was observed that there is a high positive correlation between Ca and Cl (0.99), Mg and Cl (0.97), Na and Cl (0.94), total hardness and Cl (0.98), TDS and Cl (0.94) and EC and Cl (0.99). Strong correlation of chloride with calcium, magnesium and sodium indicates non-carbonate hardness and with total dissolved solids and electrical conductivity indicates salinity (Purandara and Vardarajan, 2003; Purandara, *et al.*, 2003; referred in Sameer, *et al.*, 2010).
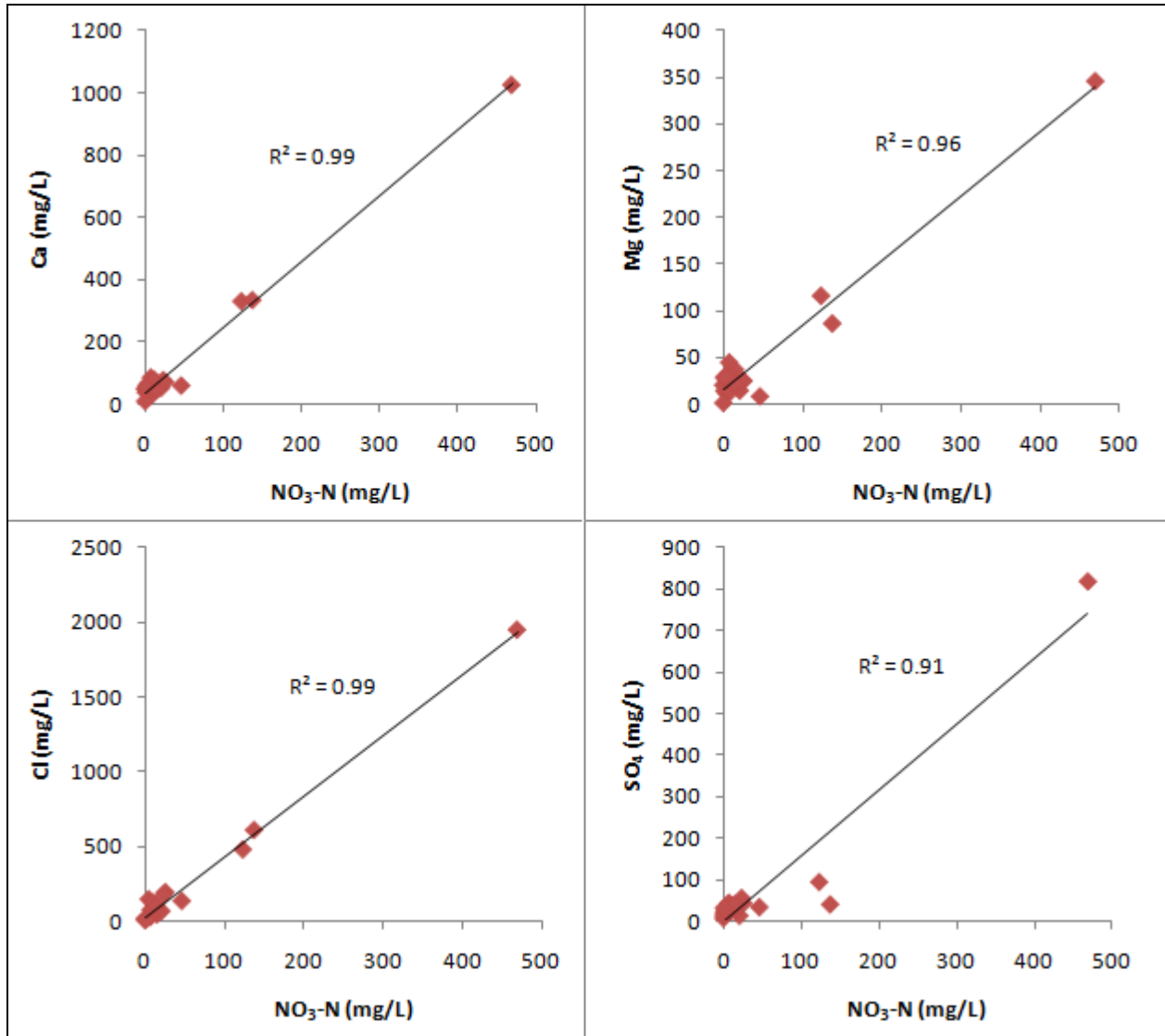
Figure 4-13: Linear regression coefficients for nitrate against calcium (Ca), magnesium (Mg), chloride (Cl) and sulphate (SO₄)

The moderate loading of phosphate (PO_4) corresponds to correlation between measured concentrations of NO_3 and PO_4 (r = -0.96). The possible sources of these contaminants could be from organic decomposition such as household solid wastes, animal and human wastes (Ishaku, *et al.*, 2011).

There is a very strong positive correlation between Br and Ca, Mg, Na, NO_3, Cl and SO_4 (0.99 ≥ r ≥ 0.94). Consequently, these high Br concentrations are probably related the agricultural land-use patterns and lend support to the significance of the contamination by rejection of treated and non-treated waste water; and return flow from irrigation water that include high amounts of fertiliser and pesticides such as methyl bromides and other organic bromyl (Zhu, *et al.*, 2007 mentioned in Moussa and Zouari, 2011).

4.3   Isotope analysis

4.3.1   Groundwater sources

Environmental isotopes data for 20 groundwater samples and one surface water sample in the study area collected in March 2012 are given in Appendix G Table 1. Deuterium (^{2}H or D) and Oxygen 18 (^{18}O) were used as tracers in the context of this study. Analyses of the stable isotopes ^{18}O and ^{2}H determine the isotope partitioning behaviour (fractionation), or the separation into heavy and light fractions that occurs from natural processes such as groundwater and surface water mixing, evaporation, precipitation events, and groundwater recharge that occurs at different elevations and temperatures. Fractionation is measured by comparing a known standard ratio with the sample ratio. For this study, samples were collected to measure the oxygen-deuterium isotopic signatures (^{18}O/^{16}O and ^{2}H/H).

Groundwater samples values ranged between -4.25 and 0.99 ‰ with a mean of -2.46 ‰ for δ^{18}O, and between -29.16 - 3.25 ‰ with a mean of -16.04 ‰ for δ^2H. Plotted in the conventional δ^{18}O *versus* δ^2H diagram together with the Global Meteoric Water Line (GMWL) of Craig (1961 cited in Diédhiou, *et al.*, 2011) which the equation is $\delta D = 8\ \delta^{18}O + 10$ and the evaporation line, the values deviate significantly from and lie below the GMWL with a best-fit curve of $\delta D = 5.35\ \delta^{18}O - 2.88$ and a correlation coefficient of $R^2 = 0.96$ (Figure 4-14). This trend is typically characteristic of the Sahelian aquifers (Fontes, *et al.*, 1991 referred in Diédhiou, *et al.*, 2011) which is due to isotopic enrichment caused by evaporation process that occurred before and during infiltration but also by probable mixing with enriched water.
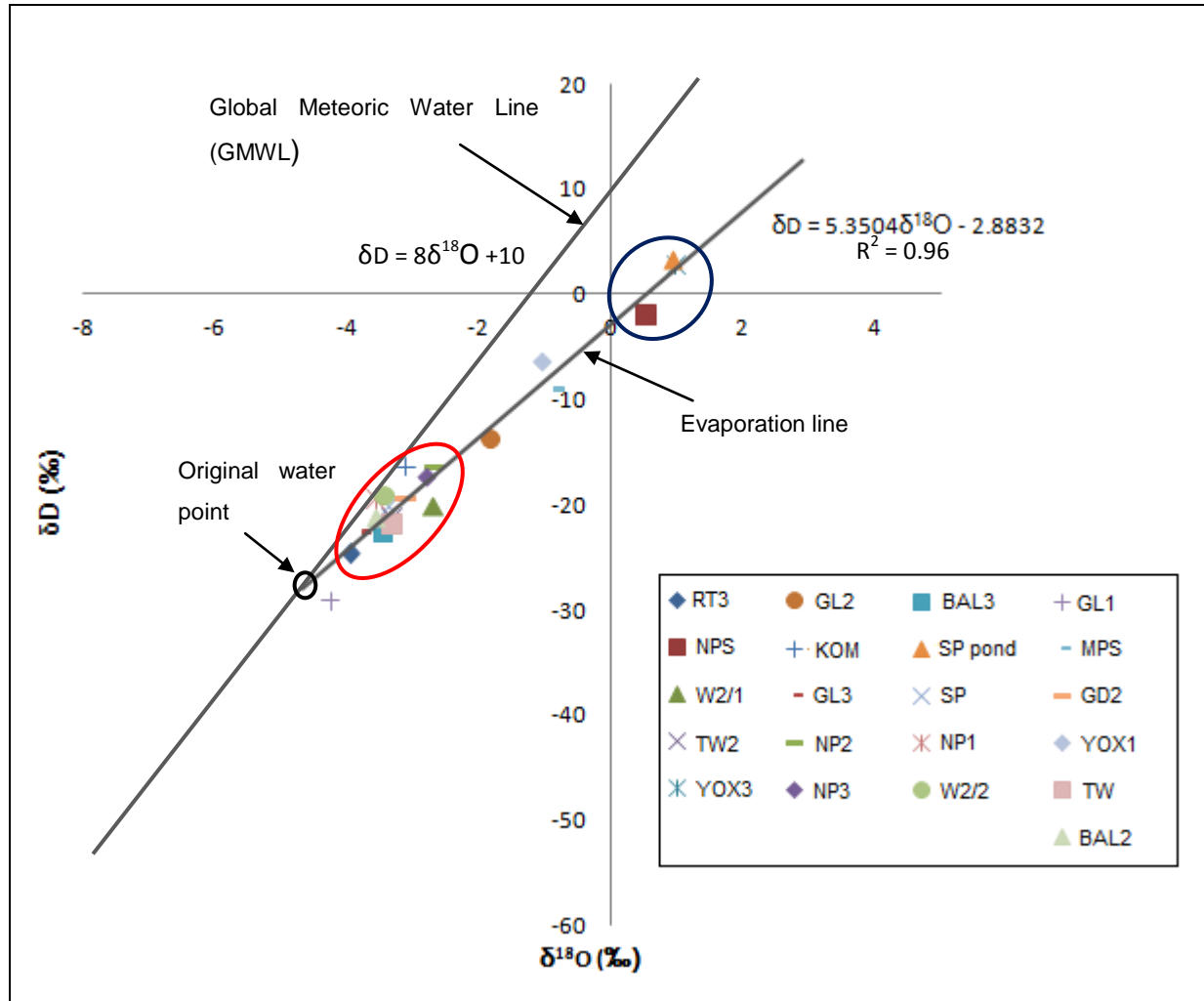
Figure 4-14: Isotopic concentrations of Deuterium and δ^{18}O of the water samples on Global Meteoric Water Line and evaporation line

There are two groups of data with distinct isotopic signatures, as illustrated by the red and blue ovals (Figure 4-14). The boreholes in the blue oval (local groundwater flow system) exhibit an enriched (less negative) isotopic signature, indicating the groundwater has possibly mixed with surface water (such as the SP pond recharging the SP borehole), shallow on-site sanitation (NPS) or the water has undergone evaporation prior to recharge. The boreholes' (regional groundwater flow system) isotopic signatures in the red oval are depleted and are consistent with water that has recharged from higher elevation and/or under cooler climatic conditions (Clark and Fritz, 1997, cited in Schorzman, *et al.*, 2009). Those in the middle experienced some degree of evaporation and contamination from on-site sanitation. Intersection point of the GMWL and the evaporation line represents the original isotopic concentration of the groundwater samples before evaporation. This point is called original water point (Gurer, *et al.*, 2008) as shown in Figure 4-14. Isotopic concentrations of the groundwater sample GL1 is closest to the isotopic concentrations of the original water point.

In the case of evaporatively labelled waters, it is particularly useful to examine the coupled enrichments of stable isotopes and solutes such as nitrate. Since evaporation produces a proportional enrichment in both $\delta^{18}O$ and δ^2H, only one isotope need be considered. Scattered plot of nitrate concentration (natural log) *versus* $\delta^{18}O$ is shown in Figure 4-15. Nitrate has a less coherent distribution, suggesting either a non-conservative behaviour or more than one source (Mohr, *et al.*, 1992). Boreholes in the green oval (GL2, NP2 and NP3) display the highest NO_3 concentrations in the moderately evaporatively enriched group waters. However, these highly elevated anion concentrations cannot be due to evaporative enrichment alone, for the isotopic enrichments would be far greater. Such solute enriched groundwaters, therefore, must have been contaminated after experiencing evaporation.

On the basis of the above evidence, four water types can be discriminated on the basis of their oxygen isotope ratios and nitrate contents:

(i) non-evaporated groundwater with very low nitrate (blue);
(ii) shallow groundwater, with possible evaporation and high nitrate (orange);
(iii) very high nitrate groundwater, with moderate evaporation (green); and
(iv) low nitrate; high evaporative enrichment (black).
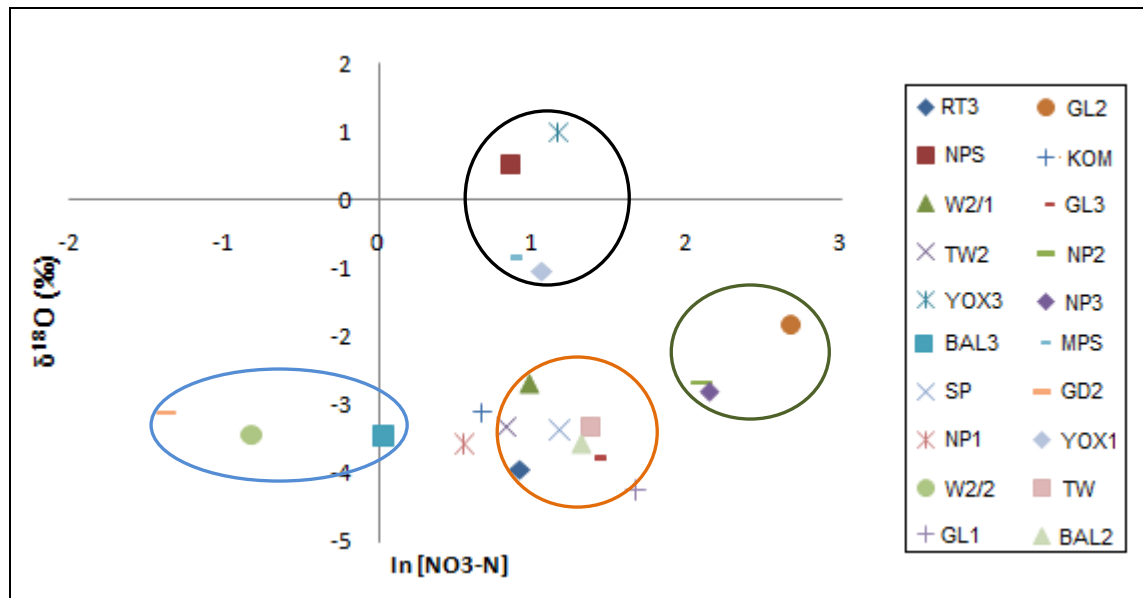
Figure 4-15: Scattered diagram of $\delta^{18}O$ *versus* natural log of nitrate concentration

4.3.2   Nitrogen and oxygen isotopes of nitrate

Appendix G Table 2 shows the values of $\delta^{15}N$ and $\delta^{18}O$ for 19 selected groundwater samples collected in March 2012. The $\delta^{15}N_{NO3^-}$ values in groundwater ranged from 3.15 - 51 ‰, and the $\delta^{18}O_{NO3^-}$ ranged between 7.19 and 27.07 ‰. A duplicate was run for GL2 sample in the laboratory with both results matching very closely. Therefore, its nitrate content value ranged differently from the original, as well as for NP2 and NP3.

The isotopic composition of groundwater NO_3^- may indicate the major contaminant source, since NO_3^- from different sources has characteristic $\delta^{15}N_{NO3^-}$ and $\delta^{18}O_{NO3^-}$ values (Clark and Fritz, 1997; Kendall, 1998; Kendall and Aravena, 2000; Kendall, *et al.*, 2007; cited in Kaown, *et al.*, 2009). The use of both nitrogen and oxygen isotopes from nitrate can often provide a more reliable distinction between the sources of nitrate than relying on nitrogen isotopes alone. In addition, the $\delta^{15}N$ and $\delta^{18}O$ values may be a useful indicator of denitrification.

The isotopic source range limits as approximated by Kendall (1998) and Mengis, *et al.* (2001) (cited in Bratcher, 2007; Diédhiou, *et al.*, 2011) were applied to the plot of $\delta^{15}N$ *versus* $\delta^{18}O$ values from collected samples in Figure 4-16. Nitrate resulting from ammonium fertilisers, organic soil matter, and animal and human wastes have $\delta^{18}O$ values that overlap, which leaves the $\delta^{15}N$ as a better discriminator for these sources. In contrast, even though $\delta^{15}N$ values are overlapping, nitrate derived from atmospheric sources or nitrate fertilisers are readily separable from soil nitrate using $\delta^{18}O$ (Fogg, *et al.*, 1998b cited in Bratcher, 2007). For the most part, the isotopic ratios of the collected samples plotted in separate distinct source areas. The plot indicated that nitrate in the aquifer was predominantly derived mostly from human and animal wastes, and to a lesser extent from organic nitrogen in the soil (BAL3) and nitrate fertilizer (W2/2).

Denitrification, as a natural process removing nitrate, can be also evaluated directly by dual ($\delta^{15}N$, $\delta^{18}O$) isotopic indicators (Einsiedl, *et al.*, 2005; Kendall, *et al.*, 2007; cited in Diédhiou, *et al.*, 2011). It is a dissimilatory, energy-generating process, which potentially can have a large effect upon groundwater geochemistry in zones in which it is occurring. As suggested by many authors (Böttcher, *et al.*, 1990; Aravena and Robertson, 1998; Mengis, *et al.,* 1999; referenced in Diédhiou, *et al.*, 2011), denitrification concurrently enriches in the residual nitrate pool the heavy isotopes of $\delta^{15}N$ and $\delta^{18}O$ in roughly a ratio between 1:1 and 2:1. Plotted in Figure 4-16, one sample, KOM, falls in this range implying that the process takes place in this borehole. The rest of the dataset lay above the predicted trend evidencing an enrichment of $\delta^{18}O_{NO3^-}$ probably generated by new input of animal and human wastes, inorganic nitrate fertilizer and atmospheric deposition which are likely to blur interpretation of fractionation (Kendall, *et al.*, 2007 mentioned in Diédhiou, *et al.*, 2011). The fractionation of nitrogen

isotopes associated with denitrification leads to significant increases in the $\delta^{15}N$ of the residual nitrate (Liu and Kaplan, 1989; Saino and Hattori, 1987; Wada and Hattori, 1976; Cline and Kaplan, 1975), generating a useful isotopic indicator of denitrification (cited in Voss, *et al.*, 2001).
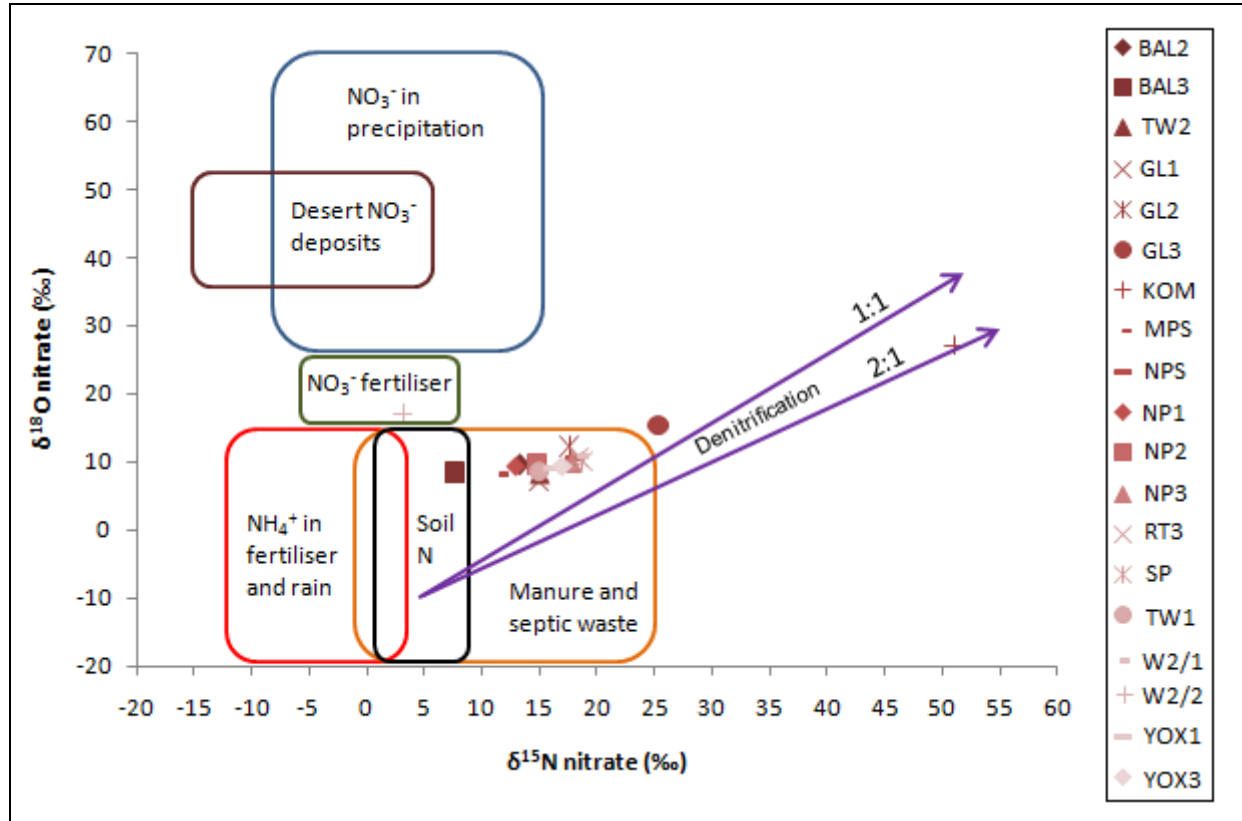
Figure 4-16: Concentration weighted mean $\delta^{18}O$ versus concentration weighted mean $\delta^{15}N$ values for groundwater nitrate. (Source: Modified from Kendall, 1998; Mengis, *et al.*, 2001; cited in Bratcher, 2007 and Diédhiou, *et al.*, 2011)

4.3.3   Nitrate concentration *versus* $\delta^{15}N$ and $\delta^{18}O$

Figure 4-17 indicates no distinguished trend of increasing $\delta^{15}N_{NO3^-}$ values with decreasing nitrate concentrations (natural logarithm), as would be expected if in-situ denitrification were controlling NO_3 concentrations in groundwater samples. It indicates in contrast a relatively poor correlation between In $[NO_3-N]$ and $\delta^{15}N_{NO3^-}$ with increasing nitrate concentrations and $\delta^{15}N$ implying nitrification or the input of new nitrates in the aquifer. However, the denitrification relationship is evident with some boreholes (KOM, GL1 and GL3).

Following the model described by Choi, *et al.* (2003 cited in Diédhiou, *et al.*, 2011) between NO_3 *versus* $\delta^{15}N$, which showed correlation patterns of groundwater nitrification and denitrification, interpretation in terms of denitrification-lowering NO_3 concentrations may be

misleading since the data did not consider temporal evolution and also sources and load patterns may be different from each point. Therefore, the trend found may obscure denitrification due to continuous mixing with new infiltrated nitrates and cycling. This hypothesis is plausible in this study area by continuous waste water infiltration in the system evidenced by the increasing nitrate trends from scattered nitrate distribution plots in Figure 4-17, following rainfall events in Figure 4-10, and Expanded Durov diagram in Figure 4-12. Despite that, the aerobic conditions in the shallow groundwater as well as assumed coarse grain texture and low organic matter content may limit the extent of denitrification process in the groundwater system (Diédhiou, *et al.*, 2011). The same non-exponential relationship applies for $\delta^{18}O_{NO3-}$ and nitrate with most of the $\delta^{18}O_{NO3-}$ isotopes stagnant as NO_3 concentration increases.
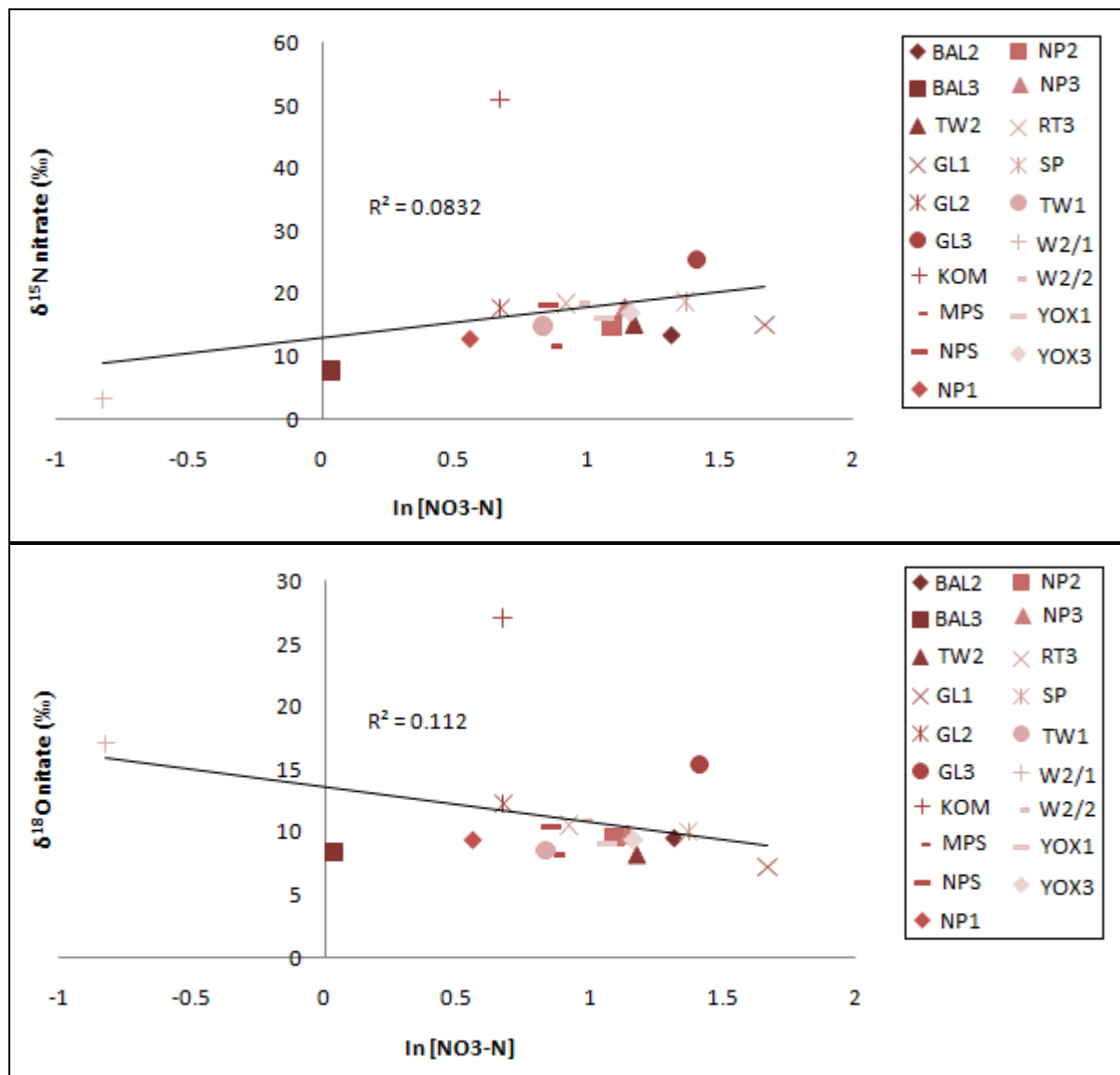
Figure 4-17: Correlations between $\delta^{15}N_{NO3-}$ (top) and $\delta^{18}O_{NO3-}$ (bottom) values *versus* the logarithm of nitrate concentrations

5. NITROGEN MANAGEMENT STRATEGY

This chapter provides an overview of some of the options for managing groundwater pollution risks derived from sanitation for on-site methods. These include planning, design and construction of facilities, as well as monitoring their safe operation. Important aspects discussed in the context of planning are siting decisions and infrastructure changes that will help reduce risks, and balancing the sometimes competing needs for better sanitation and groundwater protection. The end of the chapter summarizes some major control measures that can be used to provide protection of groundwater through effective management of sanitation.

5.1 Balancing investment decisions

In communities in developing countries where improved sanitation facilities do not exist, setting stringent requirements for sanitation facility design and construction to meet criteria to prevent groundwater pollution may be counter-productive, unless the risk is very significant. Such criteria may make sanitation improvements too expensive for many households, resulting in continued lack of sanitation and ongoing disease transmission (Mara, 1996 mentioned in Howard, *et al.*, 2006). Where the construction of sanitation will represent a very significant risk of groundwater contamination, decisions will be required as to whether changes in water supply or sanitation are more cost-effective (Franceys, *et al.,* 1992 referenced in Howard, *et al.*, 2006).

A nitrate management strategy for the region should be based on a dual approach that involves legislative control measures, as well as public information and education programs. Control measures are essential for reducing anthropogenic nitrogenous inputs to the environment that may affect groundwater quality. Such measures are also required for reducing groundwater nitrate levels in the rural areas and on farms that affect drinking water quality. Denitrification of drinking water supplies, aquifer restoration, blending of water sources, supply of bottled water for mothers and infants, and other measures are needed to reduce the risks of exposure of the population to excessive nitrate (Tredoux, 2004).

5.2 Selecting the right sanitation technology

The first stage in the management of sanitation in order to protect against groundwater contamination is to select the right technology for the local environment. This requires that data is collected on the local hydrogeological conditions and the role of groundwater in water

supplies within a region or the country. Sanitation technology selection will not be based solely on concerns regarding risks of groundwater contamination. Community preferences, usual methods of anal cleansing, available resources and costs of technology options should all be considered in this process (Franceys, *et al.*, 1992; Cotton and Saywell, 1998; cited in Howard, *et al.*, 2006). In many cases these concerns will take priority over groundwater quality concerns, but it is important that attention is also paid to groundwater pollution risks in the decision-making process.

The links between water supply service and sanitation options cannot be ignored. As water supply service level increases, so will water consumption, thus increasing the volume of wastewater that must be disposed of. Using sanitation technologies that are not designed to take large volumes of wastewater will not be appropriate and water-based systems or sanitation systems that separate effluent and solid material should be considered. Equally, the use of flush toilets and other water-based systems will not be appropriate where the water supply service is only a public tap, dug well or other form of communal supply. Intermediate levels of service (single on-plot tap) may be suitable for some forms of modified sewerage, but will not allow the use of conventional sewerage (Howard, *et al.*, 2006).

5.3   Controlling risks from on-site sanitation

In many developing countries access to water supply and sanitation remains low and there is an urgent need to provide both improved water supply and a safe means of human waste disposal (WHO and UNICEF, 2000 cited in Howard, *et al.*, 2006). In many rural and peri-urban communities (including poor marginalised communities within urban centres) it is likely that improved access to sanitation facilities will be in the form of on-site sanitation (ARGOSS, 2001; Mara, 1996; Cotton and Saywell, 1998; referred in Howard, *et al.*, 2006).

In this section some key issues relating to the risks posed to groundwater quality from on-site sanitation and the potential means by which this may be reduced through design (including siting), construction and maintenance are reviewed. It is not intended to provide a detailed description of how to design and construct such facilities, but rather the specific measures that can be used to protect groundwater.

5.3.1 Siting of on-site sanitation facilities

Site selection of sanitation facilities is an important control measure to protect groundwater from human faeces. In many developing countries, recommendations are often made regarding siting of latrines with respect to groundwater sources. These are often developed separately from (and usually before) groundwater protection zones.

Set-back distance recommendations range from simplistic to more sophisticated approaches based on hydrogeological conditions. Pickford (1995 cited in Howard, *et al.*, 2006) noted recommendations from India for pit latrines to be located some six metres downhill of the nearest water source. Xu and Braune (1995 referenced Vinger *et al.*, 2012) proposed an absolute minimum distance of 50 m between a pit latrine and a borehole in South Africa. Such recommendations should always be treated with some caution. Although the hydraulic gradient of shallow groundwater typically follows the ground surface, it should be borne in mind that where the well is equipped with an electric submersible or other form of pump, there will be a substantial drawdown. Therefore contaminants can be drawn into the well from areas downhill and physical location may not always provide adequate protection (Howard, *et al.*, 2006), which is the case in Thaba Nchu.

In many countries, single-distance criteria are used. A distance of 15 m is a commonly used criterion, based on suggestions by Wagner and Lanoix (1958 cited in Howard, *et al.*, 2006). The weaknesses in using these approaches was highlighted by Lewis, *et al.* (1982 cited in Howard, 2006) who noted that this distance may be overly conservative in some hydrogeological environments (thus limiting health gains from sanitation) and insufficient in other environments with rapid flow rates. Lewis, *et al.* (1982 mentioned in Howard, *et al.*, 2006) also suggested that set-back distances should be established based on local hydrogeological conditions (such as water table depth, nature of unsaturated zone) and the hydraulic load from the pit latrine (Howard, *et al.*, 2006).

In South Africa, DWAF (1997, cited in Tredoux, 2004) developed a framework for selecting separation distances using contaminant risk assessment based on:

- whether the site for sanitation development overlies a major aquifer;
- the proposed use of groundwater;
- the depth to the water table;
- the type of aquifer;
- presence of existing pit latrines within 50 m and up-gradient; and
- evidence of contamination.

One problem noted with the definition of set-back distances is that these do not always take into account the fact that different types of technology are likely to have different levels of pollution potential. Pit latrines usually are significantly deeper than septic tanks and tend to rely on infiltration of leachate through the surrounding soil. Pour-flush latrines have a much higher hydraulic load than dry latrines and as a result have a greater pollution potential. Septic tanks typically receive relatively large volumes of wastewater and therefore if not constructed properly, may lead to a significant hydraulic load and increased pollution potential. This is reduced through ensuring that the tank is watertight and that effluent is discharged into drain fields and soakaways at a much shallower level (Howard, *et al.*, 2006).

In addition to set-back distances, hydrogeological data are often used to identify areas where groundwater-fed sources are particularly susceptible to contamination. A widely used method is known as DRASTIC (Aller, *et al.*, 1987 mentioned in Tredoux, 2004 and Howard, *et al.*, 2006) which employs seven hydrogeological factors in order to develop an index of the vulnerability of groundwater to contamination:

- Depth to water table
- Recharge
- Aquifer media
- Soil media
- Topography (slope)
- Impact to vadose zone
- hydraulic Conductivity

An index is generated by applying a weight to each hydrogeological factor that is represented numerically. As hydrogeological factors vary spatially, the DRASTIC index provides a systematic way of mapping the relative vulnerability of groundwater to contamination and can be readily incorporated into a Geographical Information System (GIS) (Kim and Hamm, 1999; Shahid, 2000; referred in Howard, *et al.*, 2006). The method is, however, data intensive and does not include factors (for example, attenuation capacity) that relate specifically to the risk to groundwater posed by sewage and sewage-derived microorganisms. DRASTIC also does not provide any site-specific guidance. The index may, however, provide a worthwhile framework for assigning set-back distances based on different levels of risk (Howard, *et al.*, 2006).

Other work in South Africa has recommended an approach that takes into account estimation of pollution risk based on travel time for microbes, mass balance for nitrate and using a probabilistic approach for contamination exceeding specified targets (Van Ryneveld and Fourie, 1997 cited in Howard, *et al.*, 2006). De Lang (1999) calculated separation distances

related to microbial quality based on a time of travel estimation that included hydraulic and pollutant loading as well as the attenuation potential and survival of microbe. Recent research in developing countries has attempted to develop guidance without requiring detailed hydrogeological information in order to determine set-back distances for pit latrines (ARGOSS, 2001 referenced in Howard, *et al.*, 2006). Risk assessments are defined for three scenarios (localised microbial contamination, widespread microbial contamination, and widespread nitrate contamination).

More qualitative approaches to defining separation distances using available data can be used based on statistical analysis of water quality and sanitary inspection data (ARGOSS, 2001; Howard, *et al.*, 2003; cited in Howard, *et al.*, 2006). These have been shown to be robust in supporting water and sanitation planning and offer an effective way to determine siting requirements based on local conditions when there is limited hydrogeological data available.

5.4 Control measures for reducing nitrate source inputs

Control measures for reducing nitrogenous inputs to the environment are essential for protecting the groundwater resources. In view of the considerable delay (varying from years to decades) between the introduction of control measures and any decrease in groundwater nitrate levels it is a matter of extreme urgency to take action in this regard. It has been proven that stable nitrogen isotope analysis can be used successfully to identify pollution sources. This technique can be used to confirm the effectiveness of any control measures adopted. In view of the fact that the groundwater in many countries are already contaminated and that control measures will take many years (if not decades) to reduce these nitrate levels, denitrification of drinking water is widely practised. In South Africa denitrification for potable use and/or stock watering will be needed in areas where no alternative supplies are available (Howard, *et al.*, 2006).

Despite suggested control measures pollution from diffuse sources in South Africa remains practically uncontrolled. Such sources largely refer to agricultural activities and uncontrolled rural settlements. Protection of the groundwater resources is specifically of benefit to the local user but also to the country as a whole. Therefore, an information campaign bringing the detrimental effect and the hazards of nitrate pollution to the attention of farmers, owners of small-holdings and the public at large is essential for safeguarding the sparse groundwater resources. Such a campaign should complement any control measures introduced. Pollution prevention is the desired option providing the ultimate longer term cost-effective solution. The

retrospective costly approach of drinking water treatment must be avoided as the whole water supply needs treatment to protect infants (Tredoux, 2004).

As noted in Tredoux (2004) an action plan was devised for guiding the response to nitrate occurrences and for managing the nitrate concentration in groundwater. The action plan is based on the groundwater nitrate concentration which is best determined by laboratory analysis. The preliminary strategy is set out in the following diagrams. The first step, the situation assessment, is set out in Figure 5-1.
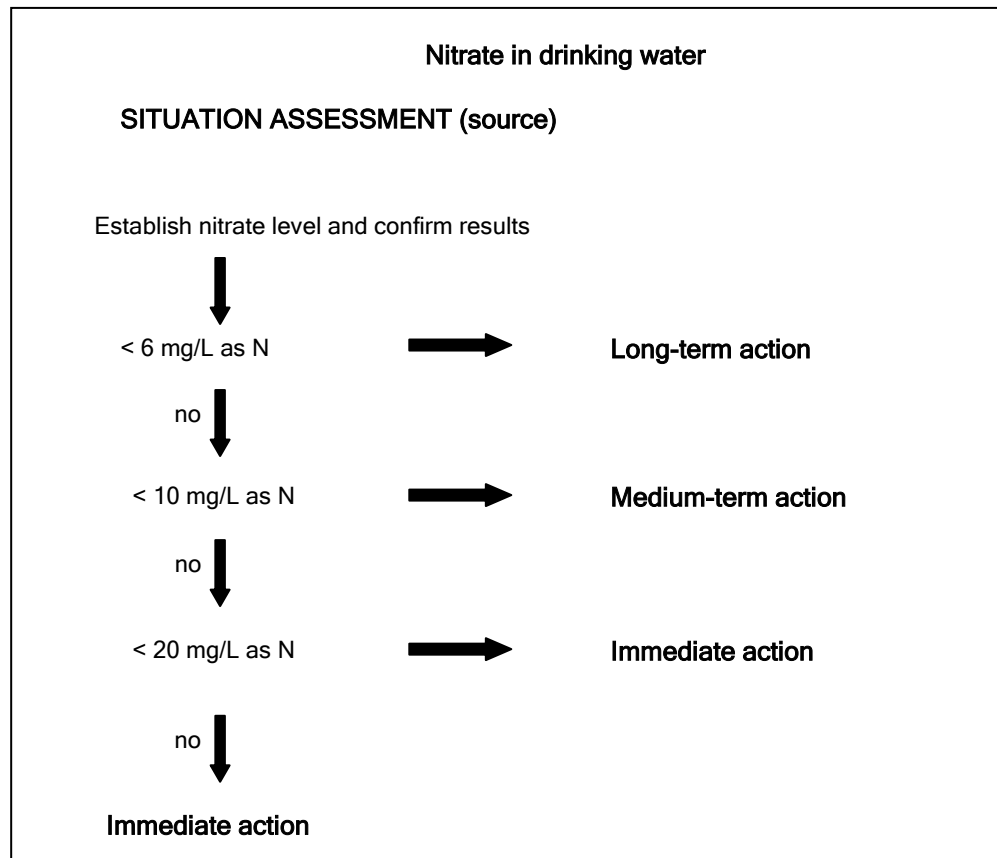
Figure 5-1: Groundwater nitrate strategy based on situation assessment (Source: Modified from Tredoux, 2004)

5.4.1 Immediate action

As set out in the specifications by the Department of Water Affairs (DWA) in Chapter 4, Table 4-1, the water is of marginal quality if the groundwater nitrate exceeds 10 mg/L (as nitrogen). However, if the nitrate concentration exceeds 20 mg/L, or if the water is bacterially polluted, immediate action is required. Such action would entail that the microbiological quality of the water be determined. All users should be alerted to the risk, and nitrate-free and bacterially safe bottled water should be provided for infants and pregnant women. If the nitrate exceeds

50 mg/L, use of the source should be terminated and an alternative nitrate-free supply found (Figure 5-2) or denitrification measures implemented. Bacterially polluted water should be disinfected, for example, chlorinated.
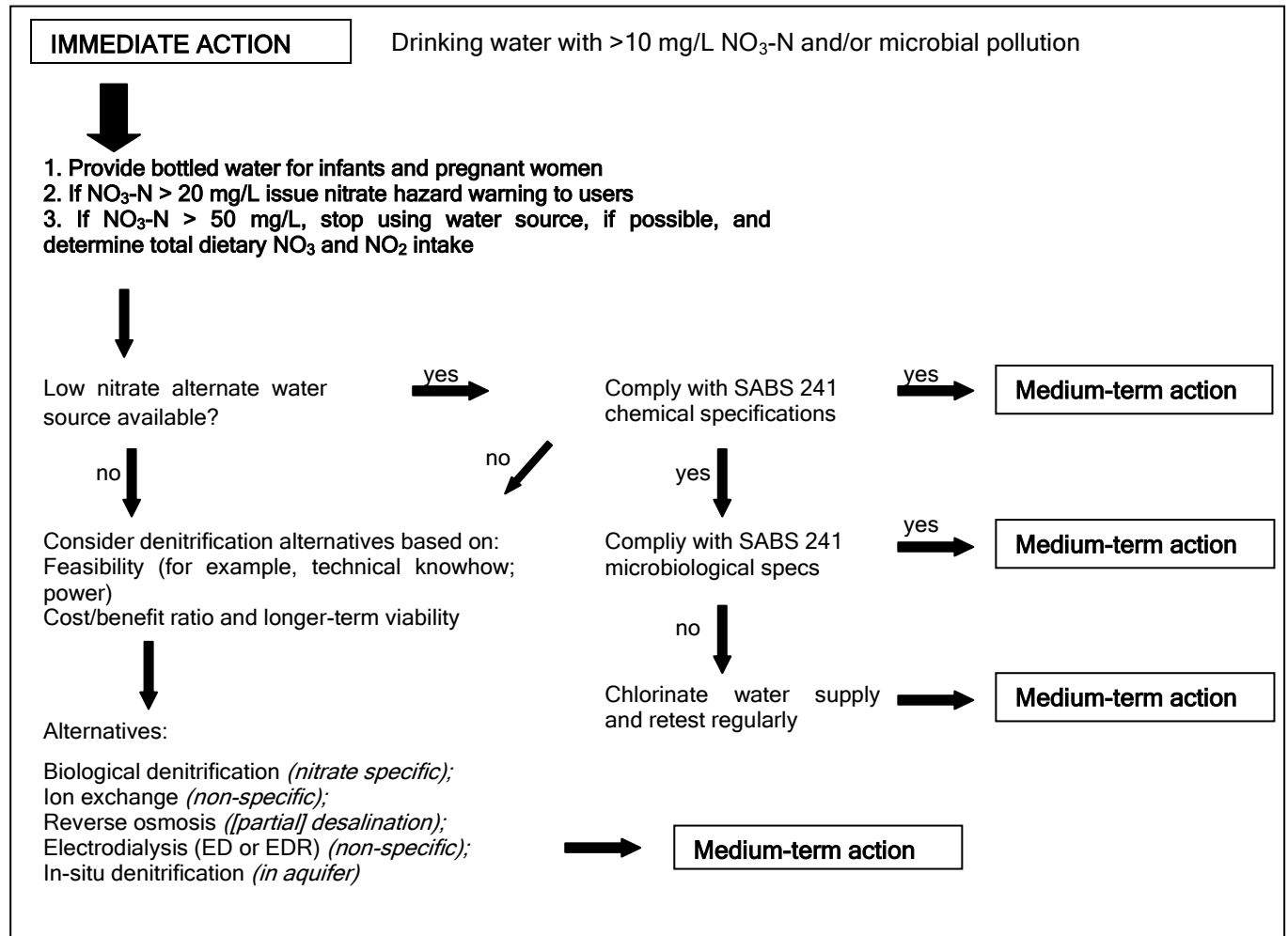
Figure 5-2: Groundwater nitrate strategy: Immediate action situation (Source: Modified from Tredoux, 2004)

5.4.2 Medium-term action

Once the immediate actions have been carried out, further steps may be needed, mostly in the medium-term situation. These are described in Figure 5-3. When nitrate exceeds 10 mg/L but is less than 20 mg/L, it can still pose a threat to certain users (immune compromised individuals, particularly infants). In such cases, all potential nitrate sources like pit latrines, septic tank soakaways, stock watering points, need to be identified. Should such pollution point sources exist then relocation of the borehole or well will be necessary.
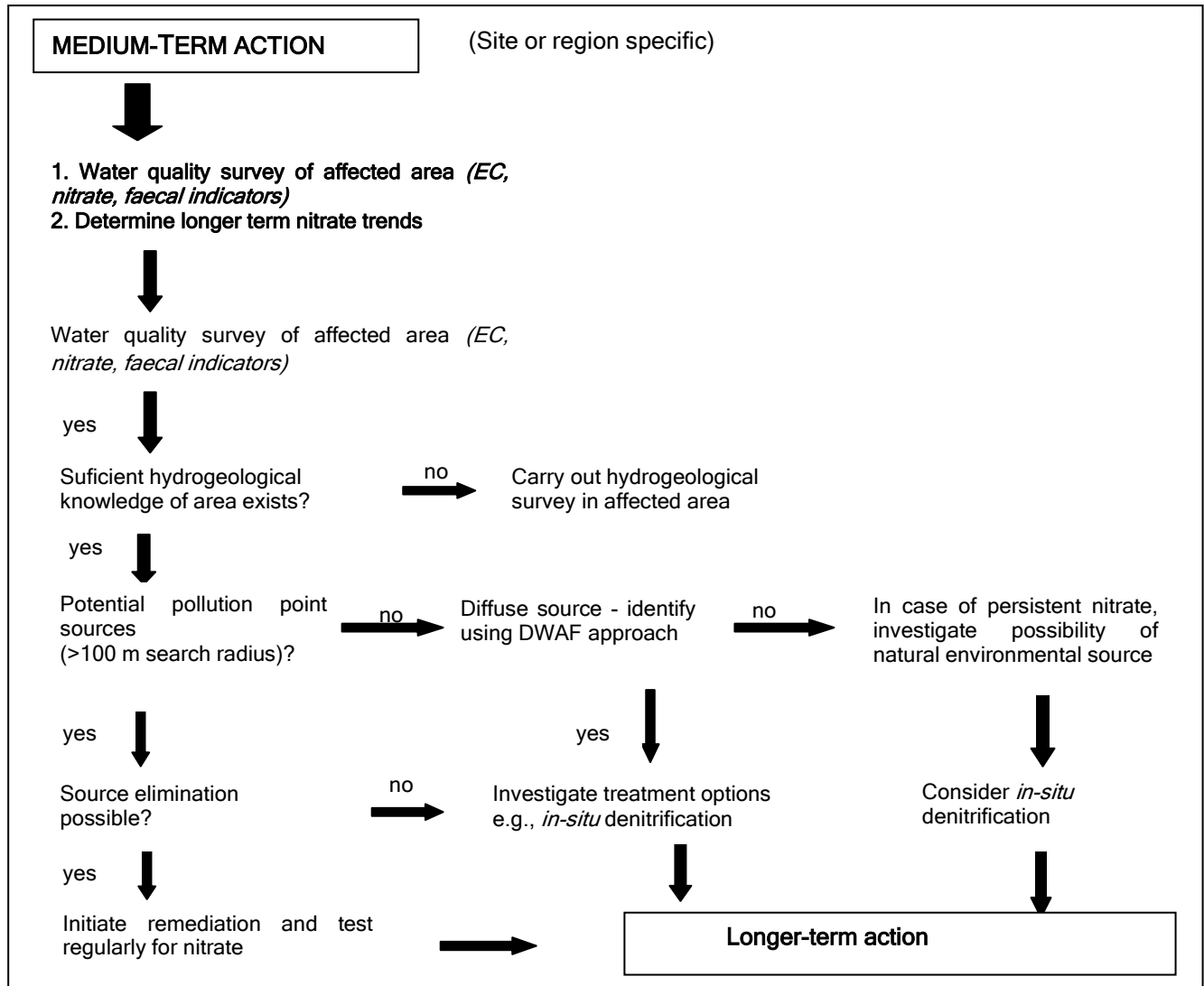
Figure 5-3: Groundwater nitrate strategy: Medium- term action situation (Source: Modified from Tredoux, 2004)

5.4.3 Long-tem action

Should the nitrate concentration exceed the recommended potability level of 6 mg/L, and pollution sources can be identified, further action may be needed, such as relocation of the well or borehole, longer-term monitoring of the nitrate levels. In the case of regionally elevated nitrate in groundwater, Tredoux (2004) noted that other measures may be needed for which expert advice should be sought. For example increase nitrate levels after high rainfall events in USA, Botswana, Namibia and South Africa.

LONGER-TERM ACTION   (Water Management Areas - CMAs, DWAF)

1. Classifying resource i.t.o. NGA requirements
2. Set management class
3. Set Resource Quality Objectives (RQOs)

Important current / future uses? — no → Implies that RQOs are met or that alternate sources are available

yes ↓

Vulnerable to pollution? — no → Avoid any action that may increase vulnerability

yes ↓

Determine present status and trends in comparison to reference conditions. Degraded? — no → Implement RDM well-head and well-field protection programmes

yes ↓   no ↗

Risk assessment to prioritise pollution sources. High priority?

Apply cooperative governance in future land-use authorisations

Longer-term monitoring and assessment (are RQOs being met?)

yes ↓

Apply relevant remediation and source directed controls: for example, statutory minimum requirements; incentive programmes; BMP guidelines (for sanitation)

Figure 5-4: Groundwater nitrate strategy: Long-term action situation (Source: Modified from Tredoux, 2004)

The control measures for pit latrines in drinking water catchments proposed by Howard (2006) range from planning the choice of site and sanitation technology in relation to aquifer vulnerability and socio-economic criteria to specific design and construction criteria for sanitation facilities. Selected examples are summarised below in Appendix H Table 1.

As discussed, monitoring and verification of the control measure implemented is crucial to ensure that they are in place and are effective. Appendix H Table 1 therefore includes options for surveillance and monitoring of the control measure examples given. Most of these focus on checking whether the controls are operating as intended, rather than on contaminant concentrations in groundwater: In the context of planning, surveillance will address whether plans exist and how they took criteria for siting and set-back distances in relationship to aquifer

vulnerability into account. Monitoring will address whether these criteria are being adhered to and plans are being implemented, for example, by site inspection to check the location of sanitary facilities and the depths of pits and sewers during their construction.

Monitoring programmes are important to verify comprehensively that contaminants from sewage are not contaminating aquifers used for drinking-water abstraction (that the management concept for the catchment is adequate and safe). With respect to human and animal deposits, this would typically include faecal indicators and potentially pathogens of particular concern in the respective setting. Where sewerage is contaminated by a range of chemicals from household use and connected enterprises, monitoring overall groundwater safety would occasionally address these contaminants (Howard, *et al.*, 2006).

5.5   Management strategies for the present Thaba Nchu groundwater quality

The water supply boreholes in the Thaba Nchu villages belong to Bloemwater and personally by the villagers. Most of the Bloemwater boreholes have a safe distance from contaminant sources (Appendix D Table 1) except SP and RT1 are very close to these sources. Therefore, these boreholes have to be relocated and treatment options must be considered. The positive actions carried out are the mixing of groundwater pumped from different boreholes and distributed for consumption (RT1 and RT2, YOX1 and YOX2, GD1 and windmill) and the chlorination for microbial elimination and frequent sampling analyses for nitrate and microbial contamination (all Bloemwater boreholes). Unfortunately, water levels could not be measured and aquifer parameters could not be calculated which would have shed more light into the vulnerability of the aquifer and determining their RQOs (Resource Quality Objectives). Most of the boreholes in the villages are much more polluted and their remediation should target their respective pollution sources such as in-situ denitrification. The set-back distance proposed by Xu and Braune (1995 cited in Vinger *et al.*, 2012) of ≥ 50 m from a pit latrine to a groundwater source does not apply in this study for some boreholes. 42.3 % of the total number of boreholes (GD1, GD2, BAL1, BAL3, KL, NP1, TW1, YOX1, YOX2, RT1 and MPS) is within the acceptable nitrate potability level with the boreholes > 50 m away from pit latrines, 30.7 % (RT2, RT3, BAL2, GL1, GL2, GL3, NP2 and NP3) is located < 50 % from contaminant sources having unacceptable levels of nitrates, 15.3 % (WD1, WD2, NPS and YOX3) is < 50 m from pit latrines with very low nitrate levels, and 11.5 % (KOM, SP and TW2) is located > 50 m from point pollution sources having high nitrate levels. This extensively shows the heterogeneity of the aquifers, therefore, different management options are required.

6. CONCLUSIONS AND RECOMMENDATIONS

An intense literature review reflected the sources of nitrates in groundwater, effects on human and animal health and on the environment, nitrate pollution estimation methods and remediation options in aquifers. In addition, the literature review showed case studies of elevated nitrate concentrations that exceed the allowed nitrate concentration of 10 mg/L in groundwater. Though frequently resulting from anthropogenic pollution, several cases of elevated nitrate in groundwater have been reported, that are suspected to stem from natural sources.

The main aim of this study was to analyse the groundwater quality in southern Thaba Nchu in the vicinity of contamination sites which was achieved by identifying the major nitrate input factors and determining their extent, degree and distribution in groundwater.

In the present study, these nitrate loadings from various sources are incorporated by interpreting NO_3 isotope and concentration data in the context of local geohydrology and land use history. Nitrate pollution characterisation of the aquifer system in southern Thaba Nchu was achieved by acquiring data from 26 boreholes and one surface water sample in November 2011, March 2012 and May 2012. A complex distribution of nitrate was found in groundwater, with concentrations ranging from 0.05 - 468.95 mg/L from which groundwater hydro-geochemistry characterisations were comprehensively undertaken. The occurrence of high nitrate concentrations is very heterogeneous and cannot be singularly attributed to the main flow path, especially not in the investigated intergranular and fractured aquifer which is additionally affected by groundwater abstraction.

65 % of the groundwater samples collected in the southern villages of Thaba Nchu had nitrate concentrations that exceeded the maximum recommended limit of < 6 mg/L set by the Department of Water Affairs (DWA) drinking water standards. When nitrate concentrations were analysed, some distinct boreholes with high nitrates were recognised. These nitrate levels came from a variety of sources. The following conclusions can be drawn from this study:

The origin and fate of nitrate in the southern Thaba Nchu aquifer was investigated, and elevated concentrations were reported that were suspected to stem from anthropogenic sources. Pit latrines are the largest sources which account for 86 % of nitrate generated in the area. Successful management options should target these sources. Other sources must not be overlooked since these have local impacts and thus could be responsible for the elevated nitrate concentrations at certain receptors.

For regional groundwater flow solution, it was assumed that shallow groundwater levels are a subdued replica of topography based on Toth, 1963. Therefore, overlying groundwater flow patterns on the topographic map of Thaba Nchu, the boreholes that were vulnerable to contamination had a distribution of high nitrate concentrations with calculated groundwater flow directions down-gradient of the contaminant sources (SP, NP2, NP3 GL1, GL2, GL3, and BAL2). Also, boreholes NP2 and NP3 and GL3 experienced increasing nitrate concentrations from November to May. Although other boreholes did not experience changes in the respective rainfall events or in reverse order, it may be cancelled due to the heterogeneity of the systems.

NO_3 showed significant positive correlations with chlorides, sodium, potassium and magnesium from groundwater samples suggesting a common source for these contaminants, such as animal wastes, fertiliser, or domestic wastes. Other strong correlations with nitrate include Ca^{2+}, SO_4^{2-}, PO_4^{3-}, Br and Ca, Mg, Na, NO_3, Cl and SO_4. Other than with NO3-, other positive correlations are SO_4 with Cl, between Ca and Cl (0.99), Mg and Cl (0.97), Na and Cl (0.92), $CaCO_3$ and Cl (0.98), TDS and Cl (0.94) and EC and Cl (1.00). Negative correlation between NO_3 and HCO_3^- is explained by the heterotrophic denitrification process.

Environmental isotopes data (^{18}O and ^2H) for groundwater and surface water samples in the study area were analysed. Groundwater samples values ranged between -4.25 and 0.99 ‰ with a mean of -2.46 ‰ for $\delta^{18}O$, and between -29.16 to 3.25 ‰ with a mean of -16.04 ‰ for δ^2H. Plotted in the conventional $\delta^{18}O$ *versus* δ^2H diagram together with the Global Meteoric Water Line (GMWL) of Craig, 1961 which the equation is $\delta D = 8\ \delta^{18}O + 10$ and the evaporation line, the values deviate significantly from and lie below the GMWL with a best-fit curve of $\delta D = 5.35\ \delta^{18}O - 2.88$ and a correlation coefficient of $R^2 = 0.96$. This trend is due to isotopic enrichment caused by evaporation process that occurred before and during infiltration but also by probable mixing with enriched water. There are two groups of data with distinct isotopic signatures; local groundwater flow system exhibiting an enriched isotopic signature indicating groundwater mixture with surface water, shallow on-site sanitation or the water has undergone evaporation prior to recharge; and regional groundwater flow system with depleted isotopic signatures consistent with water that has recharged from higher elevation and/or under cooler climatic conditions. Nitrate has a less coherent distribution, suggesting either a non-conservative behaviour or more than one source.

When isotopic data for the 19 sampled boreholes were evaluated, many of the samples were found to plot in narrow, overlapping range that included nitrate from soils, nitrate from fertilisers and manure or septic waste as possible sources of nitrate in groundwater. Data from

this study indicated that a singular source of high nitrates could not be readily differentiated from other sources based on the δ^{15}N *versus* δ^{18}O values of nitrate alone. Available historic land use and supplementary groundwater chemistry coupled with the isotopic analysis worked well together to get more distinctive picture of responsible sources.

On-site sanitation remains a viable, or only, option for vast parts of South Africa. Not all such practices lead to groundwater pollution, but in the wrong geohydrological and environmental conditions, the effects on groundwater can be disastrous. It is necessary to have a practical approach in this regard, but where sensitive and sole source aquifer systems are at risk, alternative sanitation options have to be found.

This study has identified a broad range of issues associated with the existing and future management of nitrate in groundwater in Thaba Nchu. The following recommendations are put forward to establish management actions, and to reduce gaps in our existing knowledge.

- Develop guidelines for groundwater protection zones around major potable water supply areas specifically focusing on nitrate sources;

- Develop suitable groundwater monitoring networks in key areas where nitrate contamination from existing land use is already known. Typical priority areas based on the nitrate map prepared for this study include Balaclava, Gladstone, Kommissiedrift, Noga's Post, Rietfontein, Springfontein and Tweefontein;

- An emphasis should be placed on fully categorising the extent of nitrate pollution laterally and vertically;

- Establish techniques for identifying risk to groundwater from nitrate pollution such as risk mapping in areas where there is broad area nutrient loading and development of a 'pollution index' for more localised nitrate source management, for example, point sources, taking into consideration factors such as watertable depth, lithology, groundwater flow system and groundwater beneficial use.

- Establish research into denitrification of nitrate, including determination of the key processes and conditions allowing denitrification. The relationship of denitrification to climate is an important issue.

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Appendix A

Sampling locations

Appendix A Table 1: Sampling locations

SiteName	Xcoord	Ycoord	Comments
BAL1	26.9732	-29.3803	Bloemwater, sampled once
BAL2	26.9895	-29.3978	Sampled twice
BAL3	26.9902	-29.4004	Bloemwater, sampled once
GD1	26.9241	-29.3804	Bloemwater, sampled once
GD2	26.9173	-29.3808	Hand pump, sampled thrice
GL1	26.8366	-29.3645	Handpump, sampled thrice
GL2	26.8359	-29.3625	Hand pump, sampled thrice
GL3	26.8395	-29.3602	Hand pump, sampled thrice
KL	26.9778	-29.5190	Bloemwater, sampled twice
KOM	26.7692	-29.3107	Hand pump, sampled thrice
MPS	26.7634	-29.3146	Merry-go-round, sampled thrice
NPS	26.9384	-29.4215	Merry-go-round, sampled twice
NP1	26.7820	-29.3587	Bloemwater, sampled once
NP2	26.7857	-29.3550	Hand pump, sampled twice, dry in May
NP3	26.7860	-29.3545	Hand pump, sampled twice
RT1	26.9371	-29.4236	Bloemwater, sampled once
RT2	26.9417	-29.4251	Bloemwater, sampled once
RT3	26.9386	-29.4262	Hand pump, sampled thrice
SP	26.9070	-29.4288	Bloemwater, sampled thrice
TW1	26.9378	-29.3770	Bloemwater, sampled twice
TW2	26.9414	-29.3797	Merry-go-round, sampled thrice
W2/1	26.8197	-29.4036	Hand pump, sampled thrice
W2/2	26.8204	-29.4016	Hand pump, sampled thrice
YOX1	26.8497	-29.4171	Bloemwater, sampled twice
YOX2	26.8452	-29.4156	Bloemwater, sampled once
YOX3	26.8490	-29.4165	Hand pump, sampled thrice

Appendix B

Chemistry results of boreholes from the Department of Water Affairs (DWA)

and Bloemwater

Appendix B Table 1: Chemistry data from the Department of Water Affairs (DWA) (-1.0 implies no allocated value for the chemical parameter)

SiteName	DateTimeMeas	pH	EC mS/m	Ca mg/l	Mg mg/l	Na mg/l	K mg/l	TALK (HCO$_3$) mg/l	Cl mg/l	SO$_4$ mg/l	NO$_3$-N mg/l
BAL	9/30/2000 12:00	8.46	56	41.2	15.1	59.9	9.1	240.9	10.9	61.6	2.27
GD	10/1/2000 12:00	8.59	44.7	-1.0	4.3	0.5	100.4	0.85	8	0.27	0.27
GL1	10/5/2000 12:00	8.59	44.7	4.3	0.5	100.4	0.85	208.3	8	12.9	0.27
GL2	10/6/2000 12:00	7.76	75.6	32	2.8	136.5	1.65	275.4	29	30	5.59
GL3	10/7/2000 12:00	8.22	85.4	57.4	18.4	112.2	2.14	362.9	32.3	41.1	1.59
KL	10/10/2000 12:00	8.13	55.8	56.5	30.8	22.2	0.66	279.5	7.5	23.6	1.87
KOM	10/11/2000 12:00	8.82	40.3	4.2	1	85.3	0.39	130.6	26.4	22.1	0.5
NP	10/22/2000 12:00	8.25	56.4	20	2.7	101.1	0.36	170.2	54.9	24	2.29
RT	11/1/2000 12:00	8.18	67.9	40.1	20.5	77.3	24.8	326.6	11.1	23.6	2.56
SP	11/13/2000 12:00	8.14	85.9	62.7	20.2	100.1	5.67	280.7	73.2	38.7	12.1
TW1	11/20/2000 12:00	8.04	60	58.9	26.6	32.2	0.88	263.1	18.5	26.6	4.54
TW2	11/21/2000 12:00	8.1	48.4	41.8	27.7	22.8	0.84	226.1	7.8	13.3	1.29
W2/1	9/30/2000 12:00	8.08	59.8	41.6	13.8	72.6	2.27	292.6	7.4	15	0.06
W2/2	10/1/2000 12:00	8.19	70.2	55.8	11.2	85.3	2.5	349.1	8.3	18.2	0.11
YOX	10/2/2000 12:00	8.51	52.5	6.9	0.5	115	0.58	168.4	43.9	21.1	0.17

Appendix B Table 2: Chemistry data from Bloemwater (negative values imply that the measured parameters are very small in the sample(s))

SiteName	DateTimeMeas	pH	EC mS/m	Ca mg/L	Mg mg/L	Na mg/L	K mg/L	TALK (HCO$_3$) mg/L	Cl mg/L	NO$_3$-N mg/L	SO$_4$ mg/L
BAL	4/17/2001	8.26	54.10	42.49	18.32	64.30	8.68	280.00	21.00	2.06	22.00
BAL	5/2/2001	7.88	54.90	44.56	16.79	61.99	9.06	252.00	24.20	2.60	22.00
BAL	6/12/2001	7.99	50.70	37.70	14.40	54.62	8.57	251.00	20.30	1.93	20.40
BAL	8/21/2001	8.00	53.80	44.57	18.30	62.02	9.66	253.00	16.49	2.14	19.35
BAL	10/24/2001	7.91	50.80	40.54	15.86	57.77	9.18	255.00	18.30	2.20	21.00
BAL	11/7/2001	7.92	56.80	42.91	17.09	57.36	8.88	256.00	16.80	2.16	19.80
BAL	11/27/2001	8.05	56.00	40.87	16.17	56.01	8.25	253.00	19.90	2.35	21.10
BAL	12/11/2001	8.18	56.40	42.42	16.52	58.10	8.76	258.00	20.10	2.35	22.00
BAL	7/23/2003	8.20	57.30	41.20	16.50	61.30	9.81	267.78	17.08	1.78	20.20
BAL	8/20/2003	8.24	57.50	41.30	16.20	60.00	9.64	261.00	20.76	2.02	22.11
BAL	9/17/2003	7.80	57.50	43.80	16.70	59.70	9.98	266.00	18.99	1.82	22.33
BAL	10/15/2003	8.36	57.60	43.30	16.90	62.10	10.50	269.00	19.01	1.91	20.80
BAL	11/12/2003	8.06	57.30	44.00	16.80	62.90	10.00	268.00	18.51	2.07	21.80
BAL	5/20/2004	7.84	57.00	48.18	18.47	61.97	8.96	268.00	18.89	1.57	21.77
BAL	6/22/2004	7.61	54.10	40.85	17.58	44.07	6.22	233.00	14.37	1.49	16.40
BAL	7/23/2004	7.26	46.60	47.86	22.24	21.20	11.05	212.00	13.70	0.99	15.19
BAL	8/18/2004	7.84	46.40	44.63	21.03	20.79	11.43	216.00	10.66	0.75	13.44
BAL	9/15/2004	7.91	46.90	45.58	21.38	20.43	11.44	226.00	11.52	0.83	16.04
BAL	10/13/2004	7.75	45.90	49.00	22.60	21.10	12.50	225.00	10.18	0.64	13.75
BAL	11/10/2004	7.87	47.30	43.15	20.13	18.58	11.32	221.25	9.68	0.67	14.17
BAL	12/8/2004	7.59	47.80	44.04	20.34	19.50	11.37	230.17	9.70	0.76	13.95
BAL	1/12/2005	7.09	47.50	44.55	20.85	19.18	11.79	226.00	8.98	0.73	13.94
BAL	2/9/2005	8.10	47.60	46.98	21.41	19.97	12.90	229.30	8.54	0.72	12.48
BAL	3/9/2005	7.81	45.17	47.37	22.11	20.97	14.20	226.00	8.39	0.56	13.88
BAL	4/7/2005	7.85	47.70	49.26	22.74	21.17	14.43	232.00	8.77	0.60	14.09
BAL	6/1/2005	7.53	47.90	45.46	22.21	25.24	3.82	250.00	15.61	1.54	13.59
BAL	6/29/2005	8.05	47.30	44.76	20.71	19.08	13.31	247.00	8.82	0.72	14.70
BAL	7/27/2005	7.45	47.70	43.37	20.50	19.52	13.76	244.00	8.62	0.67	14.61
BAL	8/24/2005	6.53	43.40	42.79	19.86	19.29	13.79	229.00	9.01	0.69	14.50
BAL	9/21/2005	7.73	31.50	25.84	13.53	18.40	5.73	142.00	13.17	0.18	9.46

BAL	10/19/2005	8.04	47.70	44.53	21.02	20.30	13.90	236.00	9.17	0.69	14.65
BAL	11/16/2005	7.87	49.67	46.43	21.09	19.50	11.87	235.11	8.44	0.65	12.98
BAL	3/2/2006	7.57	48.60	49.65	22.94	21.36	13.19	236.00	8.05	0.66	14.46
BAL	3/30/2006	7.55	38.90	43.55	20.67	19.91	12.50	234.00	9.46	0.68	14.57
BAL	5/25/2006	7.27	45.80	49.46	22.73	23.24	12.91	237.00	11.03	0.81	15.87
BAL	6/21/2006	7.70	47.60	47.58	21.98	22.41	12.88	234.00	12.48	1.10	14.84
BAL	7/18/2006	7.49	44.70	52.22	23.90	23.86	13.77	235.00	12.81	0.87	15.35
BAL	8/29/2006	7.40	59.10	42.96	16.02	62.82	8.51	259.00	23.31	2.11	22.17
BAL	9/12/2006	7.52	34.70	45.05	17.38	69.25	9.73	265.00	25.19	2.13	26.25
BAL	10/11/2006	7.39	46.30	39.80	15.45	54.64	7.14	258.00	18.72	1.64	23.02
BAL	11/7/2006	7.41	54.00	45.91	19.33	48.83	4.83	240.00	21.96	1.94	20.74
BAL	12/5/2006	7.58	59.00	40.94	15.85	60.35	7.73	261.00	21.94	2.20	21.78
BAL	1/4/2007	7.29	58.60	40.07	15.68	60.83	8.41	257.00	22.30	2.04	22.00
BAL	1/30/2007	7.28	48.39	44.10	21.09	22.32	2.95	221.56	17.70	1.61	16.16
BAL	2/28/2007	7.41	50.07	52.15	22.58	23.28	11.67	228.00	15.37	1.06	13.45
BAL	3/28/2007	7.58	48.70	46.93	22.17	22.93	11.59	232.00	12.12	0.96	13.32
BAL	4/25/2007	7.34	50.00	47.37	22.27	22.55	11.57	240.00	11.16	1.17	9.44
BAL	5/23/2007	8.08	47.70	46.78	22.05	22.95	12.33	227.00	13.42	1.11	13.43
BAL	6/27/2007	7.27	48.20	42.01	20.00	17.23	9.77	220.00	11.98	1.42	14.05
BAL	7/17/2007	7.19	61.69	39.28	15.71	60.61	7.81	237.02	24.71	2.13	23.57
BAL	8/15/2007	7.28	48.21	42.89	20.54	21.86	10.86	220.00	13.00	0.12	9.74
BAL	10/11/2007	7.65	47.90	42.84	20.47	22.28	11.11	226.00	10.89	0.92	13.05
BAL	11/9/2007	7.36	47.54	45.37	21.42	21.57	10.46	220.27	10.03	0.89	13.58
BAL	12/5/2007	7.78	31.00	23.24	10.21	19.66	6.05	130.00	13.05	0.31	10.38
BAL	2/6/2008	7.43	47.10	40.00	18.17	20.63	10.22	219.00	11.28	0.92	14.84
BAL	3/5/2008	7.72	46.70	44.92	20.63	21.00	11.17	216.00	9.71	0.82	14.07
BAL	4/2/2008	7.75	46.10	43.11	20.39	22.72	11.47	214.00	9.89	0.73	14.75
BAL	5/14/2008	7.56	47.50	43.14	19.64	20.41	11.37	225.00	8.41	0.71	12.68
BAL	6/5/2008	7.48	48.00	42.58	19.34	20.65	11.93	225.00	13.62	2.05	16.38
BAL	7/9/2008	7.27	47.10	43.26	18.55	21.86	11.49	224.00	8.03	2.09	13.07
BAL	7/30/2008	8.23	31.60	40.79	21.20	18.79	14.68	208.00	10.01	0.85	15.42
BAL	8/26/2008	7.52	47.50	46.92	21.34	19.49	12.28	221.00	13.62	-0.04	16.38
BAL	9/25/2008	7.82	49.10	41.70	19.71	21.91	12.61	238.00	10.63	1.01	16.31
BAL	10/22/2008	7.41	48.10	46.36	21.22	22.62	13.69	238.00	8.21	0.16	6.13

BAL	11/24/2008	7.68	48.50	42.22	19.69	21.22	10.48	234.00	11.35	1.05	16.43
BAL	12/8/2008	8.60	60.70	9.48	3.23	146.29	0.37	260.00	27.99	0.35	25.66
BAL	1/5/2009	7.90	48.10	49.52	22.34	23.22	11.09	240.00	10.46	0.85	15.59
BAL	2/3/2009	7.94	47.70	44.51	20.48	20.79	12.51	234.00	10.23	0.87	15.32
BAL	3/3/2009	8.07	48.70	49.97	22.58	23.66	13.40	238.00	10.92	0.93	15.66
BAL	3/31/2009	8.01	48.20	46.06	21.02	21.66	13.06	238.00	9.66	0.69	15.06
BAL	6/2/2009	7.97	48.80	42.67	19.73	22.83	9.13	235.00	9.84	0.68	14.63
BAL	7/14/2009	7.65	48.30	46.47	21.16	22.41	13.26	235.00	10.37	0.65	15.64
BAL	8/24/2009	7.85	58.60	40.58	15.62	63.76	9.40	267.00	20.17	1.70	22.33
BAL	9/21/2009	7.50	57.70	47.06	17.77	66.92	10.23	266.00	20.48	1.92	21.06
BAL	10/22/2009	7.56	57.20	44.67	16.88	63.82	10.27	260.00	18.17	1.64	18.28
BAL	11/19/2009	7.53	57.00	38.20	14.71	57.51	8.25	262.00	18.26	1.83	21.85
BAL	12/10/2009	7.67	51.20	42.13	16.23	59.87	9.36	262.00	18.69	1.81	22.13
BAL	1/11/2010	7.54	56.80	39.29	15.45	59.29	9.31	259.00	19.73	1.91	20.43
BAL	2/1/2010	7.76	55.50	36.56	15.95	54.82	9.20	255.00	18.03	1.89	20.92
BAL	3/8/2010	7.55	59.40	45.23	16.72	65.68	9.64	263.00	22.66	1.88	20.74
BAL	4/1/2010	7.32	48.30	48.41	21.75	28.61	4.08	221.00	17.38	1.58	15.83
BAL	5/6/2010	7.30	60.00	41.59	15.27	62.43	9.55	263.00	24.30	1.78	22.10
BAL	6/3/2010	8.14	56.70	44.18	18.08	55.09	8.03	254.00	23.56	1.82	20.21
BAL	6/28/2010	7.18	48.90	51.57	22.87	30.20	4.56	223.00	22.84	1.53	15.31
BAL	7/26/2010	7.58	51.40	45.59	19.65	36.38	5.70	235.00	20.49	1.78	19.05
BAL	8/26/2010	7.87	48.00	43.33	19.83	23.94	3.46	218.00	15.22	1.46	13.20
BAL	10/19/2010	7.30	57.00	40.24	15.40	52.78	8.29	254.00	18.99	1.68	21.53
BAL	11/25/2010	7.94	56.40	36.33	14.18	54.02	8.66	241.00	18.82	1.74	20.55
BAL	12/8/2010	7.60	56.90	48.04	15.12	61.44	11.30	257.00	17.15	1.68	19.59
BAL	1/18/2011	7.50	56.60	39.82	15.50	55.47	8.92	248.00	22.12	1.71	20.66
BAL	4/7/2011	7.30	45.00	33.45	13.02	46.60	6.69	210.00	16.61	1.43	13.87
GD	4/17/2001	8.05	39.50	41.27	24.94	18.96	0.52	198.00	10.50	1.70	10.10
GD	5/2/2001	7.94	40.30	42.00	23.12	18.57	0.46	204.00	10.90	1.61	9.10
GD	6/12/2001	7.66	37.30	36.99	19.73	17.46	0.53	196.00	11.20	1.81	8.90
GD	8/21/2001	7.53	40.00	41.49	23.08	17.60	0.37	191.00	9.66	1.16	8.21
GD	10/24/2001	7.67	36.50	38.83	20.86	18.22	0.55	194.00	10.10	1.54	8.50
GD	11/7/2001	8.02	41.30	40.62	22.42	17.92	0.50	198.00	9.30	0.45	8.00
GD	11/27/2001	8.03	41.30	41.22	22.37	18.23	0.56	198.00	10.80	1.52	8.50

GD	12/11/2001	8.02	41.50	41.03	22.18	17.91	0.54	203.00	10.50	1.34	8.60
GD	7/23/2003	7.71	36.60	37.80	19.60	17.60	0.61	192.56	7.28	0.48	5.84
GD	8/20/2003	8.07	36.80	36.60	19.90	17.00	0.45	193.00	7.15	0.50	5.92
GD	9/17/2003	7.79	36.80	38.20	20.60	18.00	0.58	195.00	6.83	0.46	5.82
GD	10/15/2003	8.32	28.10	38.40	20.60	17.30	0.56	197.00	8.17	0.53	5.76
GD	11/12/2003	8.32	36.90	39.40	20.70	18.60	0.87	196.00	7.47	0.50	6.07
GD	1/7/2004	7.40	37.60	35.20	19.32	16.50	0.74	195.00	7.87	0.50	6.16
GD	2/4/2004	7.55	37.90	36.58	20.29	17.79	0.67	196.00	7.17	0.57	6.23
GD	3/3/2004	8.13	29.10	22.97	11.23	20.82	5.98	123.00	14.64	0.25	9.28
GD	4/30/2004	7.82	37.40	34.32	18.69	16.09	0.48	193.00	7.50	0.65	6.30
GD	5/20/2004	7.74	37.10	37.52	20.28	19.15	0.60	194.00	7.08	0.61	6.27
GD	6/22/2004	7.48	37.20	33.81	18.69	14.84	0.39	180.00	7.81	0.67	6.58
GD	7/23/2004	7.16	36.90	33.39	19.32	14.86	0.48	176.00	8.47	0.74	6.67
GD	8/18/2004	7.89	36.30	36.98	20.32	17.12	0.48	190.00	8.78	0.92	7.20
GD	9/15/2004	7.21	37.60	38.81	21.34	17.40	0.52	186.00	8.79	0.79	7.02
GD	10/13/2004	7.86	37.00	38.50	20.60	16.60	0.40	190.00	8.64	0.84	7.32
GD	1/12/2005	7.05	37.90	35.70	19.64	15.87	0.46	183.00	8.60	0.10	7.43
GD	2/9/2005	8.00	38.00	38.01	20.69	17.44	0.53	186.10	8.24	1.01	6.76
GD	3/9/2005	6.90	37.40	36.60	20.00	18.85	0.65	188.69	8.40	1.05	7.69
GD	4/7/2005	7.63	39.30	41.21	22.18	18.44	0.55	195.00	8.49	0.99	8.01
GD	6/1/2005	7.47	40.20	38.79	21.28	18.88	0.60	213.00	9.24	1.16	8.51
GD	6/29/2005	7.45	39.60	39.98	19.32	17.32	0.58	206.00	9.00	1.26	8.36
GD	7/27/2005	7.79	39.40	38.31	20.91	17.88	0.71	199.00	9.11	1.33	8.45
GD	8/24/2005	6.14	38.20	35.84	19.42	16.37	0.62	197.00	8.93	1.25	8.35
GD	9/21/2005	7.96	31.20	24.44	12.88	18.06	5.57	142.00	12.98	0.17	9.51
GD	10/19/2005	7.80	39.60	36.22	20.03	17.07	0.58	195.00	9.28	1.45	8.46
GD	11/16/2005	8.64	56.71	8.30	2.15	118.82	0.48	230.79	29.40	0.02	18.38
GD	1/31/2006	7.40	40.70	40.62	22.02	18.09	0.41	195.00	9.38	1.17	9.01
GD	3/30/2006	7.50	42.10	39.61	21.93	17.49	0.46	207.00	8.81	1.17	9.78
GD	4/26/2006	7.24	36.40	39.12	20.77	17.35	0.53	200.00	9.09	1.35	9.25
GD	5/25/2006	7.31	40.70	42.15	22.72	20.87	0.72	200.00	15.57	1.40	10.11
GD	7/18/2006	7.47	40.60	41.62	22.55	20.14	0.70	198.00	10.49	1.51	10.19
GD	8/29/2006	7.50	40.10	39.59	20.44	18.60	0.47	197.00	11.17	1.52	9.13
GD	9/12/2006	7.27	40.80	40.47	21.85	20.49	0.64	197.00	8.54	1.40	9.15

GD	10/11/2006	7.19	41.50	35.99	19.25	16.15	0.02	194.00	8.25	1.20	9.50
GD	11/7/2006	7.43	40.70	40.20	21.51	20.66	0.40	193.00	11.96	1.50	10.66
GD	12/5/2006	7.45	40.50	37.21	20.12	15.57	0.38	194.00	10.06	1.52	9.52
GD	1/4/2007	7.07	40.10	36.99	19.96	18.19	0.48	190.00	9.54	1.23	8.73
GD	2/28/2007	7.14	40.68	41.54	21.30	19.28	0.01	191.00	9.60	1.07	8.38
GD	3/28/2007	7.18	39.00	40.11	21.48	21.04	0.51	192.00	8.12	1.02	8.06
GD	4/25/2007	7.26	38.90	37.62	20.50	19.28	0.61	189.00	8.23	1.53	13.51
GD	5/23/2007	7.27	38.80	37.35	20.55	18.46	0.55	188.00	8.40	1.03	7.93
GD	6/27/2007	7.03	39.10	34.90	18.40	13.85	0.21	185.00	7.79	1.15	8.84
GD	7/17/2007	7.16	40.56	35.96	19.79	18.03	0.50	170.98	9.46	0.86	8.05
GD	8/15/2007	7.23	38.98	36.75	20.30	18.75	0.59	186.00	13.37	0.12	9.47
GD	10/11/2007	7.79	38.90	35.44	19.81	18.62	0.46	189.00	8.17	0.92	7.62
GD	11/9/2007	7.17	39.56	38.17	21.17	17.84	0.31	187.81	7.93	0.93	7.85
GD	12/5/2007	7.67	25.10	18.25	8.45	19.55	5.33	108.00	9.31	0.21	9.42
GD	1/9/2008	7.15	41.00	38.60	18.22	19.34	1.08	198.00	8.88	0.88	8.18
GD	2/6/2008	7.48	39.80	34.40	18.31	17.57	0.54	188.00	9.14	0.99	8.67
GD	4/2/2008	7.32	40.50	37.61	20.71	19.43	0.53	189.00	8.98	0.91	8.74
GD	3/5/2008	7.27	39.50	38.25	20.37	17.71	0.50	186.00	8.42	1.04	8.20
GD	5/14/2008	7.35	40.50	36.82	19.66	17.38	0.53	194.00	9.33	0.93	7.77
GD	6/5/2008	7.24	40.40	37.99	20.26	18.01	0.54	192.00	9.21	0.81	7.89
GD	7/9/2008	7.05	41.00	36.97	21.07	19.25	0.84	191.00	7.94	0.35	8.53
GD	7/30/2008	7.63	41.00	36.08	27.29	16.37	0.75	193.00	9.57	1.16	10.01
GD	8/26/2008	7.33	40.60	40.96	21.60	16.85	0.37	190.00	13.10	0.32	10.93
GD	9/25/2008	7.51	41.30	39.34	22.00	21.18	0.75	200.00	10.33	1.45	10.66
GD	10/22/2008	7.24	40.10	39.09	21.07	20.39	0.77	199.00	14.68	0.54	12.86
GD	11/24/2008	7.39	40.40	36.59	19.63	15.82	0.66	198.00	9.27	1.42	9.97
GD	12/8/2008	8.60	60.30	9.66	3.27	144.69	0.36	260.00	27.98	0.33	25.77
GD	1/5/2009	7.43	40.10	39.84	21.09	19.83	0.47	201.00	9.54	1.37	10.16
GD	1/11/2010	7.33	41.10	38.45	20.87	20.79	0.81	199.00	10.78	1.49	11.32
GD	2/1/2010	7.39	41.10	37.57	22.57	19.28	0.64	200.00	9.84	1.43	10.69
GD	3/8/2010	7.27	41.80	43.98	22.15	21.09	0.79	202.00	9.95	1.29	11.00
GD	4/1/2010	7.29	41.70	40.66	21.05	21.85	0.79	199.00	10.81	1.37	11.09
GD	5/6/2010	6.90	42.20	38.91	19.51	18.24	0.72	204.00	9.60	1.17	10.63
GD	7/26/2010	7.28	41.50	40.24	21.44	19.22	1.15	198.00	11.43	1.42	11.00

GD	8/26/2010	7.90	42.90	36.11	17.55	27.06	0.70	198.00	14.89	1.21	10.20
GD	9/20/2010	7.38	40.70	28.16	14.08	38.27	1.16	189.00	10.33	0.96	10.09
GD	10/19/2010	6.99	40.80	37.97	19.50	16.91	1.86	192.00	9.76	1.30	10.05
GD	11/25/2010	7.61	40.00	35.02	18.87	16.67	1.19	189.00	9.41	1.13	9.10
GD	12/8/2010	7.20	57.90	53.13	25.40	26.21	0.89	226.00	30.58	5.12	23.11
GD	1/18/2011	7.27	43.40	41.73	21.01	18.32	1.51	205.00	10.69	0.97	9.50
GD	4/7/2011	7.22	42.80	18.28	7.09	80.86	1.44	202.00	11.07	1.07	9.45
KL	10/10/2000	8.13	55.8	-1.00	56.5	30.8	22.2	-1.00	7.5	1.873	1.873
KL	4/17/2001	8.10	44.50	45.20	27.07	22.14	0.84	206.00	14.40	3.48	18.60
KL	6/12/2001	7.81	49.70	52.18	27.93	23.62	0.62	269.00	11.30	1.94	25.30
KL	8/21/2001	7.67	52.70	57.33	31.66	22.50	0.41	260.00	9.92	1.30	27.09
KL	11/7/2001	7.75	54.60	55.91	31.22	22.51	0.58	261.00	9.20	1.07	27.00
KL	7/23/2003	7.89	57.10	56.60	29.40	32.40	0.65	269.90	14.78	1.37	29.13
KL	8/20/2003	8.39	53.70	54.20	30.10	23.20	0.52	257.00	11.11	1.45	27.77
KL	9/17/2003	8.09	55.70	56.00	30.80	23.30	0.53	275.00	10.77	1.42	27.25
KL	10/15/2003	8.37	55.90	58.80	32.60	24.50	0.60	274.00	11.64	1.54	27.03
KL	1/7/2004	7.84	57.30	54.62	29.82	29.59	0.79	271.00	13.76	1.60	28.36
KL	6/22/2004	8.04	55.50	51.42	28.56	24.11	0.47	255.00	14.77	2.78	25.26
KL	7/23/2004	7.70	55.50	58.47	33.25	27.51	0.48	261.00	15.13	2.91	24.81
KL	8/18/2004	8.14	55.80	54.89	29.80	27.81	0.55	248.00	16.32	3.00	24.26
KL	10/13/2004	8.06	55.00	56.20	29.90	25.20	0.50	251.00	15.70	3.66	21.70
KL	11/10/2004	7.33	56.00	52.02	28.00	24.55	0.58	248.13	19.86	4.01	24.44
KL	12/8/2004	8.03	57.40	50.98	27.14	24.90	0.60	242.10	18.25	4.28	21.69
KL	1/12/2005	7.22	44.00	41.48	22.87	15.63	0.53	200.00	6.70	1.34	19.30
KL	2/9/2005	7.40	43.30	41.95	23.20	17.24	0.49	195.00	8.47	1.32	18.59
KL	3/9/2005	6.99	42.20	42.07	23.04	18.78	0.66	200.00	7.55	1.34	21.38
KL	4/7/2005	7.39	43.50	39.86	21.86	18.88	0.56	206.00	7.32	0.08	20.10
KL	6/29/2005	7.79	44.00	42.21	22.82	16.27	0.54	217.00	7.99	1.32	22.29
KL	7/27/2005	7.42	44.10	40.56	22.72	17.22	0.64	213.00	8.59	1.29	22.12
KL	10/19/2005	7.97	58.50	52.74	28.15	28.50	0.68	250.00	22.99	4.95	23.32
KL	11/16/2005	7.70	60.99	55.84	29.04	30.75	0.63	255.39	22.90	4.80	23.88
KL	1/31/2006	7.37	45.10	47.15	25.63	18.17	0.56	207.00	8.77	1.26	21.54
KL	3/2/2006	7.25	5.70	56.74	30.09	27.46	0.53	234.00	20.13	5.01	22.51
KL	5/25/2006	7.26	55.80	54.53	28.75	33.46	0.65	258.00	15.62	2.51	28.03

KL	6/21/2006	7.40	42.60	41.17	22.58	17.62	0.36	189.00	9.24	1.67	21.10
KL	7/18/2006	7.54	55.50	60.04	31.12	32.37	0.77	263.00	14.20	1.72	28.50
KL	8/29/2006	7.26	54.50	54.15	27.92	23.52	0.61	256.00	12.87	1.18	27.62
KL	9/12/2006	7.43	55.30	56.79	30.95	27.37	0.72	259.00	10.37	1.08	27.29
KL	10/11/2006	8.17	20.60	22.68	8.17	13.73	4.20	111.00	9.09	0.39	8.34
KL	11/7/2006	7.46	54.50	55.63	30.26	26.40	0.45	253.00	12.76	0.98	31.32
KL	12/5/2006	7.42	53.90	53.32	28.13	20.07	0.15	254.00	9.86	0.84	25.24
KL	1/4/2007	7.37	53.70	54.32	29.68	24.33	0.58	252.00	10.67	0.71	26.99
KL	1/30/2007	7.21	53.43	50.37	27.25	22.49	0.18	252.26	11.98	0.84	31.50
KL	2/28/2007	7.04	44.68	46.95	24.37	18.74	0.04	193.92	11.13	1.64	22.43
KL	3/28/2007	7.28	43.60	45.99	26.13	19.39	0.54	197.00	9.46	1.39	22.06
KL	4/25/2007	7.33	43.30	40.94	22.32	18.81	0.53	199.00	8.92	1.70	7.89
KL	5/23/2007	7.27	53.60	54.25	29.48	25.36	0.56	256.00	10.63	0.90	26.15
KL	6/27/2007	7.13	42.60	42.76	22.12	14.48	0.22	187.00	8.85	1.55	25.67
KL	7/17/2007	7.01	44.18	36.99	19.46	20.03	0.56	178.14	9.77	0.90	22.20
KL	8/15/2007	7.21	43.02	39.18	20.84	20.48	0.72	195.00	8.36	0.33	8.76
KL	10/11/2007	7.66	42.50	37.82	19.90	22.34	0.56	199.40	8.39	0.53	20.69
KL	11/9/2007	7.31	42.67	38.36	21.18	21.46	0.37	195.01	8.35	0.04	21.09
KL	12/5/2007	7.80	31.40	26.65	11.70	22.19	6.75	131.00	13.32	0.07	10.39
KL	1/9/2008	7.15	43.50	37.16	18.54	19.44	0.56	191.00	7.86	0.83	19.49
KL	2/6/2008	7.26	40.80	35.70	19.12	17.29	0.56	185.00	8.47	1.20	20.52
KL	3/5/2008	7.37	41.40	38.81	19.15	22.03	0.64	185.00	7.99	1.02	19.34
KL	4/2/2008	7.47	56.00	55.97	30.31	28.09	0.80	256.00	11.38	1.04	24.59
KL	5/14/2008	7.52	56.40	56.30	29.97	24.97	0.66	265.00	9.08	0.83	21.75
KL	6/5/2008	7.39	41.70	43.35	21.40	27.39	0.57	193.00	20.77	7.18	14.09
KL	7/9/2008	7.34	56.10	57.02	18.44	31.38	0.96	267.00	9.26	0.10	22.84
KL	7/30/2008	7.75	56.90	52.20	35.89	22.55	0.76	263.00	11.41	1.03	24.98
KL	8/26/2008	7.53	56.90	53.99	31.33	22.43	0.45	265.00	12.60	0.32	10.28
KL	9/25/2008	7.87	57.90	55.07	31.48	28.53	0.72	283.00	12.12	1.23	26.35
KL	10/22/2008	7.41	57.00	56.64	30.23	27.95	0.83	281.00	14.44	0.51	12.84
KL	11/24/2008	7.69	57.00	52.68	27.70	24.63	0.70	274.00	12.07	1.34	26.69
KL	12/8/2008	8.15	60.30	9.72	3.28	146.52	0.36	260.00	28.20	0.35	26.02
KL	1/5/2009	7.87	57.00	60.17	31.27	29.67	0.53	282.00	12.21	1.42	24.19
KL	2/3/2009	7.64	55.60	56.56	29.65	27.05	0.62	266.00	12.29	1.70	23.36

KL	3/3/2009	8.05	57.20	60.92	31.71	28.49	0.72	275.00	13.46	1.69	24.13
KL	3/31/2009	7.47	56.60	53.86	28.23	28.15	0.72	273.00	12.66	1.25	23.50
KL	6/2/2009	7.69	57.30	52.97	28.00	26.60	0.80	273.00	11.39	0.90	23.10
KL	8/24/2009	7.90	57.80	65.33	34.23	28.31	0.81	288.00	10.95	1.09	24.07
KL	9/21/2009	7.51	57.70	64.23	32.21	29.92	0.83	286.00	13.31	1.13	23.96
KL	10/22/2009	7.32	57.30	59.83	30.53	28.15	0.75	277.00	11.34	0.93	20.57
KL	11/19/2009	7.43	57.00	52.29	26.84	26.22	0.72	279.00	12.39	1.22	23.13
KL	12/10/2009	7.52	57.30	57.98	29.76	30.23	0.89	276.00	13.88	1.40	23.75
KL	1/11/2010	7.31	57.70	55.06	28.80	28.92	0.84	274.00	14.89	1.77	23.75
KL	2/1/2010	7.61	57.60	52.81	31.04	26.60	0.72	275.00	13.22	1.70	23.23
KL	3/8/2010	7.49	57.00	58.76	28.86	27.77	0.90	267.00	14.31	1.86	23.33
KL	4/1/2010	7.20	57.00	56.17	28.30	30.53	0.87	262.00	15.22	1.84	22.75
KL	5/6/2010	7.46	56.20	51.57	24.82	26.29	0.85	261.00	15.78	1.94	23.39
KL	6/3/2010	8.04	56.10	58.47	30.04	31.12	0.93	261.00	16.51	2.07	23.32
KL	7/26/2010	7.84	79.20	31.31	11.31	121.09	12.41	317.00	39.66	2.96	39.40
KL	8/26/2010	7.92	56.90	51.96	26.58	28.10	0.92	254.00	18.62	2.37	23.80
KL	9/20/2010	7.49	57.30	57.28	28.50	28.08	1.21	253.00	18.14	2.60	22.56
KL	10/19/2010	7.28	57.80	56.86	28.29	26.59	2.02	253.00	20.55	3.17	23.07
KL	11/25/2010	7.92	56.50	47.91	24.36	27.67	1.35	242.00	21.27	3.10	21.32
KL	12/8/2010	7.60	87.30	34.91	7.44	147.99	3.09	227.00	117.00	4.67	33.94
KL	1/18/2011	7.61	90.30	32.25	10.25	135.64	3.37	222.00	118.94	5.41	31.26
KL	2/10/2011	7.61	98.90	39.63	11.63	148.07	3.59	228.00	147.62	10.99	36.80
KL	3/8/2011	7.85	106.00	48.90	15.06	168.22	4.17	252.00	153.00	11.45	49.59
KL	4/7/2011	7.74	104.00	48.90	15.06	168.22	4.17	229.00	155.00	12.69	53.00
RT	8/21/2001	8.42	72.40	33.09	13.96	129.52	13.74	304.00	35.80	4.08	36.13
RT	10/24/2001	8.15	67.80	32.04	11.81	131.45	12.53	319.00	40.60	4.90	39.20
RT	11/7/2001	8.44	76.90	34.84	13.72	117.53	12.98	318.00	38.70	5.06	37.02
RT	12/11/2001	8.54	77.30	35.37	13.19	119.58	12.68	320.00	36.90	4.98	34.90
RT	8/20/2003	7.92	83.90	39.00	14.40	129.00	15.10	311.00	65.32	10.88	33.71
RT	6/22/2004	7.92	85.30	29.01	13.21	116.48	30.59	302.00	56.60	3.56	48.80
RT	7/23/2004	8.26	84.90	32.51	14.75	142.08	32.74	316.00	57.49	3.51	42.66
RT	8/18/2004	8.40	84.70	27.64	12.35	136.50	29.24	318.00	58.21	2.67	43.20
RT	9/15/2004	8.00	87.80	37.94	17.55	118.26	36.27	316.00	71.26	3.05	41.40

RT	10/13/2004	7.90	86.70	33.10	14.70	127.50	31.30	311.00	58.70	7.86	39.10
RT	11/10/2004	8.62	89.40	32.16	14.18	124.07	29.69	307.66	62.20	10.27	39.04
RT	4/7/2005	7.90	82.30	35.25	13.65	124.54	13.93	307.00	49.62	6.18	36.48
RT	7/27/2005	8.08	86.60	24.41	10.34	135.30	23.95	322.00	52.76	6.28	40.91
RT	9/21/2005	8.04	86.20	24.94	11.34	127.48	23.16	318.00	50.46	-0.05	38.64
RT	10/19/2005	8.22	91.30	33.52	15.25	124.89	32.51	314.00	58.96	13.47	36.79
RT	11/16/2005	7.95	89.67	31.49	13.72	135.03	26.28	311.98	53.27	9.09	33.13
RT	3/2/2006	8.05	83.00	21.45	9.50	150.79	21.02	310.00	43.75	3.39	39.41
RT	3/30/2006	8.11	79.50	21.36	9.78	137.78	21.86	312.00	57.40	5.21	44.80
RT	4/26/2006	7.98	79.50	19.53	8.52	151.15	19.20	312.00	54.32	3.79	47.78
RT	5/25/2006	8.02	81.40	22.01	9.56	154.93	20.02	312.00	53.70	6.59	40.00
RT	6/21/2006	8.09	78.60	20.28	8.84	151.80	19.94	313.00	48.08	4.06	39.82
RT	7/18/2006	8.18	82.30	22.64	9.92	160.56	21.47	313.00	47.44	4.64	41.25
RT	8/29/2006	8.08	82.80	20.25	8.36	142.11	17.63	307.00	52.07	4.96	35.79
RT	9/12/2006	8.01	82.70	22.15	9.56	140.89	20.57	308.00	47.31	5.95	38.80
RT	10/11/2006	7.90	87.90	28.35	12.31	127.40	20.02	306.00	44.83	7.87	37.51
RT	11/7/2006	8.01	88.10	24.23	10.35	153.80	17.09	303.00	69.73	10.89	40.86
RT	12/5/2006	8.15	85.40	22.48	9.49	151.44	17.82	308.00	52.66	6.51	39.89
RT	1/4/2007	8.06	85.20	19.85	8.44	142.49	16.79	307.00	50.09	7.00	36.63
RT	1/30/2007	8.01	85.10	18.10	8.08	150.64	16.33	306.19	51.70	6.73	39.53
RT	2/28/2007	7.71	98.93	34.98	13.74	168.18	27.13	299.37	73.00	18.33	30.60
RT	3/28/2007	8.15	84.60	21.05	9.22	172.88	17.63	309.00	48.24	6.41	38.20
RT	4/25/2007	8.02	84.80	18.40	7.91	151.68	15.36	306.00	48.01	11.06	9.20
RT	5/23/2007	8.01	84.40	17.60	7.68	142.45	16.84	305.00	48.33	6.94	38.04
RT	6/27/2007	8.06	88.80	16.80	6.92	141.29	14.58	302.00	46.95	5.67	44.27
RT	7/17/2007	7.73	85.08	16.12	7.08	143.09	14.07	275.27	37.80	8.38	35.80
RT	8/15/2007	7.80	96.99	35.68	16.71	135.36	29.22	312.00	68.30	20.66	30.05
RT	10/11/2007	8.31	88.20	18.72	8.03	165.23	18.02	303.40	54.00	11.20	35.53
RT	11/9/2007	8.06	83.75	19.12	8.12	147.26	15.84	303.65	43.61	5.48	37.98
RT	12/5/2007	7.86	31.00	24.30	10.72	21.64	6.42	129.00	12.87	0.28	10.33
RT	1/9/2008	7.95	85.80	19.75	8.27	147.00	20.03	300.00	49.85	6.76	39.03
RT	2/6/2008	8.03	92.80	25.51	10.86	137.28	21.77	297.00	61.10	14.62	31.85
RT	3/5/2008	7.94	90.60	26.69	11.28	151.59	22.76	296.00	63.40	14.29	36.68
RT	4/2/2008	7.59	93.50	35.18	16.26	145.64	31.27	292.00	62.00	18.38	32.24

RT	5/14/2008	7.84	95.10	47.55	21.24	126.45	37.79	297.00	90.53	24.08	34.14
RT	6/5/2008	8.11	85.40	25.34	13.19	134.80	20.16	292.00	60.84	18.00	25.15
RT	7/9/2008	7.60	93.70	32.43	16.99	136.72	27.43	295.00	62.00	15.35	30.80
RT	7/30/2008	8.25	87.70	27.93	15.84	131.74	30.95	297.00	55.96	9.20	37.88
RT	10/22/2008	7.98	88.60	27.53	11.40	142.35	24.34	316.00	52.25	8.90	32.82
RT	12/8/2008	8.65	60.80	9.14	3.15	142.30	0.33	261.00	27.95	0.38	25.52
RT	1/5/2009	8.24	83.70	21.45	8.64	149.75	15.04	324.00	46.34	5.57	39.19
RT	2/3/2009	8.00	92.30	26.15	11.56	155.50	23.10	314.00	62.00	14.63	35.68
RT	3/3/2009	8.45	83.70	21.44	8.80	155.79	17.22	319.00	47.93	5.28	39.92
RT	3/31/2009	7.78	91.50	29.58	13.40	139.72	25.06	314.00	60.70	12.79	34.23
RT	6/2/2009	7.99	91.60	28.92	13.11	135.79	25.48	306.00	58.00	12.31	32.56
RT	7/27/2009	7.93	86.30	27.81	11.73	140.78	23.64	314.00	51.56	8.17	36.35
RT	8/24/2009	8.67	85.70	28.42	12.50	146.45	24.33	315.00	51.39	8.51	36.92
RT	9/21/2009	8.05	85.00	25.80	10.76	152.85	20.87	314.00	50.21	7.05	37.61
RT	10/22/2009	7.85	90.00	27.98	12.10	146.94	24.86	310.00	71.53	11.80	31.87
RT	11/19/2009	7.95	91.80	28.65	12.72	134.09	28.09	312.00	62.00	13.17	33.02
RT	12/10/2009	8.15	86.30	22.26	9.68	143.61	20.88	315.00	55.45	8.36	37.36
RT	1/11/2010	8.12	83.80	21.46	9.47	146.58	20.33	315.00	49.39	5.59	38.52
RT	2/1/2010	8.23	82.10	16.86	8.01	159.50	15.48	318.00	43.64	3.60	38.59
RT	3/8/2010	8.04	31.30	25.85	10.72	161.09	25.21	307.00	60.28	11.40	35.76
RT	4/1/2010	7.63	88.10	24.49	10.39	157.78	26.70	305.00	56.00	10.27	36.36
RT	5/6/2010	7.53	81.10	21.49	10.09	153.78	26.70	309.00	61.85	5.58	37.22
RT	6/3/2010	8.04	81.60	20.52	8.89	151.47	18.18	309.00	61.15	5.13	38.11
RT	6/28/2010	7.66	83.30	25.44	11.20	145.56	22.30	307.00	48.85	7.32	37.10
RT	7/26/2010	7.88	79.10	32.39	11.60	125.66	13.02	316.00	40.11	3.06	39.90
RT	8/26/2010	8.06	78.70	29.24	10.63	129.02	12.08	311.00	39.08	3.77	35.23
RT	9/20/2010	7.89	82.00	21.08	8.87	133.48	19.60	308.00	43.79	4.54	37.94
RT	10/19/2010	7.87	81.40	18.43	8.07	144.43	17.50	309.00	44.02	4.37	38.74
RT	11/25/2010	8.04	74.20	28.62	10.55	114.44	11.37	281.00	35.25	3.51	33.30
RT	12/8/2010	7.96	81.40	25.22	7.80	155.32	24.57	311.00	43.69	3.77	34.44
RT	1/18/2011	7.91	82.90	24.51	10.46	130.40	19.81	302.00	43.48	5.29	39.66
RT	2/10/2011	7.75	89.80	34.97	15.39	138.84	27.56	300.00	58.68	11.95	33.73
RT	3/8/2011	7.90	82.60	37.85	12.63	147.10	12.59	336.00	49.68	3.87	38.31
RT	4/7/2011	7.97	79.50	35.95	12.22	135.10	12.59	296.00	44.35	4.39	36.90

SP	6/12/2001	7.91	97.00	83.88	34.82	106.91	8.46	258.00	155.00	24.30	40.00
SP	10/24/2001	8.01	87.40	73.80	23.37	108.02	7.55	262.00	108.00	16.17	43.00
SP	11/27/2001	8.10	100.70	81.66	31.09	99.23	8.41	253.00	145.00	23.20	38.40
SP	12/11/2001	8.40	123.00	92.57	35.21	106.68	9.30	261.00	194.00	28.27	44.40
SP	7/23/2003	7.89	108.00	79.90	26.40	111.00	6.37	278.13	114.00	19.35	50.43
SP	8/20/2003	8.07	109.60	83.60	27.40	115.00	6.50	270.00	126.57	20.97	49.00
SP	9/17/2003	8.19	112.20	90.50	29.30	116.00	6.79	280.00	119.93	20.61	49.29
SP	1/7/2004	7.97	75.90	50.09	19.81	77.98	7.39	279.00	52.94	6.77	33.34
SP	2/4/2004	7.83	77.40	54.22	21.16	81.38	7.76	272.00	52.34	8.30	31.94
SP	4/30/2004	8.19	77.30	52.99	20.16	75.87	6.89	273.00	56.10	9.48	34.54
SP	5/20/2004	7.66	73.30	57.10	21.47	83.44	7.35	273.00	55.10	8.67	34.10
SP	6/22/2004	8.07	75.90	50.64	19.69	76.44	6.83	260.00	50.24	8.09	31.80
SP	8/18/2004	8.30	74.90	53.99	20.72	84.39	7.36	272.00	54.36	8.38	34.47
SP	9/15/2004	8.15	75.80	54.81	20.80	87.40	7.20	272.00	68.98	8.84	38.94
SP	10/13/2004	8.45	73.60	52.10	19.50	83.00	6.90	265.00	50.36	7.18	33.80
SP	12/8/2004	8.18	73.30	47.37	17.68	79.78	6.30	266.59	48.07	6.69	34.04
SP	1/12/2005	7.90	72.50	47.35	16.55	86.26	6.00	269.00	40.90	5.14	34.50
SP	2/9/2005	8.01	99.30	71.46	23.85	106.06	5.76	272.00	111.75	13.37	52.14
SP	3/9/2005	7.79	73.09	52.67	20.27	86.98	7.59	276.10	48.35	6.44	34.24
SP	4/7/2005	7.85	74.80	53.93	20.32	86.66	7.61	276.00	46.35	6.40	33.90
SP	6/1/2005	7.99	75.50	48.85	18.26	86.56	7.19	298.00	47.09	5.91	35.05
SP	6/29/2005	8.06	78.00	54.74	17.72	91.06	7.36	271.00	65.25	8.46	37.90
SP	7/27/2005	8.00	78.20	50.74	19.31	77.12	7.28	282.00	56.06	7.56	34.31
SP	8/24/2005	6.81	72.30	47.50	16.53	85.97	6.82	269.00	54.38	7.05	34.62
SP	9/21/2005	7.58	86.30	61.14	24.77	79.39	7.26	279.00	76.80	10.34	35.92
SP	10/19/2005	7.72	78.00	51.10	19.79	82.85	7.61	280.00	57.43	7.34	35.04
SP	11/16/2005	7.94	78.77	53.41	19.74	88.77	6.73	272.85	54.31	7.31	29.74
SP	3/2/2006	7.65	93.00	67.26	25.69	97.20	7.94	264.00	92.90	13.49	38.08
SP	3/30/2006	7.76	93.60	63.76	25.13	89.55	7.75	259.00	104.00	16.35	39.50
SP	4/26/2006	7.77	87.50	70.48	26.40	97.85	8.03	256.00	122.21	20.27	45.91
SP	5/25/2006	7.71	88.00	66.81	25.53	94.76	7.44	260.00	109.70	17.83	43.10
SP	6/21/2006	7.74	77.70	59.92	23.13	87.71	7.49	260.00	77.34	11.78	36.23
SP	7/18/2006	7.93	82.80	61.74	23.62	88.95	7.54	263.00	65.90	12.64	35.40
SP	8/29/2006	7.64	82.70	57.49	20.89	80.58	6.51	258.00	76.70	13.74	32.90

SP	9/12/2006	7.72	81.90	56.98	22.15	85.59	7.37	255.00	66.46	9.87	35.98
SP	10/11/2006	7.64	79.90	58.65	22.03	77.98	7.19	259.00	61.25	11.95	38.83
SP	11/7/2006	7.77	87.50	63.64	24.02	91.76	5.70	258.00	98.64	16.73	38.15
SP	1/4/2007	7.83	76.40	53.21	20.54	77.99	6.47	263.00	53.27	8.73	27.51
SP	4/25/2007	7.48	121.00	92.86	30.65	127.19	5.44	262.00	153.53	46.28	37.59
SP	5/23/2007	7.53	70.60	43.71	18.21	74.23	6.43	263.00	39.56	5.83	32.20
SP	6/27/2007	7.46	67.70	42.05	16.90	66.69	5.58	258.00	33.08	5.16	33.50
SP	8/15/2007	7.56	124.00	89.40	30.56	123.74	6.27	295.00	146.60	30.62	58.20
SP	10/11/2007	8.12	66.90	42.42	16.52	79.52	6.25	262.00	30.16	4.51	28.13
SP	11/9/2007	7.77	69.91	45.41	18.01	76.41	6.10	259.89	35.07	5.60	28.35
SP	12/5/2007	7.87	31.50	23.89	10.58	21.00	6.22	131.00	13.06	0.30	10.27
SP	1/9/2008	7.43	116.00	81.80	27.97	118.40	5.98	293.00	109.00	13.84	69.70
SP	2/6/2008	7.65	117.00	74.63	25.48	107.80	5.68	261.00	132.00	22.22	58.08
SP	3/5/2008	7.74	104.00	73.06	26.20	117.27	5.20	300.00	112.00	7.83	79.80
SP	6/5/2008	7.40	65.70	43.70	16.10	73.07	5.97	260.00	59.39	0.17	22.34
SP	8/26/2008	7.69	65.90	45.80	16.48	79.10	6.54	256.00	49.39	0.04	22.34
SP	10/22/2008	7.45	59.10	57.98	20.11	48.10	1.79	293.00	10.73	0.62	2.78
SP	12/8/2008	8.63	60.40	10.17	3.40	144.76	0.33	260.00	27.10	0.21	25.02
SP	2/3/2009	7.97	70.40	34.39	16.47	107.39	11.01	298.00	24.40	2.48	37.59
SP	6/2/2009	8.16	79.90	24.82	7.88	134.49	1.82	229.00	93.00	3.96	23.54
SP	7/14/2009	7.89	98.90	43.57	12.77	138.78	3.20	242.00	130.50	11.48	44.40
SP	7/27/2009	7.70	98.00	47.83	14.59	139.47	3.67	253.00	117.00	11.40	45.07
SP	8/24/2009	8.57	96.00	44.87	14.09	142.59	3.59	252.00	112.00	9.83	45.30
SP	9/21/2009	8.02	81.00	37.58	11.50	131.41	3.55	245.00	88.13	4.70	32.88
SP	10/22/2009	7.76	94.00	43.33	12.94	143.31	3.25	248.00	114.00	8.72	43.26
SP	11/19/2009	8.09	90.50	37.46	11.59	131.73	3.04	248.00	109.00	7.04	42.32
SP	12/10/2009	7.98	91.60	40.01	12.13	146.80	3.39	248.00	121.72	7.51	43.22
SP	1/11/2010	7.93	87.90	34.15	10.85	133.49	3.32	241.00	107.00	5.23	37.01
SP	2/1/2010	7.96	89.70	35.06	12.30	138.91	3.26	245.00	106.00	5.95	39.09
SP	3/8/2010	8.07	90.90	42.29	12.48	144.97	3.54	242.00	120.93	6.78	43.32
SP	4/1/2010	7.63	93.70	43.44	12.83	152.17	3.49	244.00	115.00	8.75	45.28
SP	6/3/2010	7.77	92.70	43.31	13.11	155.92	3.83	242.00	118.00	7.84	43.22
SP	6/28/2010	7.62	85.90	30.52	8.91	137.59	3.03	230.00	120.49	4.33	33.82
SP	7/26/2010	7.76	88.50	33.98	9.98	140.37	3.37	230.00	115.00	4.99	36.04

SP	11/25/2010	8.19	84.60	25.73	7.92	135.11	2.96	207.00	128.16	5.10	28.47
SP	12/8/2010	7.77	87.60	33.89	7.53	148.54	3.31	227.00	117.00	0.10	29.21
SP	1/18/2011	7.72	90.50	32.22	10.33	142.75	3.36	221.00	140.14	6.14	33.02
SP	2/10/2011	7.69	99.10	39.46	12.52	144.96	3.51	223.00	144.79	10.92	36.60
SP	3/8/2011	7.88	106.00	51.57	15.46	177.98	4.32	252.00	152.00	11.16	49.31
SP	4/7/2011	7.70	110.00	45.99	14.49	148.27	3.11	229.00	148.00	12.26	52.09
TW	4/17/2001	7.80	44.90	47.23	26.25	17.90	0.61	178.00	30.00	4.51	21.80
TW	5/2/2001	7.57	45.30	50.13	23.62	18.84	0.61	175.00	31.00	4.63	22.00
TW	6/12/2001	7.75	42.70	45.02	21.82	17.43	0.56	176.00	29.20	4.42	21.00
TW	10/24/2001	7.97	40.90	44.71	22.92	16.69	0.52	173.00	28.20	3.89	23.80
TW	11/27/2001	7.76	41.30	45.99	23.44	16.77	0.58	172.00	27.40	3.87	22.50
TW	12/11/2001	8.19	47.30	48.34	24.32	17.74	0.66	177.00	29.50	4.17	24.00
TW	7/23/2003	8.16	43.90	44.00	21.60	17.20	0.92	169.80	18.91	2.62	22.88
TW	8/20/2003	7.33	43.40	43.40	22.40	16.30	0.58	172.00	21.86	2.69	25.51
TW	9/17/2003	7.83	43.80	43.70	21.20	16.50	0.66	179.00	22.03	2.56	22.20
TW	10/15/2003	7.98	44.30	43.40	22.90	16.60	0.56	175.00	22.59	2.71	24.68
TW	5/20/2004	7.27	44.10	48.79	24.04	17.01	0.73	175.00	18.62	2.74	22.90
TW	6/22/2004	8.03	43.80	40.47	21.13	14.30	0.34	161.00	18.35	2.72	21.73
TW	7/23/2004	7.55	43.90	45.66	24.04	17.49	0.56	173.00	18.50	2.65	22.02
TW	8/18/2004	7.91	43.30	43.32	22.64	16.14	0.52	170.00	19.33	2.80	22.93
TW	9/15/2004	8.53	29.80	24.00	12.78	21.19	5.76	132.00	14.77	0.06	9.58
TW	10/13/2004	8.00	44.20	45.00	22.80	16.00	0.50	176.00	19.30	2.63	22.90
TW	1/12/2005	8.09	44.80	42.52	22.06	15.71	0.57	170.00	19.79	2.53	23.40
TW	2/9/2005	8.00	44.00	42.77	22.09	16.51	0.53	166.50	22.95	2.87	22.82
TW	3/9/2005	7.20	43.43	42.30	21.83	18.01	0.66	176.67	22.69	2.72	25.05
TW	6/1/2005	7.32	46.20	43.78	22.32	17.97	0.62	192.00	24.22	2.84	26.29
TW	6/29/2005	7.58	46.00	45.32	21.03	16.87	0.62	189.00	22.81	2.78	25.50
TW	7/27/2005	7.19	46.20	44.77	22.72	16.20	0.78	178.00	24.96	2.78	26.40
TW	8/24/2005	6.24	38.90	41.99	21.07	16.49	0.67	166.00	23.62	2.69	26.37
TW	10/19/2005	7.69	45.90	43.49	22.51	17.66	0.73	183.00	24.67	3.08	27.07
TW	11/16/2005	7.29	47.62	44.28	21.92	15.89	0.52	180.61	24.07	3.06	24.54
TW	3/30/2006	7.16	47.00	43.48	22.28	16.60	0.58	185.00	27.19	2.89	23.98
TW	4/26/2006	7.31	41.90	39.66	20.66	21.38	0.53	196.00	8.84	0.11	23.42

TW	5/25/2006	7.53	39.60	46.75	23.22	21.43	0.72	186.00	22.36	1.92	21.76
TW	8/29/2006	7.48	58.30	67.58	30.35	24.03	0.62	205.00	53.12	17.24	26.78
TW	9/12/2006	7.02	45.40	44.96	22.78	20.90	0.61	174.00	22.42	2.92	25.16
TW	1/30/2007	7.26	71.33	61.01	28.32	49.66	0.45	274.18	29.76	6.67	44.15
TW	2/28/2007	7.10	68.63	69.46	30.44	47.17	0.27	252.73	34.60	6.99	36.20
TW	3/28/2007	7.49	66.50	65.19	30.16	46.52	0.84	247.00	31.35	7.13	34.14
TW	4/25/2007	7.29	66.00	59.26	27.37	44.31	0.82	244.00	31.42	11.64	61.15
TW	6/27/2007	7.27	65.40	54.90	25.80	35.94	0.47	232.00	32.44	9.13	35.65
TW	7/17/2007	6.98	68.60	54.80	26.08	42.75	0.71	211.20	38.90	8.25	36.30
TW	8/15/2007	7.45	64.90	56.48	26.78	41.58	0.89	242.00	33.47	7.91	31.40
TW	11/9/2007	7.33	65.45	56.02	26.86	38.13	0.56	227.26	33.03	8.22	31.83
TW	12/5/2007	7.93	31.50	23.94	10.47	21.34	6.29	131.00	13.56	0.29	10.48
TW	1/9/2008	7.28	65.80	54.34	24.23	36.59	0.86	222.00	34.51	9.10	30.15
TW	2/6/2008	7.56	63.60	50.92	23.77	35.52	0.82	220.00	34.42	8.50	29.36
TW	3/5/2008	7.66	62.90	59.24	27.51	38.31	0.83	218.00	38.30	9.03	32.97
TW	4/2/2008	7.26	62.80	55.78	26.06	39.12	0.83	214.00	32.23	8.62	29.05
TW	6/5/2008	7.11	62.80	58.97	27.21	40.90	0.65	218.00	31.26	8.77	28.43
TW	7/30/2008	7.72	62.80	54.40	34.24	35.19	1.08	214.00	36.57	8.23	31.39
TW	8/26/2008	7.52	62.00	59.69	27.58	35.91	0.85	211.00	42.98	8.02	34.88
TW	9/25/2008	7.73	63.60	58.19	27.80	37.62	0.90	228.00	38.52	8.74	30.94
TW	11/24/2008	7.76	61.90	54.59	25.04	32.12	0.86	220.00	34.94	9.12	28.14
TW	1/5/2009	7.64	61.60	58.37	26.17	35.88	0.68	226.00	34.27	8.42	28.55
TW	2/3/2009	7.47	61.40	57.33	26.11	34.64	0.79	221.00	33.70	8.56	28.31
TW	3/3/2009	7.92	61.50	60.11	27.08	34.82	0.86	222.00	36.32	8.67	28.96
TW	3/31/2009	7.42	60.50	55.32	25.11	33.84	0.90	222.00	32.97	8.03	27.32
TW	7/14/2009	7.52	60.60	53.06	24.15	32.86	0.61	220.00	33.91	7.96	26.65
TW	7/27/2009	7.25	60.50	57.73	24.84	33.25	0.99	223.00	33.77	8.16	27.04
TW	8/24/2009	8.38	60.00	59.87	27.21	37.25	1.16	223.00	29.84	7.24	27.43
TW	9/21/2009	7.52	60.50	56.39	25.46	34.94	0.86	222.00	34.12	7.74	28.66
TW	10/22/2009	7.43	61.20	58.18	25.95	34.64	1.03	224.00	32.76	7.60	25.55
TW	11/19/2009	7.43	60.10	53.08	23.29	30.99	0.78	224.00	32.56	7.13	27.41
TW	12/10/2009	7.44	60.00	54.65	24.66	32.43	0.84	224.00	37.18	6.94	27.07
TW	1/11/2010	7.44	59.30	51.44	23.66	30.76	1.00	223.00	30.33	6.73	26.65
TW	2/1/2010	7.48	58.90	52.16	26.57	29.73	0.87	225.00	29.02	6.49	26.13

TW	3/8/2010	7.65	58.60	60.51	26.06	32.90	0.96	221.00	28.81	6.28	26.37
TW	4/1/2010	7.08	58.10	56.14	25.16	31.75	0.92	220.00	28.31	6.25	25.92
TW	5/6/2010	7.13	58.00	53.49	21.91	26.75	1.01	220.00	28.32	6.05	26.36
TW	6/3/2010	7.36	58.20	53.17	24.46	29.23	1.03	224.00	33.69	6.02	27.50
TW	6/28/2010	7.08	57.60	60.74	27.38	31.53	1.45	224.00	26.71	5.64	26.03
TW	7/26/2010	7.43	58.20	58.45	25.88	28.64	1.31	226.00	27.64	5.72	27.16
TW	8/26/2010	8.17	57.90	54.65	24.69	28.61	0.97	224.00	28.31	5.97	28.29
TW	9/20/2010	7.69	59.40	56.81	25.16	27.13	1.29	224.00	27.29	5.79	25.19
TW	10/19/2010	7.18	58.30	51.94	24.10	29.85	5.46	224.00	27.85	5.99	25.32
TW	11/25/2010	7.77	55.90	52.36	24.02	26.77	1.46	216.00	25.30	6.14	24.01
TW	12/8/2010	7.29	58.30	54.80	26.19	26.94	0.88	226.00	25.85	0.04	24.45
TW	1/18/2011	7.35	58.30	55.65	24.63	27.32	1.61	222.00	27.89	5.42	25.33
TW	2/10/2011	7.28	58.80	53.99	25.47	27.09	1.47	225.00	25.31	4.99	25.16
TW	3/8/2011	7.49	59.70	61.37	28.42	35.17	1.64	248.00	25.97	4.87	26.83
TW	4/7/2011	7.36	57.10	49.94	23.11	26.80	0.88	224.00	24.68	4.54	25.56
YOX	4/17/2001	8.15	90.30	90.48	30.36	92.55	2.43	402.00	40.00	2.54	62.00
YOX	5/2/2001	7.57	90.30	91.70	27.42	90.07	2.70	406.00	42.00	3.22	61.00
YOX	6/12/2001	7.86	80.00	88.72	29.07	90.61	2.36	396.00	36.00	1.63	65.00
YOX	8/21/2001	7.72	91.00	95.26	30.97	92.14	2.69	401.00	45.01	3.07	70.28
YOX	10/24/2001	8.22	88.80	99.09	33.86	94.99	2.72	446.00	44.90	3.94	61.40
YOX	11/7/2001	8.19	96.40	90.29	28.61	87.23	2.67	442.00	33.20	3.55	44.30
YOX	12/11/2001	8.44	100.10	97.45	30.98	91.08	2.57	460.00	36.60	2.70	60.00
YOX	1/16/2002	7.85	100.30	95.02	30.51	88.75	2.57	466.00	32.40	2.48	59.40
YOX	2/7/2002	8.61	97.70	97.75	30.13	93.25	2.60	482.00	29.60	1.64	59.90
YOX	3/6/2002	7.19	105.00	103.90	34.74	94.79	2.54	504.00	34.30	3.00	57.68
YOX	4/3/2002	7.94	98.90	96.26	31.56	90.48	2.54	481.00	30.92	2.80	48.73
YOX	5/29/2002	8.23	86.10	78.09	24.27	81.08	2.46	426.00	23.39	2.92	34.08
YOX	6/25/2002	8.00	82.50	76.01	23.80	79.65	2.62	422.00	21.70	2.94	30.60
YOX	9/18/2002	7.80	80.10	76.45	24.82	80.83	2.28	414.00	26.76	2.65	31.63
YOX	10/16/2002	8.32	82.70	77.37	23.03	81.01	2.22	413.00	27.53	2.36	39.45
YOX	1/15/2003	7.74	82.20	83.10	25.56	84.77	2.49	410.00	29.74	4.74	32.36
YOX	8/20/2003	7.57	78.50	70.90	22.20	81.80	2.52	375.00	32.51	4.78	28.72
YOX	9/17/2003	8.59	79.20	73.40	22.40	82.50	2.85	366.00	33.44	5.67	25.24
YOX	1/7/2004	8.31	77.80	65.12	19.52	85.91	2.75	328.00	44.04	6.24	24.17

YOX	3/3/2004	8.37	77.00	61.45	17.13	87.34	2.32	316.00	40.11	5.96	25.70
YOX	4/30/2004	8.41	75.20	57.86	16.02	80.18	2.20	312.00	40.20	6.19	27.56
YOX	5/20/2004	8.37	74.00	59.90	16.26	93.22	2.14	304.00	55.20	8.70	34.00
YOX	6/22/2004	8.50	73.30	52.81	14.50	84.22	1.78	288.00	41.00	5.95	24.70
YOX	7/23/2004	8.45	72.10	56.21	15.15	97.78	1.90	288.00	43.50	6.22	25.12
YOX	9/15/2004	8.56	74.90	62.85	17.93	92.50	2.37	305.00	52.03	6.70	27.81
YOX	10/13/2004	8.66	72.00	56.10	15.20	90.70	1.90	290.00	45.30	6.29	26.40
YOX	11/10/2004	8.51	71.60	48.75	12.86	89.40	1.81	273.92	47.77	4.93	28.03
YOX	12/8/2004	8.28	70.60	43.24	11.52	88.00	1.81	261.28	44.31	5.54	28.37
YOX	1/12/2005	8.19	71.80	49.47	13.28	91.07	1.74	270.00	57.98	6.67	29.30
YOX	2/9/2005	9.00	56.00	12.45	3.80	106.01	0.47	206.50	35.66	1.64	7.14
YOX	3/9/2005	7.70	77.55	63.52	18.81	90.82	2.55	304.50	50.09	8.61	33.20
YOX	4/7/2005	8.35	87.30	75.61	22.23	90.93	2.70	327.00	54.48	8.00	43.14
YOX	6/1/2005	8.04	66.40	62.39	21.78	73.60	1.12	302.00	38.49	1.76	27.48
YOX	7/27/2005	8.19	58.10	22.27	8.74	93.63	0.89	244.00	32.07	0.64	22.55
YOX	11/16/2005	8.60	39.50	27.21	14.35	29.88	5.24	172.51	15.28	0.44	11.16
YOX	1/31/2006	8.44	57.00	10.06	3.38	119.80	0.29	237.00	25.04	0.09	18.50
YOX	3/2/2006	7.91	62.00	30.92	12.95	98.75	0.69	260.00	28.01	0.35	23.80
YOX	3/30/2006	7.78	63.70	40.92	17.92	77.85	0.79	275.00	27.75	0.72	26.84
YOX	4/26/2006	7.79	59.10	27.51	11.35	99.27	0.58	252.00	30.91	0.16	24.90
YOX	5/25/2006	8.02	42.30	31.33	13.16	103.47	0.66	266.00	31.80	0.42	28.05
YOX	6/21/2006	8.18	58.30	19.89	7.78	111.96	0.37	245.00	28.90	0.29	26.79
YOX	7/18/2006	8.47	53.80	12.08	4.31	119.45	0.55	235.00	25.12	0.13	25.50
YOX	8/29/2006	7.98	59.40	22.48	8.76	97.24	0.67	249.00	29.29	0.42	23.69
YOX	9/12/2006	7.83	48.90	54.07	24.17	63.63	0.84	290.00	30.92	1.04	27.26
YOX	1/4/2007	7.92	61.60	27.65	11.68	92.50	0.49	257.00	29.90	0.71	19.53
YOX	3/28/2007	7.97	85.90	76.46	23.45	100.09	2.85	324.00	52.66	8.89	28.70
YOX	4/25/2007	7.87	24.10	19.30	7.64	15.93	4.38	91.10	16.57	0.70	8.21
YOX	5/23/2007	8.35	57.40	7.41	2.73	113.71	0.33	232.00	28.11	0.15	20.95
YOX	6/27/2007	7.93	66.40	33.43	12.63	90.14	0.53	254.00	36.79	2.93	25.57
YOX	8/15/2007	7.81	87.30	67.05	20.53	92.55	2.83	286.00	62.60	10.29	27.51
YOX	10/11/2007	8.49	61.00	14.15	5.35	122.70	0.42	240.00	30.69	0.44	24.39
YOX	12/5/2007	7.90	31.30	25.79	11.33	21.62	6.53	130.00	13.09	0.90	10.30
YOX	1/9/2008	8.39	60.90	8.67	2.99	120.21	0.41	235.00	26.53	0.10	21.95

YOX	2/6/2008	7.92	92.50	71.43	22.59	83.12	2.51	355.00	47.43	8.61	39.81
YOX	3/5/2008	8.26	70.00	36.46	12.07	111.03	1.07	279.00	36.95	3.01	29.17
YOX	4/2/2008	7.76	66.70	34.19	14.33	98.73	0.77	270.00	28.89	0.98	24.00
YOX	5/14/2008	8.44	61.40	21.76	8.29	113.13	0.53	257.00	24.83	0.33	24.91
YOX	6/5/2008	8.14	60.70	19.53	7.22	108.04	0.35	254.00	23.86	0.33	23.83
YOX	7/9/2008	8.18	60.60	25.29	11.64	108.68	5.78	255.00	25.64	3.85	22.04
YOX	7/30/2008	8.47	61.10	14.45	7.47	111.48	0.70	245.00	27.40	0.36	27.45
YOX	8/26/2008	8.37	59.80	15.10	4.77	121.47	0.20	242.00	32.26	0.14	27.02
YOX	9/25/2008	8.31	60.10	8.94	1.11	120.78	0.33	254.00	27.44	0.32	25.24
YOX	10/22/2008	8.32	60.80	9.17	1.95	129.87	0.43	255.00	28.40	0.35	26.00
YOX	11/24/2008	8.62	61.30	9.82	3.55	129.32	0.56	254.00	28.10	0.42	25.68
YOX	12/8/2008	8.64	60.70	9.98	3.34	131.15	0.34	260.00	26.65	0.20	24.21
YOX	1/5/2009	8.17	68.80	30.62	8.95	119.89	0.86	301.00	28.45	1.63	27.56
YOX	2/3/2009	7.88	77.50	51.03	15.69	107.56	1.54	329.00	32.18	3.49	30.49
YOX	3/3/2009	8.11	90.30	87.84	26.44	92.15	2.67	397.00	37.05	5.57	40.90
YOX	3/31/2009	7.73	88.00	76.87	23.60	86.25	2.63	387.00	35.90	5.48	33.27
YOX	6/2/2009	8.19	82.30	61.16	18.14	92.35	1.82	318.00	49.32	6.92	28.27
YOX	7/14/2009	7.99	71.60	45.54	15.53	88.95	1.23	280.00	40.95	3.29	30.14
YOX	7/27/2009	7.92	70.90	43.02	13.86	97.72	1.55	282.00	40.58	3.43	30.13
YOX	8/24/2009	8.75	60.50	15.63	6.18	117.57	0.65	251.00	25.93	0.22	29.42
YOX	10/22/2009	8.21	60.30	16.62	6.71	111.50	0.55	248.00	26.63	0.21	27.51
YOX	12/10/2009	8.13	74.00	46.77	14.11	97.36	1.89	305.00	39.42	4.18	28.22
YOX	1/11/2010	8.14	69.80	36.00	11.37	103.69	1.65	284.00	35.94	2.88	28.74
YOX	2/1/2010	8.14	67.60	35.67	11.69	114.22	1.26	281.00	33.19	2.31	28.22
YOX	6/3/2010	7.51	72.60	46.13	14.49	96.66	2.01	302.00	30.43	2.70	28.76
YOX	6/28/2010	7.19	80.60	66.51	19.66	83.42	3.41	350.00	34.41	4.93	25.87
YOX	7/26/2010	7.53	87.70	69.72	19.92	84.02	3.52	342.00	42.78	5.93	26.81
YOX	8/26/2010	8.33	72.70	43.53	12.56	100.12	2.13	302.00	39.28	4.13	27.14
YOX	9/20/2010	7.64	68.80	31.85	8.78	105.05	1.98	291.00	30.31	2.35	25.87
YOX	12/8/2010	7.65	87.50	33.70	7.27	148.88	3.26	227.00	120.00	4.60	31.43
YOX	1/18/2011	7.45	81.30	60.93	18.97	77.68	3.26	338.00	35.59	0.09	31.43
YOX	2/10/2011	7.42	75.30	68.79	26.40	59.15	2.49	308.00	30.26	2.49	35.68

Appendix C

Current chemistry data

Appendix C Table 1: Chemistry data for samples collected in November 2011 (-1.0 implies no allocated value for the chemical parameter)

SiteName	pH	EC mS/m	Ca mg/l	Mg mg/l	Na mg/l	K mg/l	TALK (HCO₃) mg/l	Cl mg/l	NO₃-N mg/l	Br mg/l	PO₄ mg/l	SO₄ mg/l	Total Hardness	TDS
BAL1	7.31	48.6	41.3	19.7	23.5	3.754	224	12.5	1.37	-0.04	-0.1	12.21	184	343
BAL2	7.54	108	59.9	19	129.7	3.701	256	132.9	30.71	0.9517	-0.1	14.46	228	753
GD1	7.24	40.2	37.4	20.6	19.4	1.123	183	9.4	0.64	0.5512	-1	3.43	178	276
GD2	7.82	23.2	11.8	4.4	27.3	2.17	108	7	0.17	-0.04	-0.1	0.9	48	238
GL1	10.1	60.4	1.5	0.2	104.3	2.25	231.8	48	-0.05	0.05	0.14	9.8	5	22
GL2	7.68	359	261.7	116.2	314.8	7.15	204	649.9	109.62	3.21	1.05	446.9	1132	5659
GL3	7.49	164	115.1	40	152.1	8.19	272	258.6	54.6	0.56	1.21	34	452	2260
KL	7.55	59.1	54.9	29.2	28.5	1.316	264	14	0.83	0.069	-0.1	30.97	257	427
KOM	7.23	109	44.2	12.5	159.7	4.2	229	147.4	18	-0.4	-1	19.1	162	809
MPS	8.6	61.4	39.4	37.9	30.9	2.62	219.3	46.9	7.44	0.37	0.18	42.8	254	1271
NP1	7.45	60.4	55.1	20.8	48.5	1.978	248	26.8	3.19	0.2291	-0.1	26.17	223	442
NP2	7.18	291	299.2	108.9	111.8	3.2	243	551	135.59	1.71	-1	91.97	1194	2010
NPS	8.62	107	27.1	31.5	132.2	44.7	372.1	97.9	6.8	-0.4	-1	38.47	197	753
RT1	8.1	87.3	21.6	9.6	161.7	19.243	318	59.6	7.52	0.1749	0.1022	39.92	93	664
RT2	7.79	92	44	18	129.6	17.742	298	84.5	11.22	0.512	0.1998	35.7	184	678
RT3	7.67	87.3	40.9	27.3	90.7	48.25	350	50.6	8.26	0.13	0.13	24	215	1073
SP	7.78	133	80.1	26.9	159.4	5	249	197.47	27.11	-0.4	-1	52.84	311	890
TW1	7.38	59.1	55.5	25.5	31.4	1.348	222	33.6	7.1	0.0821	-0.1	25.76	243	427
TW2	7.59	78.5	58	35.6	55	1.64	265	56.2	13.36	0.13	0.69	37.7	291	1457
W2/1	8.26	46.2	10	2.6	92.2	1.17	219	10	0.05	0.05	0.13	13.2	36	180
W2/2	8.18	56.1	23.4	5.3	96.5	2.03	256	20.3	0.47	0.07	0.22	17.8	80	402
YOX1	7.4	90.2	74.6	23.7	82	2.9	362	54	8.06	0.0946	0.1129	34.14	284	669
YOX2	8.04	64.9	25.1	10.6	109.7	1.154	244	49.7	2.21	0.1658	-0.1	26.47	106	478
YOX3	8.37	85	27.3	25.6	119.4	4.62	264.2	78.9	11.75	0.58	-0.1	49	174	868

Appendix C Table 2: Chemistry data for samples collected in March 2012 (-1.0 implies no allocated value for the chemical parameter)

SiteName	pH	EC mS/m	Ca mg/l	Mg mg/l	Na mg/l	K mg/l	TALK (HCO$_3$) mg/l	Cl mg/l	NO$_3$-N mg/l	Br mgl	PO$_4$ mg/l	SO$_4$ mg/l	Total Hardness	TDS
BAL2	7.15	71.7	51.8	15.1	93.5	3.9	178	69	20.7	0.58	-0.1	12.04	192	516
BAL3	7.67	51.1	37.2	14.8	61.6	3.4	231	18.6	1.08	0.18	-0.1	21.55	154	394
GD2	7.43	50.7	47.7	21	48.7	1.9	254	20.9	0.04	0.18	-0.1	5.78	206	401
GL1	7.86	121	59.4	8.8	213.7	1.4	198	137.4	46.34	0.74	-1	32.59	185	861
GL2	7.28	979	1025	344.8	739.3	12.6	302	1947.2	468.95	13.79	-10	819.76	3980	7294
GL3	7.75	116	70.4	25.5	127.5	8.2	141	196.5	25.77	0.77	-1	41.91	281	728
KOM	7.69	96.8	44.9	11.9	163.1	3.8	239	149	4.67	0.76	-0.1	33.71	161	677
MPS	7.99	72.2	85.5	45.1	27.3	2.4	299	39	7.35	0.3	-0.1	40.39	399	572
NPS	8.64	94.5	25.3	33.8	136.4	42.3	337.5	79	7.11	0.69	-0.1	43.19	202	715
NP1	7.63	57.8	65.3	26.2	36.2	1.3	252	24.3	3.58	0.2	-0.1	25.23	271	447
NP2	7.29	280	330.1	116.1	113.9	3.1	238	480.4	123.32	2.98	-1	93.39	1303	1923
NP3	7.26	302	334.1	86.6	161.2	2.5	122	611	137.43	3.77	-1	39.28	1191	1968
RT	7.69	86.5	53.2	29.9	83.5	45.2	340	48	8.27	0.42	-0.1	21.9	256	660
SP	7.7	129	76.9	25.2	176.8	4.6	250	180.3	23.43	0.92	-1	54.41	296	873
TW1	7.71	59.1	57.6	28.5	32.8	1.3	220	30.5	6.77	0.25	-0.1	25.64	261	427
TW2	7.25	68.6	69.4	37.5	39.2	1.4	236	46.7	14.87	0.41	-0.1	28.62	328	525
W2/1	8.12	95.3	54.8	14.4	122.7	2.5	255	126	9.35	0.76	-0.1	23.98	31	643
W2/2	8.21	44.2	9.3	1.9	84.9	0.8	204	9.3	0.15	0.12	-0.1	14.47	196	328
YOX1	7.87	94.5	78.6	23.1	99.1	3.1	328	81	11.52	0.66	-0.1	30.46	291	695
YOX3	7.33	94.4	44	22.5	120	4.3	249.77	107	14.55	0.86	-0.1	39.46	203	650
KL	7.55	59.1	54.9	29.2	28.5	1.316	264	14	0.83	0.069	-0.1	30.97	257	427

Appendix C Table 3: Chemistry data for samples collected in May 2012

SiteName	pH	EC mS/m	Ca mg/l	Mg mg/l	Na mg/l	K mg/l	TALK (HC0$_3$) mg/l	Cl mg/l	Br mg/l	NO$_3$-N mg/l	PO$_4$ mg/l	SO$_4$ mg/l	Total Hardness	TDS
GD2	7.72	44.8	36.3	16.7	47.4	2.15	217	20	<0.4	0.15	<0.1	2	159.1	342.3
GL1	8.41	109	30.2	4.8	214.2	1.51	161.4	136.5	0.08	37.57	<1	36	95.1	754.4
GL2	7.25	899	939.1	299.2	664.6	12.69	236	1929.3	<4	444.64	<1	752.7	3574.4	6791.5
GL3	7.35	134	98.3	32.5	152.5	9.54	172	229.1	<0.4	35.21	<1	41.4	379.2	889.8
KL	7.55	45.4	50.1	26.1	20.2	1.17	221	10.8	<0.4	0.88	<0.1	20.7	232.3	353.9
KOM	7.43	109	57.2	13.4	177.1	3.72	227	151.2	0.31	23.32	<1	33.7	197.8	765.9
MPS	8.32	66.7	70.3	40.3	30.8	3.06	262.3	41.5	0.23	7.3	<0.1	38.1	340.7	514.5
NP3	7.36	310	356.6	78.4	184.8	2.88	113	664	1.92	142.88	<1	41.3	1212.8	2073.9
RT3	7.53	86.6	55.3	29.4	90.3	49.15	334	50.2	0.3	11.3	<0.1	23.8	258.6	682.9
SP	7.92	106	51.4	16.2	171.3	4.03	238	157.1	<0.4	12.16	<1	43.3	195	735.4
TW2	7.7	68.2	65.4	32.6	41.2	1.57	224	49.6	0.27	13.3	<0.1	28.4	297.2	501.9
W2/1	7.81	96.4	69.1	19.2	148.1	3.35	260	146.2	0.66	9.37	<0.1	24.9	251.4	713.6
W2/2	8.17	43.5	14.8	3.4	99.8	1.45	209	11.1	0.09	0.06	<0.1	13.9	50.9	355.8
YOX3	8.36	84.2	34.1	18.9	142.4	4.05	219.8	114	0.74	10.02	<0.1	40.2	162.5	615

Appendix D

Location of on-ground nitrate sources

Closest distance from boreholes to on-ground nitrate sources

Appendix D Table 1: Location of on-ground nitrate sources: P = pit latrines, K = kraals and F = crop farms

SiteName	Xcoord	Ycoord	Zcoord
P1	26.8518879	-29.4136789	1536.3
P2	26.851026	-29.4139474	1531.7
P3	26.8509839	-29.4139402	1532.7
K1	26.8514007	-29.4143196	1526.7
P4	26.8511922	-29.415175	1523.3
P5	26.851176	-29.4152043	1523.8
P6	26.8504035	-29.4147477	1524.5
P7	26.8504053	-29.4147481	1524.3
P8	26.8504181	-29.4147296	1524.8
K2	26.8503579	-29.4147549	1524.8
F1	26.8493392	-29.4160028	1522.1
F2	26.8493409	-29.416004	1521.9
F3	26.8494981	-29.4161397	1520.7
K3	26.8492139	-29.4167713	1515.6
P9	26.8492184	-29.416768	1515.6
P10	26.8482212	-29.4158093	1523.1
P11	26.8482365	-29.4157777	1523.8
P12	26.8493479	-29.4160029	1524.3
P13	26.8489287	-29.4149515	1528.4
P14	26.8488735	-29.414958	1529.1
P15	26.8494966	-29.414273	1526.4
P16	26.8494833	-29.414239	1525.7
P17	26.8495079	-29.4142188	1526.2
P18	26.8494884	-29.4141961	1526.9
P19	26.8509447	-29.4139659	1531
P20	26.8509535	-29.4139674	1530.5
P21	26.8509646	-29.4139374	1530.5
K4	26.8509441	-29.4139236	1530.3
K5	26.8504075	-29.4137196	1529.1
P22	26.8504926	-29.4136255	1529.1
P23	26.8486577	-29.4136301	1529.8
P24	26.8486158	-29.4136493	1530.1
P25	26.8485981	-29.4136133	1530.1
P26	26.8485863	-29.4136311	1530.1
P27	26.8480181	-29.4143929	1532.2
P28	26.8479612	-29.4144019	1532.2
P29	26.8479552	-29.4144551	1531.7
P30	26.8479086	-29.4144446	1531
P31	26.8474374	-29.4151989	1528.4
P32	26.8473808	-29.4151948	1527.9
P33	26.8473582	-29.4151818	1528.4
P34	26.8472959	-29.4152049	1528.9
P35	26.8473061	-29.4151827	1530.3
P36	26.847134	-29.4160624	1526.7
P37	26.8468972	-29.4164632	1526.4
P38	26.8468768	-29.4164876	1526.2
P39	26.8468578	-29.4165235	1526.4
P40	26.8468363	-29.416552	1526.4
P41	26.8467989	-29.4167654	1525.7

P42	26.8468488	-29.4167001	1526.4
P44	26.823444	-29.4033588	1491.1
K5	26.8227315	-29.4026827	1489.2
K6	26.8227861	-29.402699	1489.9
K7	26.8228608	-29.4029124	1489.4
P45	26.8227773	-29.4029441	1489.9
P46	26.8227353	-29.4019002	1489.4
P47	26.8227302	-29.4019134	1489.4
P48	26.822604	-29.4015929	1489.4
P49	26.8223993	-29.4016487	1489.7
K8	26.8222419	-29.4015724	1489.2
K9	26.8222987	-29.4016873	1489.7
K10	26.8225065	-29.4008419	1489.9
P50	26.8224561	-29.4007334	1489.9
P51	26.822337	-29.4004523	1489
K11	26.8210296	-29.4010679	1482.5
P52	26.8213968	-29.4012873	1484.4
P53	26.8216069	-29.4016418	1489.4
P54	26.8214116	-29.4017301	1488.7
P55	26.8218191	-29.4020528	1486.1
P56	26.8226546	-29.4024652	1486.3
P57	26.8199686	-29.4033543	1488.5
P58	26.8197481	-29.4034729	1484.4
K12	26.8196129	-29.4032956	1486.8
K13	26.8196116	-29.4032956	1486.3
P59	26.8200087	-29.4014838	1488.2
K14	26.8200062	-29.4014786	1488.5
P60	26.8203512	-29.4016333	1483.7
P61	26.820349	-29.4016305	1484.2
P62	26.8198281	-29.4019483	1490.4
P63	26.8198672	-29.4021963	1489.7
P64	26.8366122	-29.3645242	1498.6
P65	26.8367655	-29.3648097	1511.8
P66	26.8367319	-29.3641736	1508.2
P67	26.8377808	-29.3634737	1511.3
P68	26.8356223	-29.3618224	1501.5
P69	26.8358406	-29.3619728	1500.5
P70	26.8378861	-29.3615818	1506.3
P71	26.8379588	-29.3614213	1502.9
P72	26.8383555	-29.3614466	1503.6
P73	26.9170555	-29.3795029	1554.8
P74	26.9171223	-29.379547	1560.1
P75	26.918319	-29.3801712	1559.4
P76	26.9199229	-29.3809361	1560.3
P77	26.9212446	-29.3815234	1560.6
P78	26.9414302	-29.3797153	1571.9
P79	26.9372599	-29.3754914	1586.3
K15	26.937215	-29.3754732	1586.3
P80	26.9369124	-29.3752943	1588.2
P81	26.9367047	-29.3752057	1587
P82	26.9362891	-29.3749728	1586
P83	26.9342007	-29.374704	1591.3

P84	26.9336762	-29.374602	1593
P85	26.9334556	-29.3744632	1592.8
P86	26.9331988	-29.3743456	1593.3
P87	26.9324199	-29.3747736	1596.6
P88	26.9321961	-29.3746824	1597.8
P89	26.9328236	-29.3751377	1596.9
P90	26.9334336	-29.3755115	1595.9
P91	26.9335949	-29.3755877	1595.7
P92	26.9340181	-29.375824	1596.4
P93	26.9350326	-29.3763986	1593.7
P94	26.9350365	-29.3765886	1592.3
P95	26.9363102	-29.3769401	1587.5
P96	26.9386258	-29.4262372	1599.7
P97	26.9385565	-29.426878	1600.7
K16	26.9385568	-29.4269361	1601.2
P98	26.9386776	-29.4269479	1600.9
P99	26.9387078	-29.4260732	1599
K17	26.9388543	-29.4260803	1599.7
P100	26.9069781	-29.4287774	1582.4
P101	26.9070578	-29.428933	1586
P102	26.9067463	-29.4301714	1583.2
P103	26.9064114	-29.4297846	1585.6
P104	26.9056685	-29.4295172	1584.1
P105	26.9049397	-29.4297662	1581.7
P106	26.9021843	-29.4271639	1578.8
P107	26.9029833	-29.4272774	1580.8
P108	26.9034431	-29.4267528	1584.1
P109	26.9033234	-29.4267196	1580
P110	26.9036464	-29.426545	1577.9
P111	26.97982	-29.52059	1622
P112	26.97982	-29.52058	1623
P113	26.97986	-29.52059	1620
P114	26.9799	-29.52061	1622
P115	26.97995	-29.52058	1623
P116	26.98001	-29.5206	1622
P117	26.98028	-29.52043	1621
K18	26.98947	-29.39777	1586
P118	26.9895	-29.39792	1589
P119	26.92262	-29.38091	1555
P120	26.92309	-29.38157	1564
P121	26.92313	-29.38164	1563
P122	26.92275	-29.38214	1563
P123	26.92275	-29.38215	1563
P124	26.92387	-29.38179	1564
K19	26.93708	-29.42352	1615
K20	26.93707	-29.42352	1613
P125	26.93713	-29.42368	1607
P126	26.93756	-29.42365	1599
P127	26.93792	-29.42377	1598
P128	26.93753	-29.42412	1600
P129	26.93752	-29.42414	1601
K21	26.94062	-29.42417	1601

P130	26.9408	-29.42426	1601
P131	26.94062	-29.42463	1603
P132	26.94059	-29.42465	1603
P133	26.94036	-29.4246	1604
P134	26.94044	-29.42426	1604
P135	26.76809	-29.312923	1495.98547
P136	26.768547	-29.313087	1448.98743
K22	26.768582	-29.313031	1449.77429
K23	26.768117	-29.312893	1449.87036
P137	26.766586	-29.312278	1448.42395
P138	26.766084	-29.31226	1450.68835
P139	26.764689	-29.312622	1447.84436
P140	26.76505	-29.313186	1444.07361
P141	26.762923	-29.314319	1439.25147
P142	26.762943	-29.31433	1441.64014
P143	26.764691	-29.311492	1448.01563
P144	26.766665	-29.311338	1447.32983
P145	26.766638	-29.311803	1449.05762
P146	26.768628	-29.311503	1448.10169
P147	26.770821	-29.311335	1452.08362
P148	26.770284	-29.311297	1453.62647
P149	26.769681	-29.310549	1454.92712
P150	26.768013	-29.311047	1451.40674
P151	26.767641	-29.310441	1451.59094
P152	26.766304	-29.310738	1450.23279
P153	26.764789	-29.310302	1451.23694
P154	26.764887	-29.310901	1448.91919
P155	26.76521	-29.309425	1451.85608
P156	26.76495	-29.310045	1452.01367
K24	26.765297	-29.309797	1452.99719
P157	26.767252	-29.309577	1453.23584
P158	26.769315	-29.310219	1452.34448
K25	26.769291	-29.310223	1451.29309
P159	26.77077	-29.309959	1451.75317
P160	26.77017	-29.310336	1453.31458
K26	26.770227	-29.310148	1452.00171
P161	26.771234	-29.309651	1452.24805
P162	26.771253	-29.309333	1452.92847
P163	26.770235	-29.309258	1453.31372
P164	26.784675	-29.356248	1458.57813
P165	26.784686	-29.356222	1456.68543
P166	26.786513	-29.356352	1463.08533
P167	26.785405	-29.356191	1458.60303
P168	26.78534	-29.35557	1457.17468
P169	26.785463	-29.354894	1458.98853
P170	26.786041	-29.355366	1459.59766
K27	26.785949	-29.355286	1457.74915
P171	26.785879	-29.354164	1457.35767
P172	26.786334	-29.354857	1460.2135
P173	26.786356	-29.354837	1458.34399
P174	26.7868	-29.352871	1458.58691
P175	26.786857	-29.353294	1458.82727

P176	26.787329	-29.355144	1461.37488
P177	26.787318	-29.354665	1464.50818
P178	26.787649	-29.35383	1463.2915
P179	26.787627	-29.353398	1465.44409
P180	26.78755	-29.352813	1462.07568
P181	26.788557	-29.353322	1468.40991
K28	26.788643	-29.353283	1469.21716
K29	26.790175	-29.354811	1475.34241
P182	26.790271	-29.353949	1473.39917
P183	26.790214	-29.353307	1476.52759
P184	26.790216	-29.353357	1475.76294
K30	26.790524	-29.349917	1474.57141
P185	26.79074	-29.349874	1474.99255

Appendix D Table 2: Closest distance from boreholes to on-ground nitrate sources

Boreholes	Closest distance to contaminant sources (m)
BAL1	2200.36
BAL2	17.31
BAL3	156.01
GD1	115.42
GD2	123.00
GL1	34.45
GL2	61.89
GL3	48.06
KL	262.23
KOM	46.54
MPS	52.14
NP1	372.75
NP2	25.46
NP3	43.61
NPS	24.78
RT1	115.08
RT2	7.67
RT3	19.70
SP	73.01
TW1	142.40
TW2	583.18
W2/1	13.09
W2/2	1.73
YOX1	58.57
YOX2	194.68
YOX3	38.20

Appendix E

Hydrochemical facies concepts for Piper and Expanded Durov diagrams
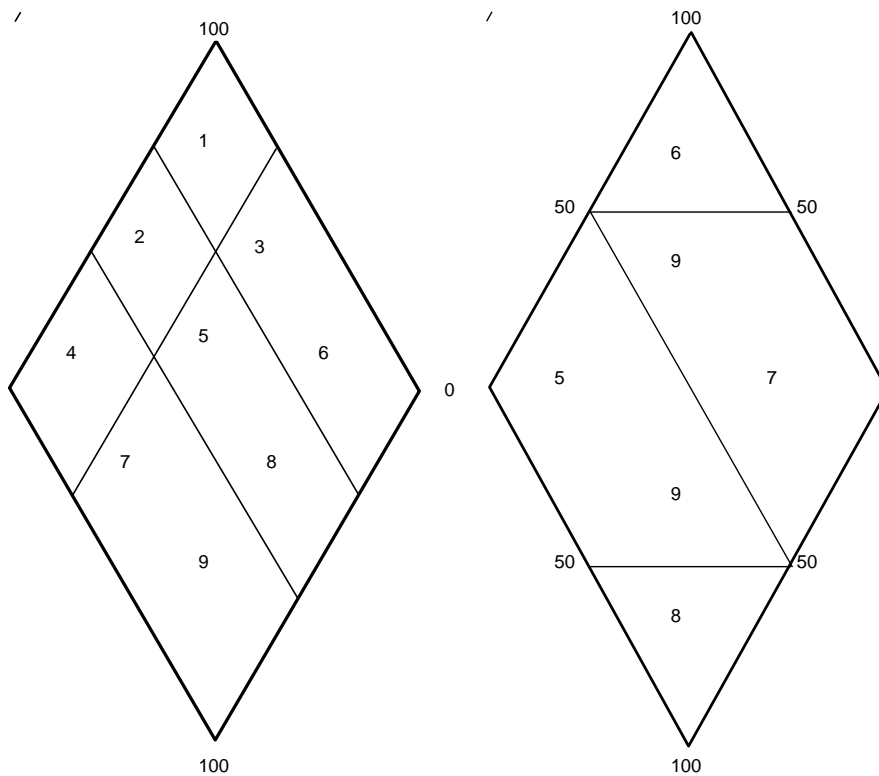
Appendix E Figure 1: Subdivisions of the diamond-shaped field of the Piper diagram (9 facies) (Source: Walton 1970, cited in Tank and Chandel 2009
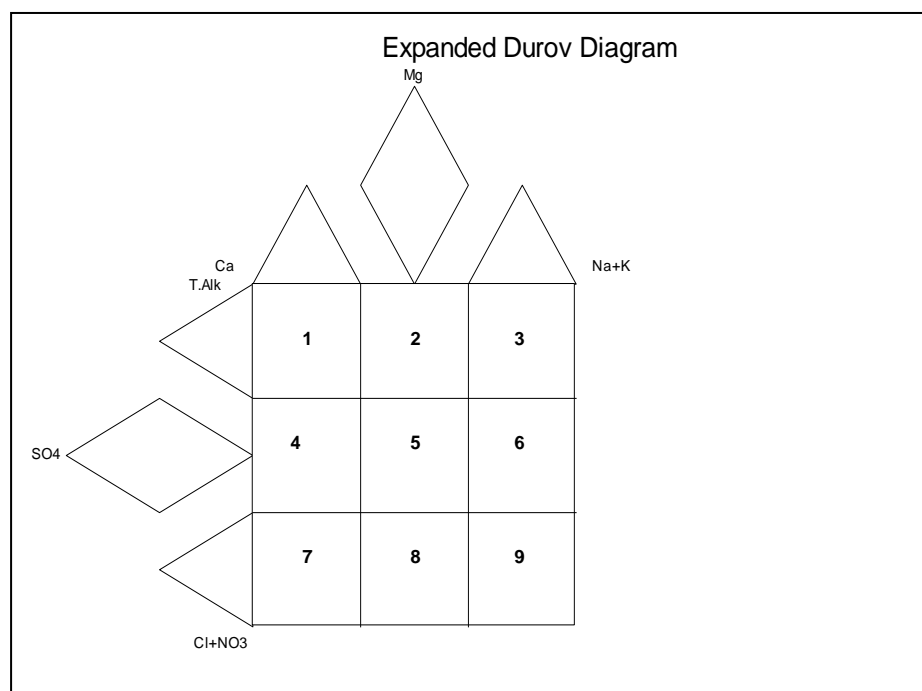
Appendix E F   jram (9 facies)
(Source: IGS

Appendix E Table 1: Characterisation of groundwater of Thaba Nchu on the basis of Piper tri-linear diagram (Source: Walton 1970, cited in Tank and Chandel 2009)

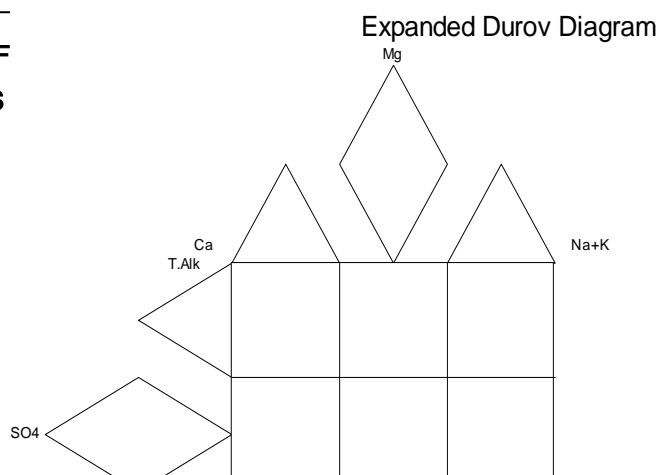| Subdivision of the diamond	Characteristics of corresponding subdivision of diamond-shaped field	Samples
1	Alkaline earths (Ca^{2+} + Mg^{2+}) exceed alkalies (Na^+ + K^+)	3 (NP2, NP3 and GL2)
2	Alkalies exceeds alkaline earths	0
3	Weak acids (CO_3^{2-} + HCO_3^-) exceed strong acids) (SO_4^{2-} + Cl^- + F^-)	1 (GL3)
4	Strong acids exceed weak acids	7 (TW1,TW2, MPS, NP1, KL, GD1 and BAL1)
5	Carbonate hardness (secondary alkalinity) exceeds 50% (chemical properties are dominated by alkaline earths and weak acids)	4 (SP, BAL2, YOX3 and W2/1)
6	Non-carbonate hardness (secondary salinity) exceeds 50% (chemical properties are dominated by alkaline earths and strong acids)	0
7	Carbonate alkali (primary salinity) exceeds 50% (chemical properties are dominated by alkalies and weak acids)	4 (YOX1, RT3, BAL3 and GD2)
8	Carbonate alkali (primary alkalinity) exceeds 50% (chemical properties are dominated by alkalies and weak acids)	3 (GL1, KOM and RT2)
9	No cation-anion pair exceeds 50%	4 (W2/2, YOX2, NPS and RT1)

Appendix E Table 2: Characterisation of groundwater of Thaba Nchu on the basis of Expanded Durov diagram: Source: IGS shared database

Fields	Characteristics of corresponding subdivision of square-shaped field	Samples
1	Fresh, very clean.recently recharged groundater with HCO_3^- and CO_3^- dominated ions.	0
2	Fresh clean, relatively young groundwater that has started to undergo Mg ion-exchange, often found in dolomitic terrain.	11 (RT3, BAL1, BAL2, BAL3, GD1, GD2, KL, NP1, MPS, TW1 and TW2)
3	Fresh, clean, relatively young groundwater that has undergone Na ion-exchange, or because of contamination effects from a source rich in Na.	7 (W/2/1, W2/2, NPS, YOX2, YOX3, RT1 and RT2)
4	Fresh, recently recharged groundwater with HCO_3^- and CO_3 dominated ions that have been in contact with a source of SO_4 contamination.	0
5	Groundwater that is usually a mix of different types - either clean water from Fields 1 and 2 that has undergone SO_4 and NaCl mixing / contamination, or old stagnant NaCl dominated water that has mixed with clean water.	0
6	Groundwater from field 5 that has been in contact with a source rich in Na.	2 (KOM and BAL2)
7	Water rarely plots in this field that indicates NO_3 or Cl enrichment, or dissolution.	2 (NP2 and NP3)
8	Groundwater that is usually a mix of different water types - either clean water from fields 1 and 2 that has undergone SO_4, but especially Cl mixing/contamination, or old stagnant NaCl dominated water that has mixed with water richer in Mg.	1 (GL2)
9	Very old, stagnant water that has reached the end of the geohydrological cycle like in deserts, salty pans … , or water that has moved a long time and/or distance through the aquifer that has undergone significant ion exchange.	3 (GL1, GL3 and SP)

Appendix F

Results of multi-variate correlation analyses

Appendix F Table 1: Results of multi-variate correlation analyses r: Pearson correlation coefficient p: p-value (the correlation is regarded as significant when p < 0.05)

		pH	EC	Ca	Mg	Na	K	TALK (HCO$_3$)	Cl	NO$_3$-N	SO$_4$	Br	PO$_4$	Total hardness
EC	r	-0.33												
	p	0.15												
Ca	r	-0.39	0.99											
	p	0.08	0.00											
Mg	r	-0.35	0.98	0.99										
	p	0.12	0.00	0.00										
Na+	r	-0.18	0.94	0.89	0.88									
	p	0.44	0.00	0.00	0.00									
K	r	0.33	0.08	0.03	0.10	0.13								
	p	0.15	0.72	0.89	0.67	0.56								
TALK (HCO$_3$)	r	0.36	0.09	0.08	0.17	0.12	0.54							
	p	0.11	0.67	0.73	0.45	0.61	0.01							
Cl	r	-0.34	0.99	0.99	0.97	0.94	0.06	0.05						
	p	0.13	0.00	0.00	0.00	0.00	0.80	0.84						
NO$_3$-N	r	-0.37	0.99	0.99	0.98	0.93	0.05	0.05	0.99					
	p	0.10	0.00	0.00	0.00	0.00	0.84	0.84	0.00					
SO$_4$	r	-0.25	0.96	0.95	0.96	0.94	0.10	0.23	0.95	0.95				
	p	0.28	0.00	0.00	0.00	0.00	0.66	0.32	0.00	0.00				
Br	r	-0.33	1.00	0.99	0.98	0.94	0.08	0.10	0.99	0.99	0.97			
	p	0.14	0.00	0.00	0.00	0.00	0.74	0.68	0.00	0.00	0.00			
PO$_4$	r	0.27	-0.97	-0.95	-0.95	-0.96	-0.07	-0.13	-0.95	-0.96	-0.99	-0.97		
	p	0.23	0.00	0.00	0.00	0.00	0.75	0.58	0.00	0.00	0.00	0.00		
Total hardness	r	-0.37	0.99	1.00	0.99	0.89	0.05	0.11	0.98	0.99	0.95	0.98	-0.95	
	p	0.10	0.00	0.00	0.00	0.00	0.82	0.65	0.00	0.00	0.00	0.00	0.00	
TDS	r	-0.32	1.00	0.99	0.98	0.95	0.09	0.13	0.99	0.99	0.97	0.99	-0.98	0.99
	p	0.16	0.00	0.00	0.00	0.00	0.69	0.57	0.00	0.00	0.00	0.00	0.00	0.00

Appendix G

Environmental and nitrate isotope results

Appendix G Table 1: Environmental isotope results

Sample	$\delta^{18}O$ Reportable Value (permil)	$\delta^{2}H$ Reportable Value (permil)	$\delta D = 8d^{18}O + 10$
BAL2	-3.57	-21.30	-18.56
BAL3	-3.45	-22.58	-17.61
GD2	-3.12	-19.38	-14.95
GL1	-4.25	-29.16	-23.97
GL2	-1.82	-13.74	-4.55
GL3	-3.77	-22.57	-20.19
KOM	-3.12	-16.38	-14.94
MPS	-0.85	-9.10	3.18
NP1	-3.57	-19.43	-18.55
NP2	-2.68	-16.44	-11.41
NP3	-2.80	-17.31	-12.39
NPS	0.53	-1.94	14.26
RT3	-3.95	-24.71	-21.59
SP	-3.32	-21.84	-16.60
SP. pond	0.95	3.25	17.58
TW1	-3.32	-21.29	-16.59
TW2	-3.36	-20.17	-16.91
W2/1	-2.69	-20.09	-11.54
W2/2	-3.44	-19.11	-17.50
YOX1	-1.04	-6.45	1.70
YOX3	0.99	2.81	17.89

Appendix G Table 2: Nitrogen and oxygen isotopes of nitrate

Sample	NO$_3$ concentration (mg N/L)	δ^{15}N$_{Air}$ (‰)	δ^{18}O$_{VSMOW}$ (‰)	Comments
BAL2	20.70	13.32	9.53	
BAL3	1.08	7.68	8.40	
GL1	46.34	14.93	7.19	
GL2	4.69	17.60	12.29	Diluted 100:1
GL2	4.69	17.58	11.95	
GL3	25.77	25.33	15.38	
KOM	4.67	51.00	27.07	
MPS	7.35	11.52	8.17	
NPS	7.11	18.14	10.39	
NP1	3.58	12.92	9.39	
NP2	12.33	14.83	9.60	Diluted 10:1
NP3	13.74	17.84	9.78	Diluted 10:1
RT3	8.27	18.45	10.57	
SP	23.43	18.68	10.01	
TW 1	6.77	14.90	8.51	
TW2	14.87	15.07	8.16	
W2/2	0.15	3.15	17.05	
W2/1	9.35	18.39	10.93	
YOX1	11.52	16.15	9.08	
YOX3	14.55	17.03	9.30	

Appendix H

Examples for control measures for sanitation systems and options for their monitoring and verification

Appendix H Table 1: Examples for control measures for sanitation systems and options for their monitoring and verification (Howard, *et al.*, 2006)

Process step	Control measures (examples)	Monitoring and/or verification (examples)
Planning	Require set-back distances for sanitation facilities in relation to travel time to aquifer, as adequate in local hydrogeological conditions	Review (applications for) permits for construction of new on-site sanitation systems or sewers
	Locate sewers outside drinking-water protection zones	Monitor land-use within zone and ensure that set-back distances are implemented
	Ensure sufficient distance (at least 2 metres) between base of latrine pit, soakaway or infiltration trench and highest water table	Inspect sewer laying and pit construction to verify that safe distances are implemented
		Conduct tests with tracers and/or indicator organisms to verify adequate siting
	Determine sludge disposal or re-use options in relation to aquifer vulnerability and contaminants	Review (applications for) permits for sludge disposal
		Conduct tests with tracers and/or indicator organisms to verify safety
Construction	Make vault latrine pits impermeable	Inspect during construction
	Fit sewers with linings to reduce breakage	Tracer tests
	Fit waste stabilisation ponds with linings	Monitor selected groundwater parameters (indicator organisms, substances typically occurring in the sewage) which would indicate leakage
Operation	Maintain on-site sanitation facilities in good condition and encourage use	Inspect regularly
	Prevent sewer leakage	Run sewer leak detection programmes
		Review records of sewer leak detection and repairs
	Implement adequate final disposal of sludge as designated	Inspect disposal

ABSTRACT

Enrichment of nitrate in groundwater is a worldwide phenomenon, mostly resulting from anthropogenic activities in densely populated areas. The objective of this study was to analyse the groundwater quality in Thaba Nchu in the vicinity of contamination sites, where the nitrate contamination of groundwater has been increased along the last decades. This is important to control and manage groundwater quality of aquifer systems in the rural areas. A multi-approach methodology was followed. During this approach, the hydrogeochemistry of major constituents (both hydrodynamic and hydrochemical parameters), as well as the concentrations of environmental isotopes (^{18}O, ^2H) and nitrate isotopes (^{15}N and ^{18}O) were used to provide information on land use in order to trace sources of waters and solutes, and to study associated processes in shallow groundwater systems of the Thaba Nchu rural villages. According to the spatial distribution of nitrate contents, nitrate concentrations exhibit very high concentrations in BAL2, GL1, GL2, GL3, NP2, NP3 and SP. 65 % of the sampled wells exceeded the value of 6 mg/L as NO_3-N. On-site sanitation in the study sites were the main cause of serious nitrate contamination given the superimposition of high nitrate concentrations with the distribution of on-ground nitrogen loadings. A connection of nitrate concentrations to rainfall conditions was found: High nitrate concentrations were recharged under drier conditions while lower nitrate concentrations appeared to be recharged under much wetter conditions. From the Piper diagram calcium chloride/nitrate water type showed significantly higher NO_3-N concentrations (NO_3-N > 100 mg/L) than the other water types. The Expanded Durov diagram showed a range of water types from fresh, clean water to mixtures from different sources. Nitrate has a less coherent distribution associated with high $\delta^{18}O$ values, clearly suggesting either a non-conservative behaviour or more than one source. Different $\delta^{18}O$-NO_3 trends suggested isotopically distinct, non-point source origins which varied spatially and temporally, due to different degrees of evaporation/recharge and number of on-ground nitrogen loadings. The plot of $\delta^{15}N$ *versus* $\delta^{18}O$ values indicated that animal and human wastes were the predominant NO_3^- sources, and a few boreholes from ammonium fertilisers and organic soil matter. KOM was the only borehole experiencing denitrification. A management strategy was developed consisting of a situation assessment, immediate actions, medium and longer-term actions. The management and reduction of groundwater nitrate levels depend on an understanding of the nitrogen sources and the pollution and nitrification mechanisms.

Keywords: Groundwater quality; contamination; nitrate; environmental isotopes; nitrate isotopes; pit latrines; manure; denitrification; management; Thaba Nchu

OPSOMMING

Verryking van nitraat in die grondwater is 'n wêreldwye verskynsel, meestal as gevolg van antropogeniese aktiwiteite in digbevolkte gebiede. Die doel van hierdie studie was om die grondwaterkwaliteit te analiseer in besoeldelde areas in Thaba Nchu omgewing waar die nitraatbesoedeling van grondwater die afgelope dekades 'n bekommernis was. Dit is belangrik om grondwaterkwaliteit van waterdraergesteentes in die landelike gebiede te beheer en te bestuur. 'n Multi-benadering-metode is gevolg. In hierdie benadering word die hidrogeochemie van die makro-parameters (beide hidrodinamiese en hidrochemiese parameters), asook die konsentrasies van omgewings-isotope (^{18}O, ^{2}H) en nitraatisotope (^{15}N en ^{18}O) gebruik om inligting te verskaf oor die grondgebruik om sodoende waterbronne en bronne van opgeloste stowwe op te spoor, en om verwante prosesse in vlak grondwaterstelsels van Thaba Nchu landelike dorpies te bestudeer. Volgens die ruimtelike verspreiding van nitraatinhoud toon nitraatkonsentrasie baie hoë waardes in BAL2, GL1, GL2 GL3, NP2, NP3 en SP. 65 % van die gemonsterde putte oorskry die waarde van 6 mg/L as NO_3-N. Sanitasie op die perseel in die studie-area was die hoofoorsaak van ernstige nitraatbesoedeling gegewe die korrelasie van hoë nitraatkonsentrasies met die verspreiding van oppervlak-grondstikstofbeladings. 'n Verbinding van nitraatkonsentrasies tot reënvaltoestande is gevind: hoë nitraatkonsentrasies is onder droër toestande aangevul, terwyl laer nitraatkonsentrasies blyk te wees onder baie natter toestande. Van die Piper-diagram kalsiumchloried/nitraat watertipe het aansienlik hoër NO_3-N konsentrasies (NO_3-N> 100 mg/L) as die ander watertipes. Die Uitgebreide Durov-diagram toon 'n verskeidenheid van watertipes, van vars, skoon watermengsels uit verskillende bronne. Nitraat het 'n minder samehangende verspreiding wat verband hou met hoë $\delta^{18}O$-waardes, wat duidelik dui op 'n nie-konserwatiewe gedrag of meer as een bron. Verskillende $\delta^{18}O$-NO_3-tendense dui op isotopies-afsonderlike, van nie-punt bron oorsprong wat gewissel het tussen ruimtelik en tydelik, as gevolg van verskillende grade van verdamping/aanvulling en aantal oppervlak-grondstikstofbeladings. Die grafiek van $\delta^{15}N$-versus $\delta^{18}O$-waardes het aangedui dat dier- en menslike afval die oorheersende NO_3-bronne was, en 'n paar boorgate van ammoniumkunsmis en organiese grondmateriaal afkomstig. KOM was die enigste boorgat wat denitrifikasie ervaar het. 'n Strategie vir die bestuur is ontwikkel wat bestaan uit 'n situasie-assessering, onmiddellike optrede, medium- en langtermynaksies. Die bestuur en die vermindering van grondwaternitraatvlakke is afhanklik van 'n begrip van die stikstofbronne en die besoedeling en nitrifikasiemeganismes.

Kernwoorde: Grondwaterkwaliteit; besoedeling; nitraat; omgewingisotope; nitraatisotope; putlatrines, mis; denitrifikasie, bestuur; Thaba Nchu