

CHAPTER 1: INTRODUCTION

1.1 BACKGROUND AND PROBLEM STATEMENT

The origin of nitrate in groundwater in southern Africa, especially at higher concentrations that impair potability, has been the subject of numerous studies (e.g. Heaton 1984, 1985; Stadler 2006; Talma and Tredoux 2005; Tredoux 1993; Taussig and Verhagen 1991). The general opinion has been that higher concentrations that exceed potability limits are probably of anthropogenic origin, over and above natural production. Because of the complexity of processes leading to the formation of nitrate in groundwater, origins cannot be readily established.

Results obtained in the course of a groundwater resource investigation in the Taaibosch area of Limpopo Province (IAEA 2002; Verhagen et al. 2004a,b; Verhagen et al. 2005), lead to a model for the formation of high nitrate levels by natural processes. This was seen as probably associated also with hydrological, hydrochemical and biological processes in the conditions peculiar to the basalt aquifer. An area around the settlement of Bochum, to the south of the Blouberg, was selected for the extension of this study (WRC 2008). The Bochum area is underlain by two contrasting hydrogeological regimes: metamorphic granites and sandstones, presenting a quite different hydrogeological environment.

The study described in this thesis is aimed at investigating the sources of high nitrate levels in groundwater of the Bochum area, Limpopo Province. The Bochum settlements lie in the northwestern part of central Limpopo Province, located some 80km northwest of Polokwane and 25 km from Dendron.

1.2 RESEARCH OBJECTIVES

The main objective of this study is to investigate high levels of nitrate in groundwater in terms of the local hydrogeology and hydrochemistry and their relationship to possible sources, be the sanitation, agriculture, cattle concentrations or natural occurrence and/or a combination of these. In the light of the foregoing background, this study seeks to accomplish the following key objectives:

- ❑ To obtain an overview of the hydrogeology of the area
- ❑ With cosmogenic isotopes to obtain information on the mean residence times (age) of groundwater occurrences as an indicator of groundwater mobility
- ❑ With non-radioactive (stable) isotopes to obtain information of the origins (recharge) of groundwater and solute elements, N and C
- ❑ To determine dominant groundwater types (hydro-geochemical) and groundwater quality in the Bochum area with specific reference to nitrate
- ❑ To understand the genesis of nitrate in groundwater in the context of its hydrology and hydrochemistry.

1.3 THESIS STRUCTURE

Chapter 1. The introductory information is given in this chapter including background, problem statement to the study, as well as the research objectives.

Chapter 2. A review of relevant literature is given in this chapter, specifically of the occurrence of nitrate in Southern Africa but also from the general literature. The information presented gives insight into some of the concepts and available techniques (i.e. hydrochemistry, and isotopes). It is mostly concerned with anthropogenic pollution as opposed to the examination of natural mechanisms of nitrate production.

Chapter 3. In this chapter the study area description is outlined i.e. the locality, topography, climate and rainfall, drainage, land use, vegetation, geology and hydrogeology.

Chapter 4. This chapter outlines a comprehensive summary of research methods and materials used.

Chapter 5. In this chapter analytical data are presented in tabular form for both 2005 and 2007 sampling campaign. Also presented in these tables are geographical coordinates and collar elevations for the individual borehole sampling points.

Chapter 6. In this chapter data and results are extensively discussed and analysed. The chapter gives insights into aspects related to the sources of nitrate in Bochum study area.

Chapter 7. This chapter presents concluding remarks based on results and observation to the area understudy.

CHAPTER 2: LITERATURE REVIEW

2.1 Nitrate occurrence in southern Africa

2.1.1 Introduction

According to Stadler (2006) nitrate is one of the major pollutants of drinking water worldwide. The single most important reason for groundwater sources in South Africa to be declared unfit for drinking is nitrate levels exceeding 10 mg/L as $\text{NO}_3\text{-N}$ (Tredoux and Talma, 2006). The exposure to high doses of nitrate in drinking water causes severe health effects, e.g., methaemoglobinaemia in humans and livestock poisoning. Both are potentially fatal. It is known from the literature that infant methaemoglobinaemia occurs in southern Africa. No statistics are available on morbidity and mortality. Considerable losses of livestock due to nitrate poisoning, are known to have been incurred over the last three decades (Tredoux *et al.*, 2005).

The origin of nitrate in groundwater in southern Africa, especially at higher concentrations that impair potability, has been the subject of numerous studies (e.g. Heaton 1984, 1985; Stadler 2006; Talma and Tredoux 2005; Tredoux 1993; Taussig and Verhagen 1991). The general opinion has been that higher concentrations that exceed potability limits are probably of anthropogenic origin, over and above natural production.

2.1.2 Isotope concepts

The isotopic study of the origins and development of nitrate in groundwater is based on the measurement of the isotope ratios ($^{15}\text{N}/^{14}\text{N}$ and $^{18}\text{O}/^{16}\text{O}$) of the elements making up the nitrate ion.

The measured ratios are expressed as relative differences (δ , in per mil = parts per thousand) from a universal standard, atmospheric air (AIR) for nitrogen and Standard Mean Ocean Water (SMOW) for oxygen. The two isotope ratios of NO_3 are, therefore, reported as $\delta^{15}\text{N}$ (‰ AIR) and $\delta^{18}\text{O}$ (‰ SMOW). This is discussed more fully in section 4.2.

2.1.3 $^{15}\text{N}/^{14}\text{N}$ ratios

Kreitler (1975) was the first to show that different sources of nitrate in groundwater in Texas can be distinguished by their different $^{15}\text{N}/^{14}\text{N}$ ratios. This established the basis for the use of this approach by many studies for the source apportionment of nitrate.

Table 1. Nitrogen isotope ranges in water from different sources (after Talma and Tredoux 2005). Data from: Kreitler (1975), Heaton (1986) and Kendall (1998)

SOURCE	$\delta^{15}\text{N}$ ‰ (AIR)
Rain	−12 to +3
Fertilizer	−5 to +5
Soil nitrogen and natural groundwater nitrate	0 to +9
Nitrate from animal and human waste	+8 to +20

Distinct isotopic differences can be seen when the nitrate sources are classified as rain, animal and human waste, natural soils and fertilizers. While there is an overlap of ranges between the different sources, a practical distinction for most samples can be made (Table 1.) and is frequently used as such.

2.2 Environmental isotopes in identifying the source of nitrate in groundwater

In the pioneering work of Kreitler, (1975) it was realized that the applications of ^{15}N in tracing relative contributions of fertilizer and animal waste to groundwater (see also Kreitler et al., 1978; Gormly and Spalding, 1979) are complicated by a number of reactions including ammonia volatilization, nitrification, denitrification, ion exchange, and plant uptake. These processes can modify the $\delta^{15}\text{N}$ values of N sources prior to mixing, and the resultant mixtures, causing estimations of the relative contributions of the sources of nitrate to be inaccurate.

Gormly and Spalding (1979) in addition attributed the inverse correlation of nitrate- $\delta^{15}\text{N}$ and nitrate concentration beneath agricultural fields to increasing denitrification with depth. The state of knowledge on the application of nitrogen-15 in the environment was summarized by L  t  lle (1980).

Amberger and Schmidt (1987) showed that denitrification results in enrichment in $\delta^{18}\text{O}$ of the residual nitrate, as well as enrichment in $\delta^{15}\text{N}$. Therefore, analysis of both $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of nitrate should allow denitrification effects to be distinguished from mixing of sources. This dual isotope approach takes advantage of the observation that the ratio of the enrichment in ^{15}N to the enrichment in ^{18}O in residual nitrate during denitrification appears to be about 2:1. The approach was applied to study the denitrification of groundwater in a sandy aquifer (B  ttcher et al. 1990).

Mariotti et al. (1988) demonstrated that dual porosity aquifers, in which both slow-moving and actively circulating groundwater is present, denitrification in the pores could make the N-isotope composition change with changes in aquifer conditions, e.g. even with borehole pump rate.

It was shown by Aravena et al. (1993) that $\delta^{15}\text{N}$ in groundwater nitrate below a septic tank is up to 10‰ higher than regional groundwater levels. Elevated values could be traced in the contamination plume, identified by elevated Na^+ values, at a distance of up to 90m. The dual isotope approach was employed by Wassenaar (1995) to conclude that the high nitrate concentrations of shallow groundwater in British Columbia were due to the nitrification of poultry manure and ammonia fertilizers.

Distinctly different $\delta^{15}\text{N}$ values were found in two streams draining adjacent agricultural catchments (Bohlke and Denver 1995). These authors conclude that storage time in the sub-surface is less important than the geochemistry of the geological units involved. The motivation for the present study was to compare nitrate formation processes in two different geological environments

Kendall et al. (1995) and Kendall (1998) in wide-ranging overviews deal with tracing nitrogen sources and cycling in catchments, methods of analysis, the fractionation of nitrogen isotopes and the processes affecting their isotopic composition principally in terms of water pollution. The isotopes of nitrogen and also that of the oxygen in the NO_3 molecule can be of value in identifying its origin(s) and tracing its hydrological pathway through a catchment. The relative paucity of $\delta^{18}\text{O}$ values for nitrate may be sought in the labour intensive analytical procedure and the requirement of hazardous chemicals, however important such values may be in understanding and identifying the chemical and hydrological processes.

An overview is given also of microbial activity in nitrogen cycling and its role in both nitrification and de-nitrification processes and attendant isotope fractionation. An important consideration is the process of mixing and that of denitrification, and the difficulties that may arise in interpreting nitrogen isotopic values when considering the operation of these two processes. An interesting observation is that in groundwater often the concentration of dissolved organic nitrogen (DON) may be higher than that of the mineralised form – dissolved inorganic carbon (DIN). As dissolved organic carbon (DOC) is associated with DON, this may have a bearing on the results obtained from the present study.

Kendall (1998) also extensively surveys the application in studies of agricultural and urban nitrate sources, forestry catchments with specific reference to acid rain, and land management. At the time, relatively little had been reported in terms of nitrogen isotopes in the study of catchments, and in particular, groundwater hydrology.

The theory and application of hydrochemistry and of environmental isotope techniques as tools in hydrogeology have been extensively reviewed in i.e. Freeze and Cherry, 1979; Lloyd and Heathcote 1985; Mazor, 1991; Fritz and Fontes 1989; Clark and Fritz, 1997; Kendall and McDonnell, 1998

2.3 Sources of nitrate in Southern African perspective

Nitrogen input into groundwater can be related to different processes. These can be natural and/or anthropogenic. The distribution and sources of nitrate in groundwater have been studied in some detail in the southern African region such as Botswana, Namibia, and South Africa. Most of these studies, many of them employing environmental isotopes, have shown that anthropogenic activities are the main source of high and variable nitrate levels (Stadler, 2006).

2.3.1 Natural origin

It has become evident that natural nitrate is a significant component of the large number of high nitrate groundwater occurrences in southern Africa (Talma and Tredoux, 2005). These authors further explain that this was supported by their first isotope survey of this nature in Namibia when high nitrate values up to 1000 mg/l NO₃ were found. Many more examples of natural nitrate have been found in the region, mainly around the rim of the Kalahari basin. Natural nitrate was found in Limpopo Province, with high nitrate levels in many boreholes in the Drakensberg/Letaba basalts (Talma and Tredoux 2005; Verhagen et al. 2004a).

According to Talma and Tredoux (2005) recent sampling in the Springbok Flats has shown that there is still a large number of boreholes with high nitrate levels and $\delta^{15}\text{N}$ between +5 and +10‰. Similar high nitrate levels are also known to occur in groundwater in the basalt of Kalkrand (Namibia), and at other locations in South Africa. They postulate that there are distinct properties of these soils that promote such high nitrate levels since adjacent sandstone soils in the Springbok Flats (Irrigasie

formation) have much lower nitrate levels. This evidence supports observations by Verhoef (1973) who completed the first extensive investigation of water quality in the same area and found that higher nitrate values were largely confined to areas with black turf soil. Studies by Verhagen et al. (2004a) of the basalt aquifer at Taaibosch (Limpopo Province) suggest that high nitrate values can be produced at depth by natural processes.

Heaton (1985) presented evidence that boreholes with high nitrate content in the Springbok Flats had increased their nitrate levels during the preceding decade and that those with low nitrate content had been higher a decade earlier. He postulated that the high nitrate levels were caused by the conversion of the natural veld to agricultural land since the late 1940's. During this process, considerable quantities of soil organic matter mineralised and the excess nitrogen not used by the remaining vegetation was transported to the groundwater as nitrate.

2.3.2 Anthropogenic origin

Nitrate derived from the excrement of wild animals could represent a potential source of "natural" nitrate in localised areas (e.g., waterholes), and the accumulation of domestic livestock around boreholes has been proposed as a possible cause of nitrate pollution in phreatic groundwater (Heaton et al, 1983).

The isotopic data by Conrad et al. (1999), Kreitler (1975) and Gormly & Spalding (1979), therefore support the observation of Xu *et al.* (1991) that boreholes with "high-nitrate" groundwater are commonly located close to livestock enclosures.

On-site sanitation is economically attractive, but often entails a groundwater pollution risk (Tredoux & Talma, 2006). Several studies on nitrate pollution related to on-site sanitation have been undertaken in southern Africa, notably also in Botswana, e.g. Lewis *et al.* (1978), Palmer (1981), Jacks *et al.* (1999) and Staudt (2003), in Moçambique (Muller, 1989) and this study. Taussig and Verhagen (1991) and Tredoux and Talma (2006) reported many cases of high nitrate concentration in many boreholes in rural settlements near Makhado (formerly Louis Trichardt) in Limpopo Province. The nitrate was ascribed to two possible sources: mobilisation of natural nitrate by cultivation of the soil, or on-site sanitation.

Xu *et al.* (1991) ascribed the high nitrate concentrations in the Northwest Province to the placement of kraals close to water sources, as well as the effect of sewage effluent and sewage sludge disposal to land overlying aquifers. Hesseling *et al.* (1991) studied the occurrence of nitrates at Rietfontein in the arid western part of Northern Cape Province. They found unacceptably high levels of nitrate in the centre of the village, considered to likely be due to human and animal pollution. Depending on local geohydrological conditions, on-site sanitation can cause serious pollution if precautionary measures are not taken (Tredoux and Talma., 2006).

In the southern African region the contribution of on-site sanitation and congregation of cattle at watering points as a nitrate source near boreholes, seems to be on the increase and constitutes an alarming feature. Contamination of groundwater by excessive use of fertilizers does not appear to be a significant problem in this region. Tredoux & Talma (2006) concluded that inorganic nitrogen fertilizer application rates in South Africa are generally too low to cause significant leaching of nitrate derived from the fertilizer to the subsurface. However, tilling the (virgin) soil probably plays a key role in oxidizing soil organic nitrogen and mobilising nitrate for leaching to the subsurface.

2.4 Denitrification

As noted previously, denitrification denotes the bacterially catalyzed process where NO_3^- is reduced to N_2O or N_2 , which only takes place below a threshold oxygen concentration that depends on the respective bacteria species as well as on the redox environment. While ^{15}N in nitrate is generally a conservative quantity, it can be altered by denitrification. This involves various bacterial processes during which nitrogen gas is produced with a preference for ^{14}N and the remaining nitrate being enriched in ^{15}N .

Denitrification will influence the conclusions on source apportionment of nitrate based solely on ^{15}N , if the process is not recognised in a field study. Usually, denitrification will not occur in water with high levels of dissolved oxygen. The statement (above) supports the observation of Heaton (1984) that high dissolved oxygen concentrations constitute a simple indicator that isotopic values are unlikely to have been modified by denitrification.

CHAPTER 3: DESCRIPTION OF THE STUDY AREA

3.1 LOCALITY

The community of villages of Bochum, is situated some 80km northwest of Polokwane in the Limpopo Province of South Africa, and lies in the Brak river catchment basin, with the Mogalakwena to the west and the Hout and Sand river basin to the east. The study area (Figure1) is framed by the lines of latitude: $23^{\circ}05' \Rightarrow 23^{\circ}45' \text{ S}$ and lines of longitude: $28^{\circ}45' \Rightarrow 29^{\circ}30' \text{ E}$.

The Brak River, which is one of the tributaries to the Sand River, traverses the study area. Regionally, surface run-off water flows towards the perennial Sand River in the north. Maximum discharge is usually recorded in late summer, especially from January to March (inclusive), and minimum flows normally occur in July or August.

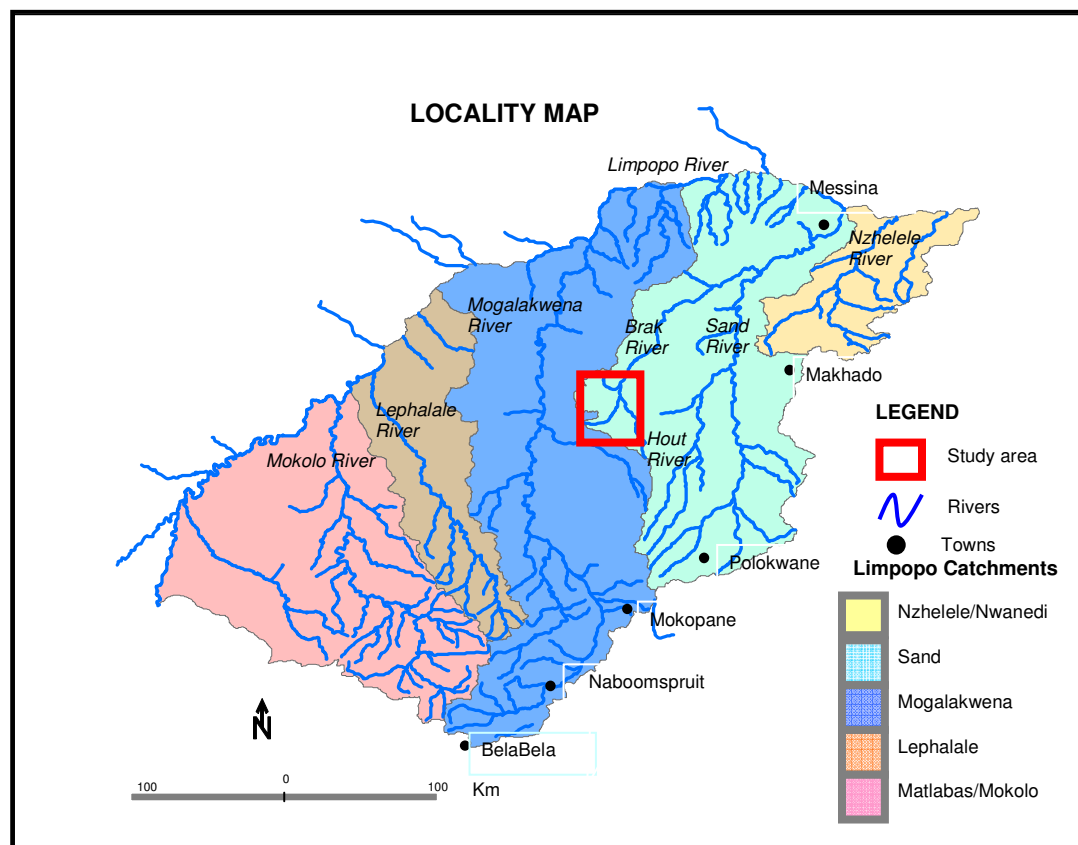


Figure 1: Map detailing Limpopo drainage basins and showing the location of the study area

As the country rocks exhibit low storage capacity and transmissivity most of the water courses are predominantly ephemeral, active during the wet season only, flowing after heavy local rainstorms. In the Sand River basin, due to the seasonal nature of rainfall, the discharge is highly variable, pointing to a strong need to consider groundwater as an alternative source for both domestic use and socio-economic development (IWMI, 2002).

3.2 TOPOGRAPHY

The Limpopo Province is characterised by its contrasting landscapes. The topographical map for Bochum (Figure 2) shows a topographically diverse area, lying south of Blouberg Mountain and east of the Waterberg plateau. The lowest point is located in the north at approximately 900m above sea level. Most villages are located in the south, some situated on the southern slopes of the Blouberg. The western part, underlain by sandstones, is sparsely populated.

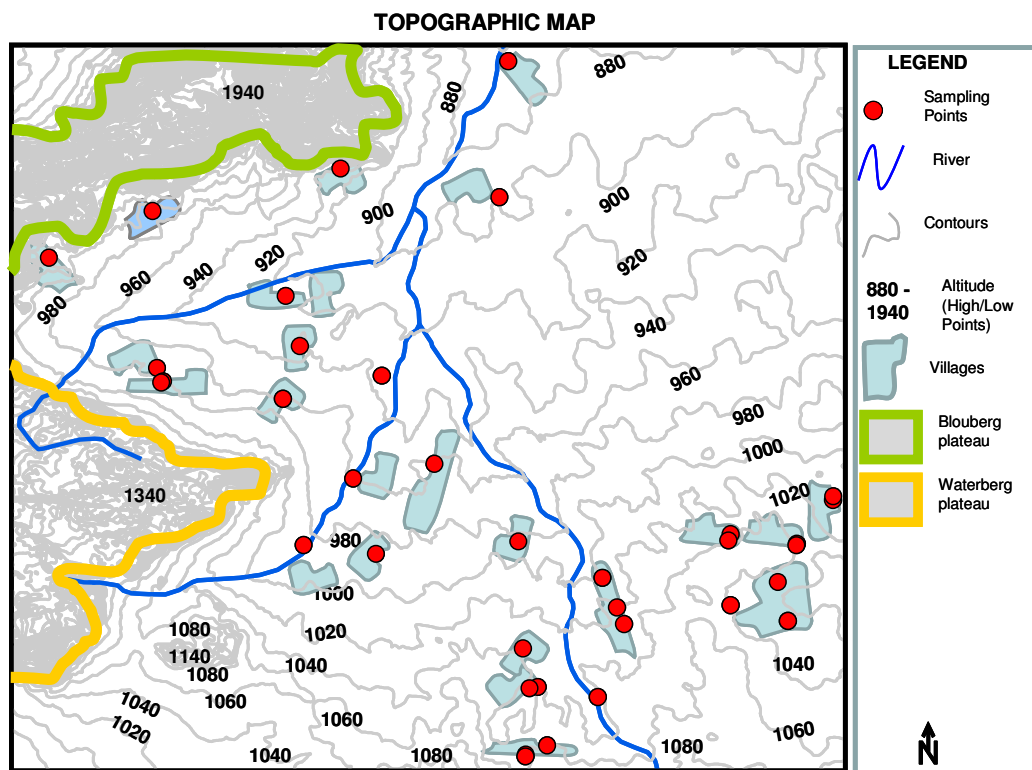


Figure 2. Topographical map for the Bochum study area, showing equal altitude contours, rivers, village outlines, and points (boreholes) sampled in this study

3.3 CLIMATE AND RAINFALL

The climate of the Bochum area is semi-arid subtropical. The summers are very hot whilst the winters are mild. The area enjoys summer rainfall that tends to be erratic (Vegter, 2001). Mean annual precipitation in the Bochum area is 453mm as recorded at Bochum rainfall station (0721/257). Yearly rainfall varies from less than 300 mm in the extreme north to 500mm in the southern portions. However, on the mountain peaks of the Soutpansberg and Blouberg range, over 900 mm of rainfall per annum is often recorded, with rainfall of about 1000 mm per annum on the southern slopes of the Soutpansberg. Approximately 95% of the mean annual precipitation is lost through evaporation in the Sand River catchment. The mean annual temperatures in the Bochum area vary between 15⁰C and 30⁰C (DWAF, 2003).

3.4 REGIONAL AND LOCAL GEOLOGY

The geological map of the study area is shown in Figure 3. Most of the area, part of the southern zone of the Limpopo Mobile Belt, is underlain by medium to coarse grained, pinkish grey and pink leucocratic Hout River Gneiss, partly exposed in higher lying areas. The deposition of Hout River gneiss is dated between 3.2 to 2.8 Ga (billion years). The magnetite quartzite rocks belonging to the Bandelierkop complex is about 2.8 Ga (billion years) (Kramers et al. 2006).

Sedimentary rocks belonging to either the Waterberg or Soutpansberg Groups of rocks form the higher lying and mountainous areas to the north and west of the study area. These rocks include sandstone, conglomerate, grit, quartzite, arkose, mudstone, volcanic and volcano-clastic rocks. Another regional feature that also forms part of higher lying areas in north-western part of the study area is the Blouberg mountain, the deposition of this formation being between 2000 and 1900 Ma (Million years) (Barker et al, 2006).

There are no radiometric ages of the rocks of the Makgabeng formation of the Waterberg group, but there are new U-Pb baddeleyite crystallization ages, reported by Hanson et al (2004) for the dolerite sills that intruded the upper strata of the Waterberg group. The ages are between 1879 to 1872 Ma (Million years). Within the study area, the sandstone is usually covered by younger Quaternary sedimentary rocks which were deposited $\pm$ 1 million years ago (Mukosi C., personal communication).

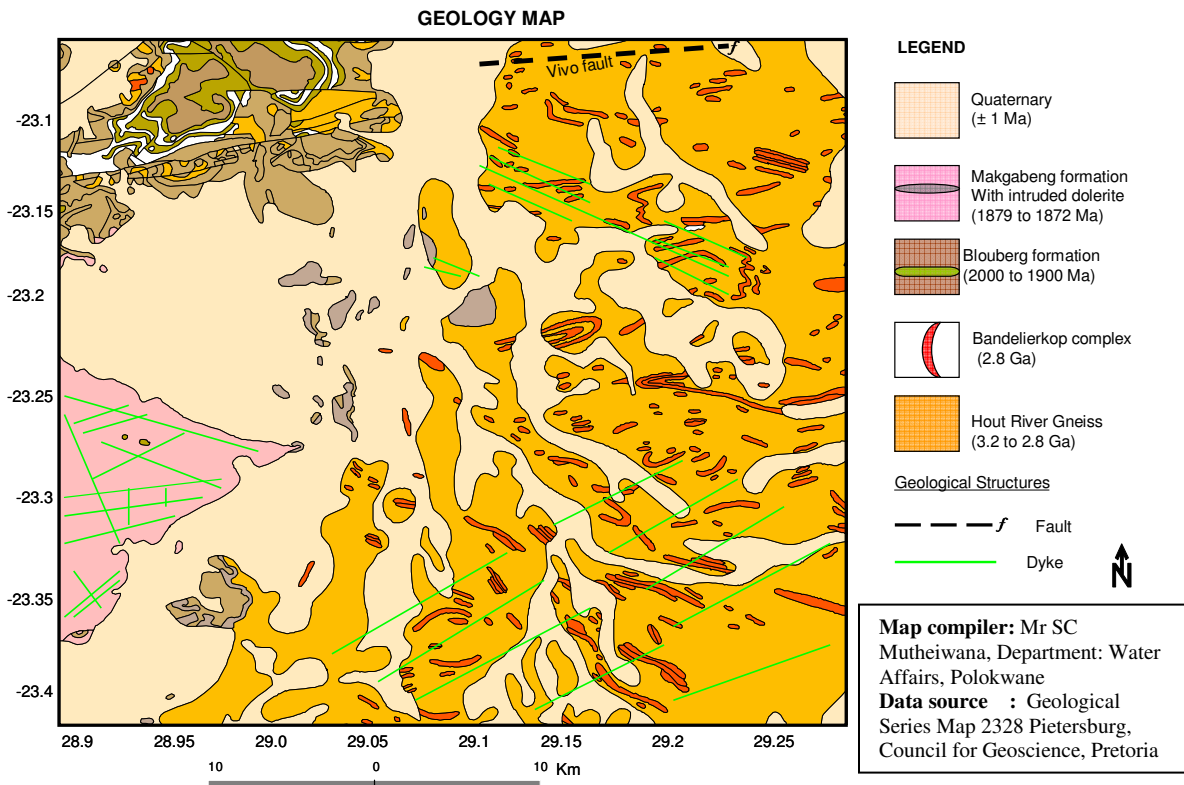


Figure 3: Geological map of the Bochum study, showing geological structures and geological units in stratigraphic order.

3.5 HYDROGEOLOGY

The potential for exploiting groundwater varies dramatically throughout the study area and is determined mainly by the specific lithologies underlying each terrain. Higher groundwater potential (yield and storage) is found in unconsolidated sand and gravel deposits associated with the Brak River drainage which in turn provides enhanced recharge potential towards the deeper lying fractured aquifers. The map of piezometric levels in the study area is shown in Figure 4.

In the sedimentary rocks of the Waterberg and Soutpansberg Groups, higher groundwater potential is associated with dolerite contact zones. The groundwater potential in the metamorphic and associated rocks is generally determined by the grade of metamorphism. Rocks subjected to higher grade of metamorphism typically display a resistance to weathering of fractures. The depth to groundwater is generally greater in the sandstones in the west than in the metamorphic rocks. This may be controlled

by contrasting depth of fracturing and weathering in the two terrains and have a bearing on the pollution potential.

Where they could be measured, depths to water levels were found to range between 10m and 17m. The generalised isopiezometric contours were constructed on the basis of the topographic map (Figure 2) by subtracting an average depth to water level of 15m from sampled borehole collar elevation (see Tables 2a and 3a). Overall, groundwater flows away from the Blouberg and Waterberg sandstone plateau and the higher terrain of the gneisses in a northerly direction, coinciding with the local surface drainage.

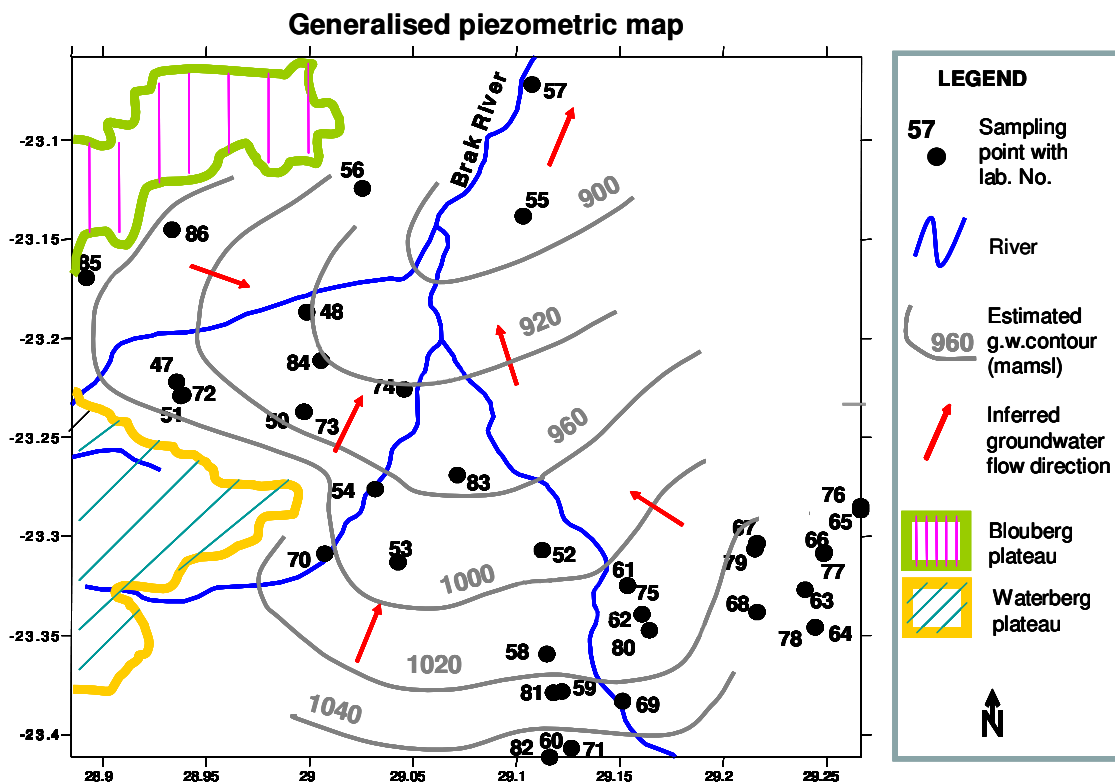


Figure 4: Hydrogeology map for the study area, showing sampling point locations with laboratory numbers (see Tables 2a and 3a) estimated equipotential lines and inferred regional groundwater flow directions. Note: apparent anomaly in SE (cf. topographical map Figure 2)

3.6 LAND USE

Rural human settlement accounts for the largest portion of the study area with a spread of villages (Figure 2), with Senwabarwana, formerly known as Bochum, the only town within the study area. Other towns outside the study area located south east and north east are Dendron and Alldays respectively. The R521 all-weather road from Dendron passes through Bochum town, towards Kobe, Blackhill, and through the Blouberg range. Gravel roads are most dominant within the study area.

Cattle raising is practiced in the Bochum area along with tillage farming and pockets of domestic garden, with no significant mining or industrial activity. Commercial irrigated agricultural activities account for the smallest land use in the Bochum area. South of study area commercial agricultural activity constitutes the dominant land use (Dendron area).

3.7 VEGETATION

The most dominant vegetation in the Limpopo area is tropical bush and savannah (Vegter, 2001; DWAF, 2003). Inland tropical forest occurs in the eastern portions. In the far western parts, bushland occupies the lower-lying ground bordering the Limpopo River as well as the Lephalala and Mogalakwena river valleys. Rolling bushveld, subtropical forest and highveld grassland savannah are common types in the Limpopo region. In the vicinity of Bochum, grassland is very common. In Bochum and its vicinity, this ranges from densely vegetated to short bushveld as well as open tree savannah to moist mountain bushveld in the lower-lying areas.

CHAPTER 4: RESEARCH METHODS

4.1 Field procedures

Fieldwork was conducted to obtain current information on the boreholes (borehole census), geology and geo-hydrology. The x, y, and z location of the boreholes was measured in the field using the Trimble GPS. The x-y accuracy of the GPS without differential correction is about 5 metres.

Sample collection in the field followed as far as possible standard procedures (e.g. Clark and Fritz 1997; Weaver 1992) to ensure representivity of *in situ* water. Samples are taken straight from the outlet where wells, either motorised or hand-pumped, are in regular production at the time. Where the pump had been idle, the pump is operated until well-head observations (e.g. temperature, dissolved O₂, electrical conductivity and total alkalinity) on the water stabilise.

Samples for tritium and chemical analyses were taken in 500ml PVC containers. Only for ¹⁵N analysis were the water samples (250 ml) preserved from biological degradation by freezing immediately, being thawed only immediately before analysis. Large volumes of up to 100 litres of sample water are required to harvest enough total dissolved inorganic carbon (TDIC) for conventional radiocarbon analysis. The water is rendered alkaline (pH > 9) in a drum and the TDIC precipitated by adding BaCl₂. The usual well head observations are performed for temperature, EC, pH and TAlk (where pH > 6).

4.2 Environmental isotope analysis.

The ratios ¹⁸O/¹⁶O were analysed by equilibrating (Brenninkmeijer, 1987) for 1 hour at 50±0.1°C a small aliquot of water in a vial briefly flushed with CO₂ gas. The gas is then extracted and introduced into an isotope ratio mass spectrometer (IRMS: GEO 20/20) via a vapour trap. In ²H/¹H analysis, water is equilibrated with H₂ gas for 6 hours, also at 50±0.1°C in the presence of a platinum catalyst. In both cases, isotope ratios are measured w.r.t. a reference gas and expressed as relative differences $\delta = \{(R_s - R_r)/R_s\} * 1000 \text{ ‰}$ (Craig, H. 1961) along with two laboratory working standards, where R_s and R_r represent isotope ratios of the sample and reference standard, respectively. Hydrogen isotope ratios are automatically corrected for H₃ contribution. The results are then normalised as $\delta^2\text{H}$ and $\delta^{18}\text{O}$ in ‰

with respect to the international standard VSMOW on the VSMOW-VSLAP scale. The results of the high and low laboratory standards measured with each batch of samples are used to check slope and offset for normalisation. Analytical precision is usually better than 0.1 ‰ for $\delta^{18}\text{O}$ and 0.5 ‰ for $\delta^2\text{H}$ as assessed on the basis of long-term data for laboratory standards. For values used and normalisation procedure see Appendix (M.J. Butler, pers. comm)

Stable carbon isotope ratios ($^{13}\text{C}/^{12}\text{C}$) are determined on CO_2 gas by acidification with orthophosphoric acid of the field precipitate for ^{14}C analysis. They are expressed as $\delta^{13}\text{C}$ in ‰ with respect to the international VPDB standard with typical 1σ errors better than ± 0.2 ‰.

Stable nitrogen isotope ratios ($^{15}\text{N}/^{14}\text{N}$) in nitrate are determined by reducing the total dissolved inorganic nitrogen to NH_3 which is allowed to diffuse quantitatively through a membrane to react with H_2SO_4 . The resulting $(\text{NH}_4)_2\text{SO}_4$ is then pyrolysed on line and reduced to N_2 gas which is introduced into an IRMS. The results are expressed as $\delta^{15}\text{N}$ in permille w.r.t. atmospheric N_2 . The intrinsic accuracy of the method is comparatively low, with errors of the order of ± 0.5 ‰.

Radiocarbon was measured by acidifying the bulk field precipitate with orthophosphoric acid, the evolved CO_2 being absorbed in a cocktail consisting of organic scintillation and spectral shift compounds held in a K-free glass vial, which in turn is introduced into an ultra-low level liquid scintillation spectrometer (Verhagen et al. 2004). Results are normalised to the results from NBS and IAEA standards and background values determined on CO_2 produced from ^{14}C -free marble and expressed in pMC (per cent modern carbon). Typical 1σ errors are better than ± 2 pMC respectively, assessed from running calibrated sub-standards. Present-day radiocarbon values in atmospheric CO_2 are about 110 pMC.

In tritium (^3H) analysis the water samples are first electrolytically pre-enriched by a factor of 20 in batches of 16, the enrichment factor for each run checked by calibrated sample or “spike”, with a tritium-free “blank” run to check for possible batch contamination. The distilled product water is mixed with a cocktail consisting of organic scintillation and spectral shift compounds held in a K-free glass vial and measured in an ultra low-level liquid scintillation spectrometer (Morgenstern and Taylor, 2009). The results are expressed as tritium units ($\text{TU} \equiv ^3\text{H}/^1\text{H} = 10^{-18}$) normalised to an NBS

and IAEA standard. The 1σ precision (in the range up to ~ 5 TU) is ± 0.2 TU. Present-day rainfall tritium values are in the range of 3-5 TU in southern Africa (GNIP - <http://isohis.iaea.org>).

4.3 Calculation of ^{14}C mean residence time, or age

Under phreatic aquifer conditions, the isotope-based age, mean residence time (MRT in years) of groundwater was calculated (Maloszewski and Zuber 1982; Verhagen et al. 1991) from the ^{14}C content using

$$\text{MRT} = 8267 * \{(A_0/A) - 1\}$$

where A is the analysed ^{14}C activity of the sample and an appropriate initial, or recharge value of the ^{14}C activity A_0 .

Corrections for isotopic exchange and fractionation factors for ^{14}C on the basis of observed $\delta^{13}\text{C}$ values of TDIC may be applied according to various proposed models (e.g. Fontes, J-C. and Garnier, J-M. (1979); see also Clark & Fritz (1997)). Such corrections may introduce even larger errors because of uncertainties in the parameters used (Verhagen et al. 1991). Assuming an initial (recharge) value of 80% to 90% of atmospheric CO_2 is often a safe value of A_0 to adopt in the present environment (see also: Vogel, 1970).

4.3.1 Exponential model plot

Plotting radiocarbon against tritium data may be employed to assess aquifer behaviour as well as estimate mean residence time. Such plots can be fitted with curves of the known isotope input function (e.g. records of tritium in rain (monthly) and radiocarbon in atmospheric CO_2 (yearly)) based on different models of aquifer behaviour. A convolution integral expresses the well-mixed model (Maloszewski and Zuber 1982; Verhagen et al. 1991).

$$A(t) = \int_0^{\infty} A_0(t - \tau) e^{-\lambda t} f(\tau) d\tau$$

In this equation, $A(t)$ is the observed tracer concentration at time t ; $A_0(t-\tau)$ is the (known) input concentration as a function of time t and the transit time τ ; λ the decay constant of the relevant isotope and $f(\tau)$ is the aquifer response function.

The exponential model approximates the response of an ideal phreatic aquifer.

$$f(\tau) = \frac{e^{-\tau/T}}{T}$$

where T is the mean groundwater residence time. (Maloszewski and Zuber 1982)

Reverse modeling of the time series of atmospheric ^{14}C and ^3H in rainfall values calculates the expected tracer concentrations in a well-mixed borehole sunk in an ideal, uniformly recharged phreatic aquifer as a function of mean residence time. Plotting the two isotope responses against each other for different mean residence times results in a curve of the expected locus of pairs of isotope concentrations (see e.g. Figure 11)

4.4 Chemical and Biological analysis

In this study, in addition to the larger sample for ^{14}C , three (3) samples were collected from each borehole, two (2) for isotope analysis and one (1) for major ion chemical analysis. Samples for biological analyses were analysed for faecal coliforms only for Koekoek 1 borehole groundwater, the only clear case of sewage pollution. The parameters included for chemical and biological analysis were: NO_3^- , SO_4^{2-} , Cl^- , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , CaCO_3 and faecal coliforms.

4.5 Standard chemical laboratory techniques:

Dissolved nitrates (NO_3^-) were analysed using automated determination of dissolved nitrates by cadmium reduction; sulphate (SO_4^{2-}) using automated turbidimetric determination; Chloride (Cl^-) by automated determination using ferric thiocyanate using a TRAACS 800 instrument. Sodium (Na^+) and potassium (K^+) were analysed by automated flame emission photometry. Calcium (Ca^{2+}) was analysed using atomic absorption method, and fluoride (F), using an ion selective method. Magnesium (Mg^{2+}) was analysed by automated atomic absorption, total alkalinity (as CaCO_3) by automated titration using

bromophenol blue; potentiometer determination. TDS and total hardness were determined by calculation. Faecal coliforms were analysed using a membrane filtration method.

4.6 Displaying isotopes and chemical results

Graphical methods for displaying and analysing results are discussed below:

4.6.1 Trilinear / Piper diagram

Ratios of individual ions w.r.t. total ions are displayed on Piper plots. In a Piper diagram cations Ca-Mg-(Na+K) were plotted as percentage of total cations; anions HCO_3^{2-} , SO_4^{2-} and Cl^- are plotted as percentage of total anions on separate triangular fields (Piper 1953). Ionic balance is first ensured for concentrations in meq/l. Points on the anion and cation diagrams were projected to where they intersect on the diamond field, where characteristic ionic compositions are indicated. This plot reveals dominant chemical types, useful trends, relationships and mixing of water for large sample groups and clustering of data points to indicate water samples that have similar compositions and classification in the study area. It is important to note that ionic ratios only are displayed, with no reference to concentrations.

4.6.2 Schoeller diagram

Individual major ion concentrations in meq/l or mg/l are plotted on vertical logarithmic scales, usually grouped in cation and anion sections (Clark and Fritz 1997). Thus sample concentrations are displayed and compared demonstrating different hydrochemical water types on the same diagram. The advantage is that many analyses can be plotted and compared in terms of differing composition and concentration and as such complement a Piper diagram that does not reflect concentrations. It should always be considered that the concentration scale is logarithmic, and that care should be taken when comparing chemical types at highly different concentration

4.6.3 X-Y plots

In order to investigate possible correlation between different measured sets of parameters x-y plots were employed. Scales can be either linear or logarithmic, depending on the range of values displayed.

4.6.4 Areal distribution plots

Surfer-7 plots were employed to display areal spreads of the concentrations of NO_3^- , ^{14}C , EC, Ca^{2+} , Na^+ , and Cl^- in Bochum groundwater and proved to be useful in highlighting regional similarities and contrasts for different parameters. Microsoft PowerPoint was used to edit and finalise draft of the geology, hydrogeology and topographic maps.

CHAPTER 5: DATA PRESENTATION

Geographical, climatic and hydrogeological data has been presented in earlier chapters. All analytical data are presented in Tables 2 (a) and (b) for the 2005 sampling campaign and in Tables 3 (a) and (b) for the 2007 sampling campaign. Also presented in these tables are geographical coordinates and collar elevations for the individual borehole sampling points.

All environmental isotope analyses were conducted by the Environmental Isotope Laboratory, iThemba LABS (Gauteng), in Johannesburg. The major ion analyses for March 2005 were conducted by the Resource Quality Services (RQS) laboratory of the Department of Water Affairs in Pretoria. The major ion analyses for October 2007 were conducted by UIS Analytical Services in Centurion.

Table 2a. Field data and Isotope data for Bochum study, March 2005

Lab No.	Villages	Latitude	Longitude	Collar elevation (mamsl)	E.C. (µS/cm)	Temp (°C)	pH	Alkali (meq/l)	Diss O ₂ (mg/l)	TAL (mg/l)	δ ² H (‰)	δ ¹⁸ O (‰)	Tritium (T.U.)	Carbon-14 (pMC)		δ ¹³ C (‰)	δ ¹⁵ N (‰)
TN 47	Udneey	-23.22201	28.93562	980	2730	24.2	7.22	578.3	0.6	447.0	-23.0	-3.90	1.2	94.7	±2.0	-7.20	+6.7
TN 48	BrodieHill	-23.18677	28.99861	946	899	25.7	6.33	65.9	1.6	40.8	-24.2	-4.31	1.7	96.1	±2.0	-10.34	+9.5
TN 50	Miltonduff	-23.23712	28.99725	960	5210	25.4	6.90	634.4	0.5	462.0	-28.3	-4.65	1.3	93.0	±2.0	-7.14	+13.3
TN 51	Milbank	-23.22861	28.93861	980	1636	25.8	7.20	524.6	0.7	401.0	-27.1	-4.53	1.3	104.7	±2.1	-8.16	+8.4
TN 52	Overdyk	-23.30695	29.11252	990	2450	26.8	7.47	378.2	0.3	318.4	-24.3	-3.91	1.4	104.0	±2.1	-5.49	+5.6
TN 53	Gemarke	-23.31306	29.04278	985	1727	25.9	7.40	500.2	2.7	393.1	-29.1	-4.50	0.7	85.4	±2.0	-5.76	+5.1
TN 54	Rittershouse	-23.27615	29.03170	960	1195	24.8	7.57	624.6	0.0	499.0	-24.6	-4.16	1.1	94.5	±2.0	-5.68	+5.6
TN 55	Avon	-23.13839	29.10329	898	1649	24.4	7.41	592.9	3.5	487.0	-30.3	-4.62	0.5	97.7	±2.1	-5.55	+6.0
TN 56	Dansig	-23.12437	29.02552	940	413	24.9	7.31	258.6	0.9	190.4	-32.5	-6.18	0.1	83.7	±2.0	-11.54	
TN 57	Indermark	-23.07189	29.10757	870	1292	26.0	7.46	556.3	5.2	441.0	-29.6	-5.10	4.6	94.8	±2.0	-4.33	+2.2
TN 58	Bouwlust	-23.35938	29.11477	1035	1473	24.2	7.32	451.4	0.5	365.3	-28.6	-4.74	0.0	92.9	±2.0	-6.55	+12.0
TN 59	Bouwlust2	-23.37827	29.12201	1040	1757	25.9	7.35	446.5	0.9	365.9	-29.9	-4.79	0.3	87.3	±2.0	-6.46	+8.8
TN 60	Reinland1	-23.40693	29.12661	1060	1027	24.9	7.31	373.3	2.1	305.2	-29.7	-4.80	0.2	99.1	±2.1	-6.57	+5.1
TN 61	Koekoek1	-23.32484	29.15374	1002	1781	27.1	7.22	463.6	1.8	360.3	-27.1	-4.41	0.0	84.7	±2.0	-6.38	+8.1
TN 62	Koekoek2	-23.33932	29.16084	1020	1709	25.7	7.05	400.2	0.6	306.9	-25.1	-3.94	0.9	96.6	±2.1	-6.41	+10.7
TN 63	Wurthsdorp	-23.32692	29.23967	1043	1781	24.1	7.35	388.0	6.1	305.0	-30.7	-4.59	0.7	100.8	±2.1	-6.37	+0.3
TN 64	Mohodi	-23.34590	29.24459	1052	1270	23.8	7.57	483.1	5.8	362.7	-35.3	-5.13	0.3	96.9	±2.1	-6.20	-2.3
TN 65	Stettin1	-23.28667	29.26667	1036	815	24.8	7.75	436.8	0.0	353.1	-21.1	-2.99	0.9	89.0	±2.0	-5.40	
TN 66	Stettin2	-23.30811	29.24892	1040	1071	26.2	7.84	480.7	5.3	390.2	-31.2	-4.91	0.0	81.9	±1.9	-7.03	
TN 67	Koningkratz	-23.30345	29.21642	1040	1070	24.9	7.91	473.4	0.0	363.1	-32.2	-4.93	0.0	86.9	±2.0	-5.80	
TN 68	Schellenburg	-23.33821	29.21646	1040	1711	24.7	7.51	366.0	2.0	274.0	-26.5	-4.26	1.3	107.1	±2.1	-5.91	-3.5
TN 69	Brussels	-23.38317	29.15143	1040	1326	24.8	7.50	568.5	0.5	447.0	-33.7	-5.01	0.0	93.1	±2.0	-7.10	+8.0
TN 70	Skoonveld	-23.30872	29.00734	985	829	25.0	8.05	258.6	0.2	178.5	-25.5	-3.78	0.4	95.5	±2.0	-5.74	
TN 71	Reinland2	-23.41144	29.11610	1060	1252	25.6	7.54	446.5	5.7	340.6	-30.3	-4.45	0.3	87.5	±2.0	-4.84	-1.0

Table 2b. Geology and major ion data for Bochum study, March 2005

Lab No.	Villages	Geology	NO ₃ -N	NH ₄ -N	F	Si	PO ₄	SO ₄	Cl	K	Ca	Na	Mg
			(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)
TN 47	Udneey	Sandstone	14.3	<0.04	0.80	36.0	<0.011	56.7	559.4	1.3	117.3	385.2	68.0
TN 48	BrodieHill	Sandstone	39.0	<0.04	0.20	20.4	0.09	27.4	136.4	17.9	58.8	45.8	31.9
TN 50	Miltonduff	Sandstone	52.0	<0.04	0.31	27.5	0.01	98.6	1316.5	13.1	171.2	604.2	195.5
TN 51	Milbank	Sandstone	14.2	<0.04	0.55	34.2	0.01	18.3	268.3	1.9	101.0	183.1	47.0
TN 52	Overdyk	Granite	3.4	<0.04	0.58	38.9	0.01	110.6	291.6	19.4	106.4	264.1	96.2
TN 53	Gemarke	Granite	156.5	<0.04	0.43	35.3	<0.011	38.6	267.2	18.2	78.6	176.9	73.7
TN 54	Rittershouse	Granite	121.3	<0.04	0.77	39.3	0.01	21.3	95.9	16.3	43.2	126.6	67.6
TN 55	Avon	Granite	20.2	0.20	0.26	29.8	<0.011	58.0	202.0	12.7	76.5	105.8	120.3
TN 56	Dansig	Granite/Sst	0.5	0.05	0.20	26.1	0.03	6.8	12.3	0.9	38.6	17.8	20.4
TN 57	Indermark	Granite	9.3	<0.04	0.27	39.2	<0.011	38.4	147.0	8.4	58.6	86.0	95.4
TN 58	Bouwlust	Granite	25.5	<0.04	0.33	37.8	<0.011	32.4	198.0	24.5	62.1	167.1	56.2
TN 59	Bouwlust2	Granite	52.4	<0.04	0.40	36.1	<0.011	48.2	231.4	19.4	87.1	176.5	81.7
TN 60	Reinland1	Granite	8.0	<0.04	0.44	39.8	0.02	20.9	143.5	4.3	32.6	147.5	37.1
TN 61	Koekoek1	Granite	20.3	<0.04	0.21	37.5	0.01	45.0	306.2	11.7	88.4	191.6	70.1
TN 62	Koekoek2	Granite	41.5	<0.04	0.29	39.7	0.01	68.8	259.3	12.8	59.3	177.3	88.4
TN 63	Wurthsdorp	Granite	20.3	<0.04	0.25	36.1	<0.011	55.9	336.9	9.2	91.7	143.3	91.7
TN 64	Mohodi	Granite	9.5	<0.04	0.29	38.6	<0.011	40.7	174.6	13.9	63.2	120.2	61.4
TN 65	Stettin1	Granite	0.1	0.06	0.21	39.3	0.04	14.9	52.3	9.4	31.0	71.9	50.9
TN 66	Stettin2	Granite	2.0	<0.04	0.21	39.7	0.02	24.2	123.6	12.2	48.4	113.7	56.1
TN 67	Koningkratz	Granite	5.1	<0.04	0.18	39.6	0.01	25.9	122.6	11.8	39.0	89.3	67.9
TN 68	Schellenburg	Granite	63.9	<0.04	0.44	38.8	0.02	67.2	202.0	16.4	78.5	164.1	77.6
TN 69	Brussels	Granite	55.9	<0.04	0.42	34.0	0.01	28.4	156.1	14.0	57.6	144.3	61.0
TN 70	Skoonveld	Granite	0.7	3.76	0.21	2.2	<0.011	8.4	152.9	11.3	21.6	112.0	19.4
TN 71	Reinland2	Granite	12.4	<0.04	0.37	30.9	0.23	39.9	155.3	11.5	59.6	143.9	47.5

Table 3a. Isotope data for Bochum study, October 2007

Lab	Villages	Collar elevation	Latitude	Longitude	δ D	$\delta^{18}\text{O}$	Tritium		Carbon-14		$\delta^{13}\text{C}$
No.		(mamsl)			(‰)	(‰)	(T.U.)		(pMC)		(‰)
TN 72	Milbank	990	-23.22908	28.93769	-33.6	-4.80	0.5	±0.2	93.0	±2.0	-8.41
TN 73	Miltonduff	960	-23.23712	28.99725	-30.1	-4.46	0.8	±0.2	94.7	±2.0	-7.37
TN 74	Terwichen	940	-23.22583	29.04569	-33.6	-4.73	0.7	±0.2	96.2	±2.0	-5.90
TN 75	Koekoek1	1002	-23.32484	29.15374					94.5	±2.0	-6.20
TN 76	Stettin1	1036	-23.28482	29.26668	-22.5	-2.94	1.5	±0.3	91.4	±2.0	-8.21
TN 77	Stettin2	1040	-23.3088	29.24869	-34.4	-4.84	0.4	±0.2	88.8	±2.0	-7.32
TN 78	Mohodi	1052	-23.3459	29.24459	-37.4	-5.28	0.8	±0.2	105.8	±2.1	-5.91
TN 79	Koningkrantz	1040	-23.30645	29.21542	-34.4	-4.91	0.0	±0.2	86.9	±2.0	-7.19
TN 80	Koekoek3	1030	-23.34743	29.16436	-30.6	-4.46	0.9	±0.2	89.4	±2.0	-5.05
TN 81	Bouwlust3	1051	-23.37894	29.11798	-32.9	-4.75	0.3	±0.2	85.1	±2.0	-6.32
TN 82	Reinland1	1060	-23.41223	29.11601	-31.7	-4.69	1.5	±0.2	89.4	±2.0	-6.01
TN 83	Witten	960	-23.26904	29.07143	-32.6	-4.78	0.4	±0.2	87.9	±2.0	-4.74
TN 84	Miltonduff2	935	-23.21126	29.00547	-28.1	-4.53	2.4	±0.3	108.9	±2.1	-13.60
TN 85	Ga-Kobe	1032	-23.16807	28.88263	-33.4	-5.53	1.9	±0.3	109.8	±2.1	-16.42
TN 86	Buffelshoek	1000	-23.1452	28.93339	-34.9	-5.66	1.0	±0.2	99.2	±2.1	-6.98

Table 3b. Geology and major ion data for Bochum study, October 2007

Lab	Villages	Geology	Ca	Mg	Na	K	Si	HCO ₃	SO ₄	Cl	NO ₃	F	NO ₃ -N
No.			mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
TN 72	Milbank	Sandstone	173	107	393	0.97	36.3	563.6	48.3	799.7	63	0.4	14.2
TN 73	Miltonduff	Sandstone	210	214	868	11.2	32.2	556.3	125.3	1541.2	565.5	0.1	127.7
TN 74	Terwichen	Sandstone	135	251	793	9.72	40.3	571.0	203.8	1762.5	44.3	0.0	10.0
TN 75	Koekoek1	Granite	115	88.3	200	15	37.4	537.0	48.8	435.1	0.0	0.1	0.0
TN 76	Stettin1	Granite	31.4	52.7	75.1	9.4	42.4	507.5	16.7	60.9	13.5	0.1	3.0
TN 77	Stettin2	Granite	51.6	58.4	103	11.9	41.3	356.2	28.3	126.9	11.6	0.1	2.6
TN 78	Mohodi	Granite	64	62.1	119	13.4	40.2	319.6	42.5	168.6	37.4	0.2	8.4
TN 79	Koningkratz	Granite	35.6	65.4	77	9.33	40.1	385.5	21.3	108.1	10.0	0.1	2.3
TN 80	Koekoek3	Granite	49.6	42.7	160	12	35	456.3	20.2	118.7	53.1	0.3	12.0
TN 81	Bouwlust3	Granite	58.1	52	127	15.2	34.5	370.9	34.1	159.6	38.8	0.3	8.8
TN 82	Reinland1	Granite	66.5	48.4	140	11	32.7	482.0	47.0	147.8	75.0	0.2	16.9
TN 83	Witten	Granite/Sst	62.9	65.3	183	14.8	40	588.0	103	205.8	37.3	0.3	8.4
TN 84	Miltonduff2	Sandstone	7.7	7.0	27.8	31.8	41.9	83.0	12.8	54.9	12.3	0.1	2.8
TN 85	Ga-Kobe	Granite/Sst	5.1	5.01	9.61	1.12	7.42	14.2	0.7	22.8	18.2	0.0	4.1
TN 86	Buffelshoek	Granite	47.2	41.5	28.2	0.37	24.1	344.0	5.8	49.7	13.2	0.2	3.0

6.1 The areal distribution of NO_3^- , ^{14}C , EC, Ca^{2+} , Na^+ , and Cl^- in Bochum groundwater

Groundwater varies greatly in its total dissolved solid concentration. Ions are dissolved from the rocks of the aquifer or transported from the land surface and soil. In general, and depending on the aquifer material, the longer water has been underground, the greater the mineralisation¹. This should, however not been taken as a rule. As was shown by Verhagen (1992), recent Kalahari groundwater was found to be underlain by deeper and older groundwater at considerably lower mineralization. The high groundwater concentration of calcium and sodium in Bochum is influenced by the geology of the area, which is largely granite gneiss.

The areal distribution of nitrate and ^{14}C concentrations is presented in Figure 5 (a) and (b) respectively. The distribution of electrical conductivity (EC), calcium, chloride and sodium concentrations is depicted respectively in Figure 6 (a), (b), (c), and (d). Note that the contours shown take no account of the topography. The maps show that the major ions except nitrate show the same general trends. As illustrated on Figure 4 (hydrogeology map), this increase in mineralisation seems to co-incide with an area of slow drainage – possibly even stagnation of groundwater flow. The similarity in trend and build-up of mineralisation suggests evapotranspirative enrichment in this location and thus possibly more generally in the Bochum area.

A consistent radiocarbon gradient corresponding to inferred regional flow is seen clearly only in the N-W on the slopes of the Blouberg and to a lesser extent on the gneisses in the S-E. Elsewhere, the map of the distribution of radiocarbon concentrations shows little correspondence with ionic concentrations, suggesting that the hydrological influences on the chemistry are rather localised.

Nitrate shows a completely different set of contours or behaviour, which do not seem to relate to any drainage features or association with human habitation (see Figure 2). Nitrate concentrations in the area seem to be similarly localised and can either be of natural or anthropogenic origin.

¹ The term: mineralisation is defined here as the concentration of all the dissolved major ions - as opposed to salinity, which strictly applies only to (sodium) chloride.

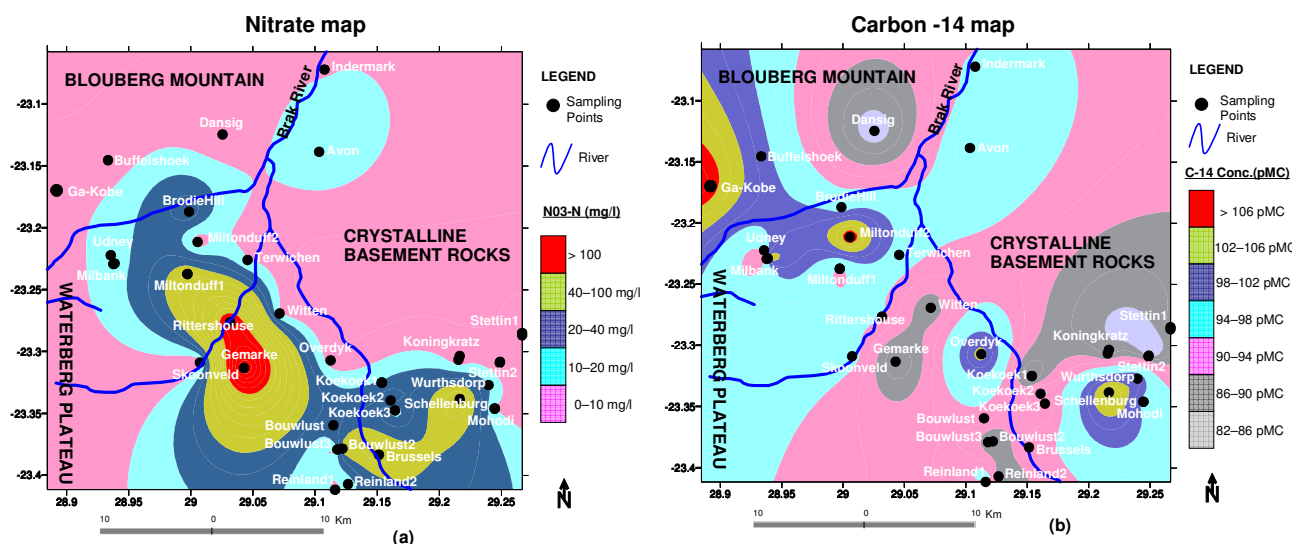


Figure 5. Spatial concentration distributions of (a) Nitrate-N and (b) Carbon-14,

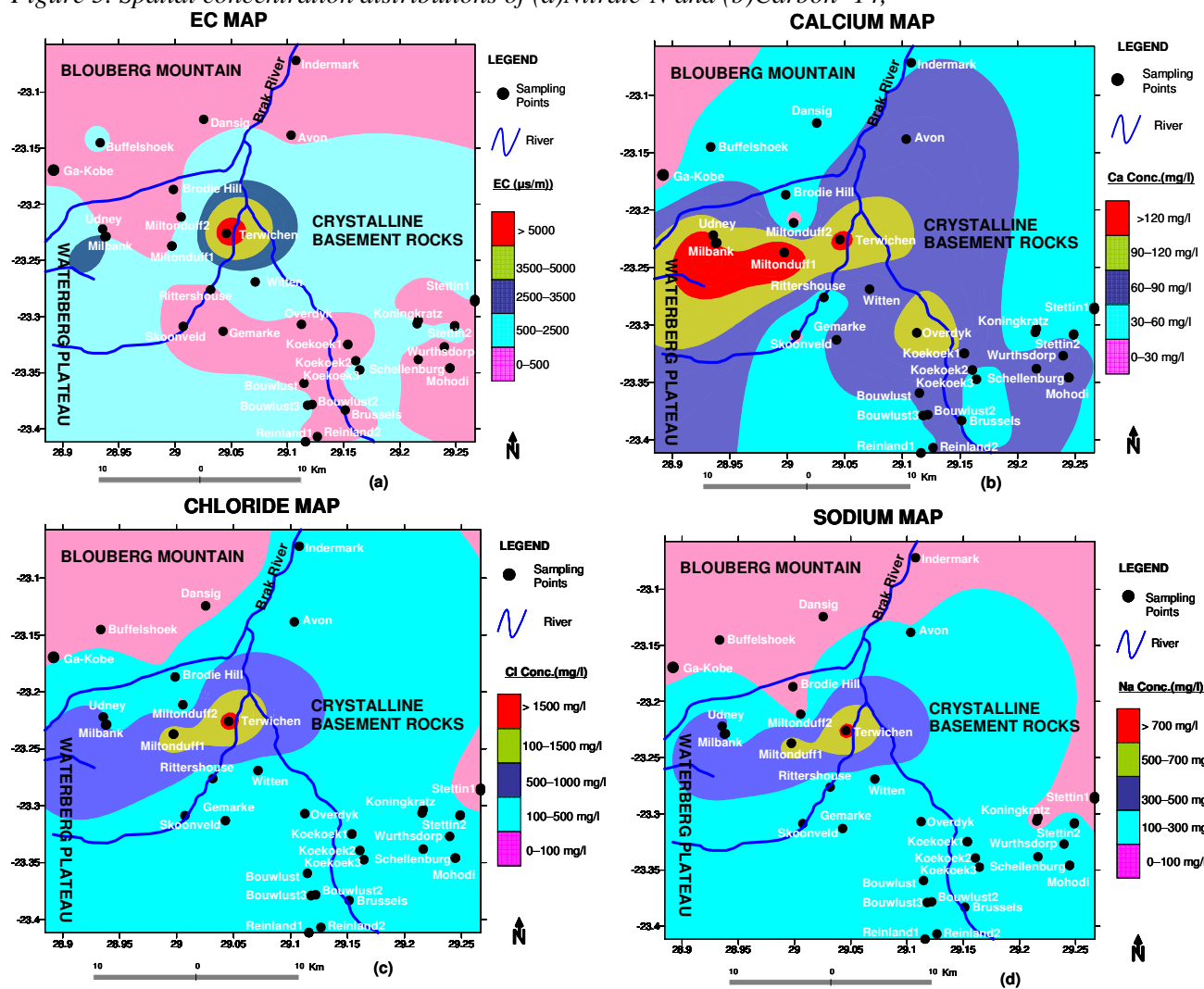


Figure 6. Spatial concentration distributions of (a) EC (b) Calcium (c) Chloride and (d) Sodium. *Note:* The EC unit is in ($\mu\text{S}/\text{cm}$) and Calcium, Chloride, and Sodium are in (mg/l).

6.2 Hydrochemistry

The results of all analyses have been plotted on both Schoeller and Piper tri-linear diagrams. All samples were obtained from equipped boreholes both motorised and hand pumped. Well-head measurements of temperature, pH, conductivity, and alkalinity were taken at each borehole during both sampling exercises.

The major ion chemistry for Bochum groundwater is presented in Table 2b for samples taken in 2005 and Table 3(b) for 2007. Hydrochemical plots are presented in Figures 7 and 8.

With few exceptions, the overall mineralisation of the groundwater samples is in the potable range. Samples with NO_3 concentrations above the potable limit of $\text{NO}_3\text{-N} \geq 10 \text{ mg/l}$ account for some 53%, a percentage very similar to that found at Taaibosch. The majority of the samples for both 2005 and 2007 (Figures 7 and 8) cluster in the centre of the Piper diamond field, with a developmental trend of a gradual mineralisation in especially Na^+ and Cl^- , but also in Ca^{2+} , Mg^{2+} , and HCO_3^{2-} .

There is no evidence of significant ion exchange, as no points fall in the Na:HCO_3 sector of the Piper diagram and the ratio of Ca/Na is rather constant. This is suggested too by a rather constant $^{13}\text{C}/^{14}\text{C}$ relationship, with only few exceptions. The clustering seen in both Piper and Schoeller diagrams is very similar for the 2005 and 2007 sample sets.

An interesting feature of especially the Schoeller diagrams is the great similarity in relative ionic concentrations (pattern) of the plots for all samples from the metamorphic granite. Most ionic concentrations, except SO_4 vary by a factor of about 2-3. A much greater spread is seen in the sandstone samples (mostly taken in 2007), where the most noticeable feature is the differences in Na and Cl . This suggests that the chemistry in the sandstone is determined more by extraneous influences, and topography, whilst in the granite, often exposed, the development is indigenous to the aquifer, determined by decomposition of the abundant feldspars.

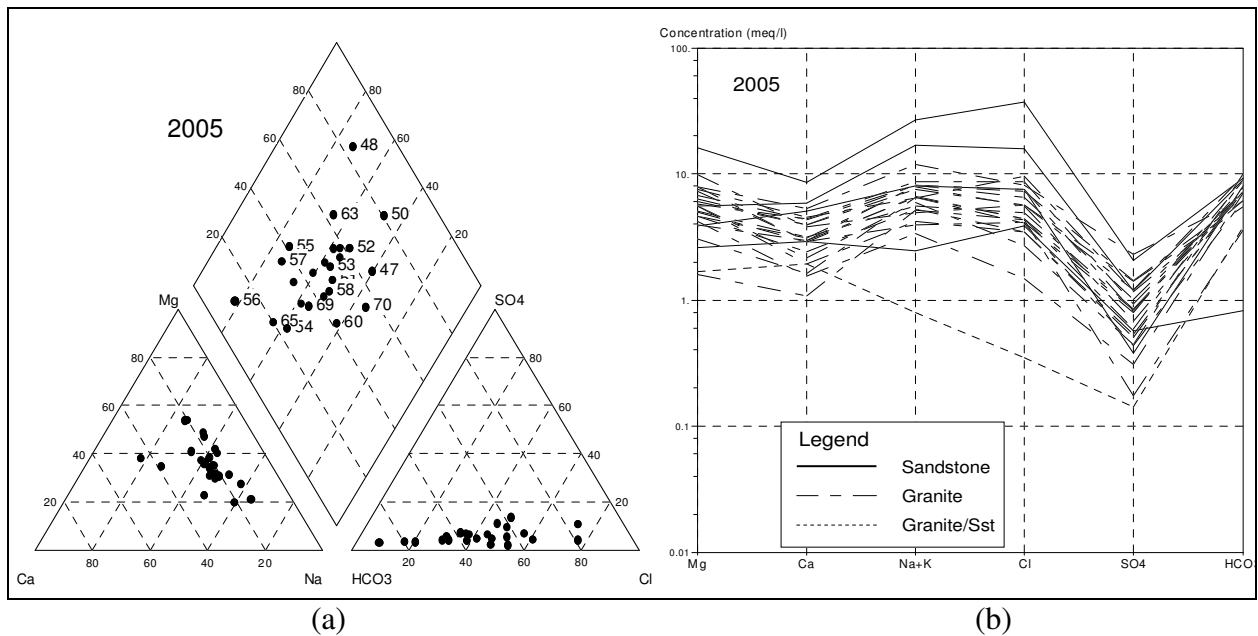


Figure 7. Major ion chemistry for 2005 water samples displayed on (a) a Piper and (b) a Schoeller diagram for ground water in different lithologies

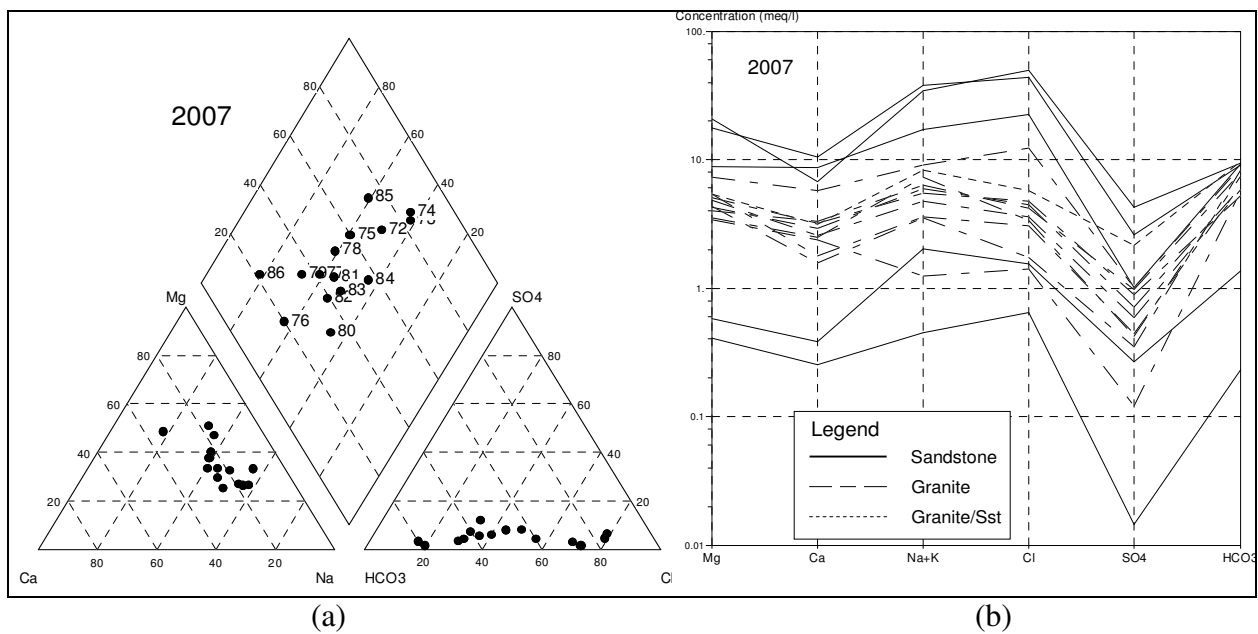


Figure 8. Major ion chemistry for 2007 water samples displayed on (a) a Piper and (b) a Schoeller diagram for ground water in different lithologies

A Piper diagram for all the sample points coded for the different lithologies is displayed in Figure 9. This shows clearly the development of the granite groundwater from Ca,Mg-HCO₃ dominance to more mineralised types, although within a relatively narrow range of mineralisations. The sandstone samples plot quite separately, especially the more highly mineralised cases, whilst the few mixed cases tend to have quite different signatures.

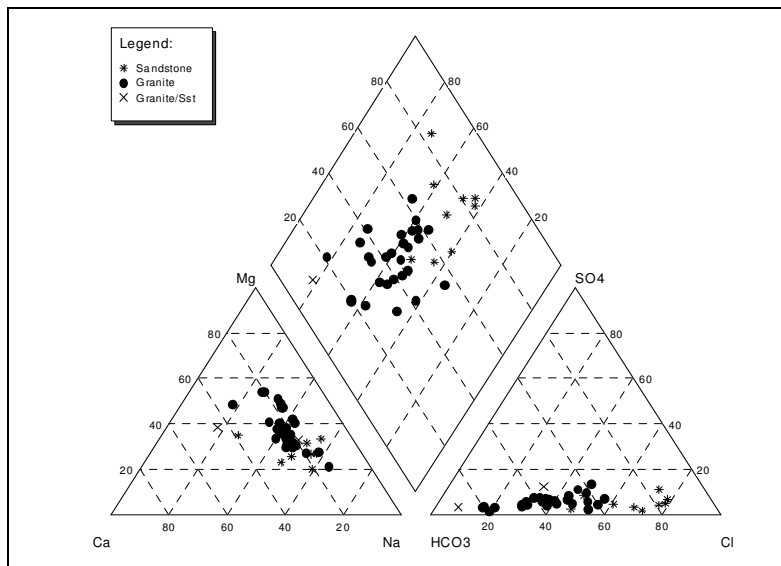


Figure 9. *Piper diagram of combined major ion data for 2005 and 2007, grouped into three hydrogeological categories (Butler 2008)*

6.3 Nitrate development

The most prominent hydrochemical feature observed in Table 2b and 3b is the high proportion (53%) of samples with nitrate concentrations exceeding the generally accepted potable limit (WHO 1995) of 45 mg/l for NO₃⁻ or 10 mg/l for NO₃-N (Verhagen et al. 2004a), as well as some exceedingly high values > 100 mg/l. This percentage is similar to that found in the Taaibosch area. Especially in densely populated rural village areas such as Bochum, such figures tend to be associated with anthropogenic sources, such as sewage, cattle concentrations etc. Nitrate concentrations do not appear to be influenced either by the aquifer environment, or major ion development.

In the Taaibosch study (Verhagen et al. 2004a,b) many cases of high nitrate concentration in the basalt aquifer were found well away from human settlements and cattle concentrations. Nitrate

furthermore did not correlate with any dissolved ion concentration or other quantitative parameter. However, it was found that high nitrate concentrations ($> 10 \text{ mg l}^{-1} \text{ NO}_3\text{-N}$) were observed only for Si(OH)_4 (expressed as Si) values $> 25 \text{ mg l}^{-1}$ see Figure 9(b)). This provided an important clue to the model of natural development of high(er) NO_3 concentrations in groundwater through the following steps. The decay of discarded functional (fine, annual) root material mobilises reduced nitrogen. Fluctuations in groundwater level could subsequently produce oxic conditions enabling mineralisation to NO_3^- . The concomitant production of CO_2 from the organic material reduces the pH of groundwater. Feldspar dissolution recommences in the aquifer thus mobilising dissolved Si (Verhagen et al. 2004a,b). The model proposes an indirect association involving many local rate-determining factors, rather than a strict correlation between NO_3^- and Si, and one of the motivations for the present study was to establish whether similar processes would/could operate in a geological environment other than basalt.

The comparative plot for Bochum and Taaibosch in Figure 10(a) and (b) shows a similar trend of higher NO_3 values associated with the Si concentration range of 30-40 mg/l, suggesting a similar mechanism of NO_3 production. It should be noticed that, in spite of the larger total number of data points for Taaibosch, the number of high nitrate cases is similar for the two areas.

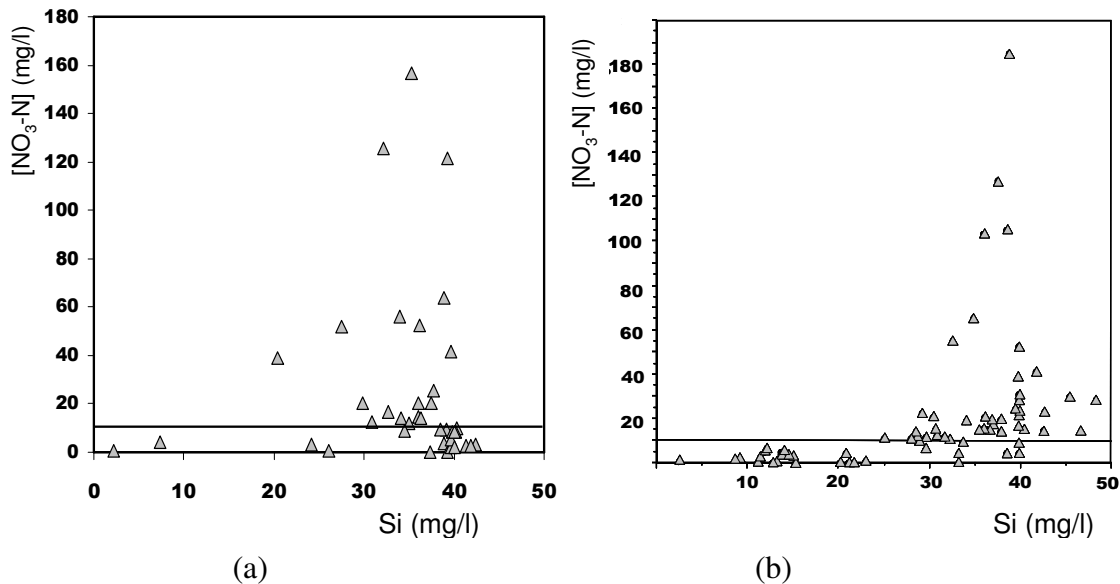


Figure 10. X-Y plots of (a) NO_3 concentration against Si concentration for Bochum (b) plot of NO_3 against Si for Phase I (Taaibosch).

6.4 Radiocarbon corrections

A plot of $\delta^{13}\text{C}$ against ^{14}C for groundwater in the Bochum area for both the 2005 and 2007 sample series is shown on Figure 11. The 2005 data set shows a negligible regression correlation coefficient ($R^2 = 0.0144$). The 2007 set has a coefficient of $R^2 = 0.4995$. However, if the two samples taken from the sandstone on the slope of the Blouberg are removed from the 2007 sample set, the correlation drops to $R^2 = 0.0008$. These two samples (TN 56, 86), with high ^{14}C and ^3H and low TAlk, EC and pH, show the low $\delta^{13}\text{C}$ values that characterise e.g. recent Table Mountain Sandstone water (Mazor and Verhagen 1983; Diamond and Harris 1997; Verhagen et al. 2009). The samples that fall in the main cluster are chemically mature, the “youngest” of which have ^{14}C values that trend only marginally below those of the mountain slope samples.

This suggests that there has been no major dilution of ^{14}C which reflects on relative ages or residence times. This is in accord with both the geology of the area as well as observed soil conditions that are essentially free of limestones and secondary carbonate deposits (calcretes).

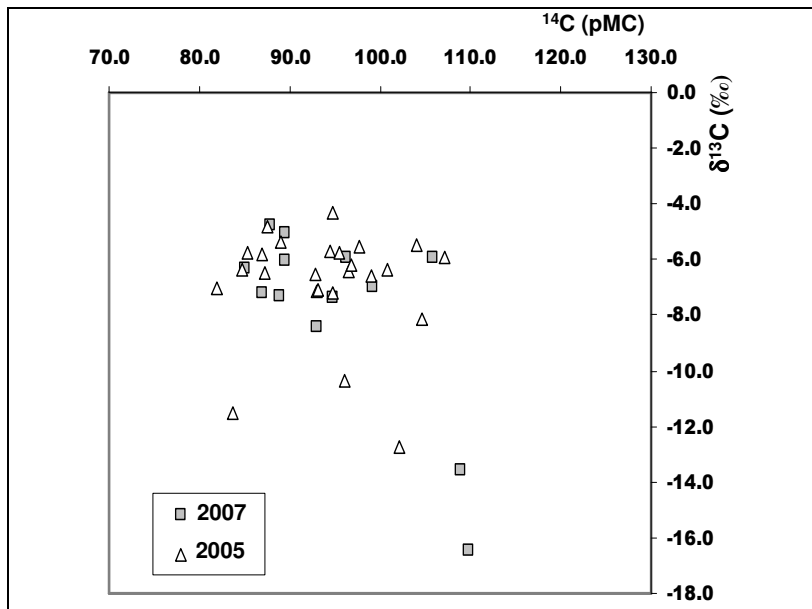


Figure 11. X-Y plot of $\delta^{13}\text{C}$ against ^{14}C for the two sampling periods. Correlation coefficients for the data sets are: 2005: $R^2 = 0.014$; 2007: $R^2 = 0.4995$; 2007 (minus the Blouberg samples): $R^2 = 0.0008$

6.5 Radiocarbon and tritium

Radiocarbon and tritium data for the two sampling periods are presented in Table 2a and 3a.

Radiocarbon values are plotted against tritium values for both 2005 and 2007 samples in Figure 12.

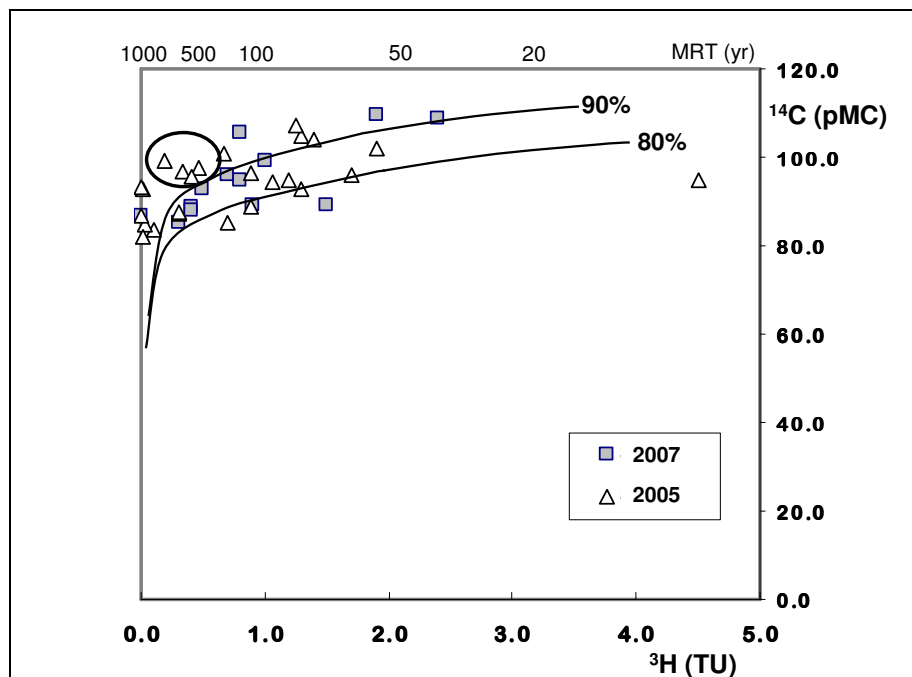


Figure 12. X-Y plot of ^{14}C against ^3H for both sampling periods. Also shown are plots of expected exponential model values for different initial ^{14}C values and estimated mean residence time as shown along the top of the diagram (Section 4.3.1)

Whereas tritium values range from 0 TU up to 4.6 TU, the range of ^{14}C values is relatively narrow, from 80 pMC to 107 pMC. Superimposed on this plot are the exponential model curves (Maloszewski and Zuber, 1982; Verhagen et al. 1991; See Section 4.3.1) of atmospheric ^{14}C against ^3H values in rain for southern Africa. The two curves are for initial, or recharge, ^{14}C concentration in DIC: A_0 of 90% atmospheric that gave the best fit for the Taaibosch data, and of 80%.

The general trend of the plotted data conforms to the idealised model. There is a (small) category of points that lies well above the model plot $^{14}\text{C} \geq 100$ pMC; $^3\text{H} \leq 0.5$ TU as in the Taaibosch area, which could be ascribed to phreatophyte root transport of ^{14}C (Verhagen 2004a,b). Where the results differ radically from those for Taaibosch is that the characteristically lower values of

^{14}C ($< 80\text{pMC}$) are missing for ^3H values trending towards 0 TU, as are mixed values $^{14}\text{C} < 80\text{pMC}$ and $^3\text{H} > 0.5$ TU i.e. plotting well below the curves. This suggests a completely different hydrology of fairly shallow circulating, very recent ($\text{MRT} < 50\text{a}$) to sub-recent ($\text{MRT} < 500\text{a}$) phreatic groundwater, in both the sandstones and the crystalline rocks. Especially in the latter, the (fracture) porosity may be expected to decline rapidly with increasing depth below surface.

The ^{14}C values as shown in Figure 12 can be interpreted as groundwater mean residence times ranging from a few decades to about 1000 years, depending on corrections applied in age calculations, implying fairly rapidly turned-over groundwater. As the soil cover in the area is generally thin, both the aquifer groups therefore should be vulnerable to surface pollutants. In the absence of details on probable aquifer porosities or borehole depths, isotope-based recharge rates cannot as yet be determined with these residence times.

6.6 Stable isotopes – $\delta^2\text{H}$ and $\delta^{18}\text{O}$

Figure 13 shows a plot of $\delta^2\text{H}$ against $\delta^{18}\text{O}$ for the combined sampling periods with the global meteoric water line (GMWL): $\delta^2\text{H} = 8\delta^{18}\text{O} + 10$ (Craig, 1961) as reference. The range of values is similar to those observed for the Taaibosch area. As at Taaibosch, the linear regression line for all the points (A-A') has a slope of 5.3, suggesting evaporative losses of rainwater before infiltration. Closer inspection however, shows that the low slope of the regression line is influenced strongly by a few outlier points at either end of the cluster, especially at $\delta^{18}\text{O} > -3\text{‰}$ and $< -6\text{‰}$.

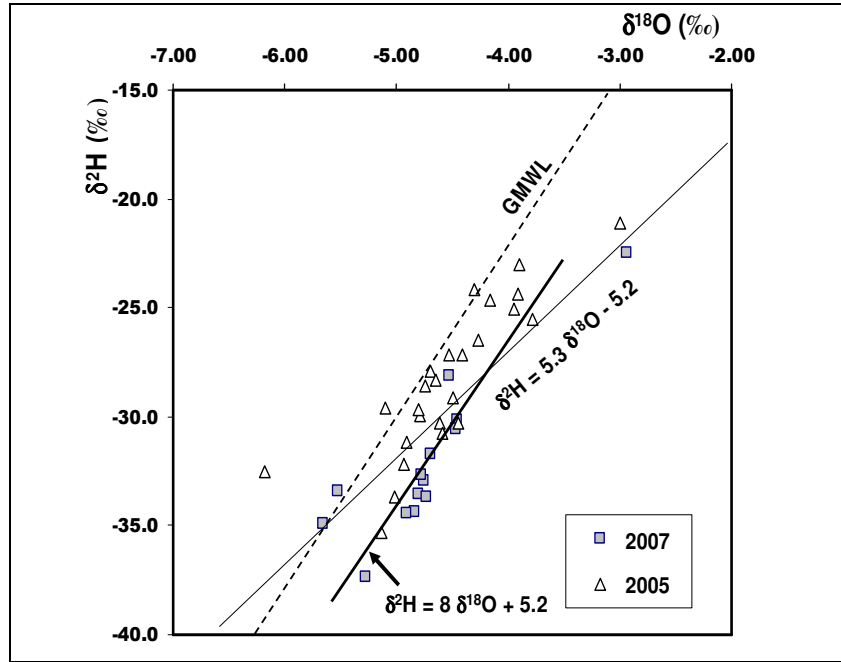


Figure 13. X-Y plot of $\delta^2\text{H}$ against $\delta^{18}\text{O}$ for the two sampling periods, with a least mean squares fit to all the points, the GMWL and a possible local meteoric water line (LMWL)

The larger body of points seems to be contained between the GMWL and a parallel line with a $\delta^2\text{H}$ intercept of +5.2 ‰. This lower bounding line may be interpreted as a local meteoric water line (LMWL) as was inferred for the Taaibosch area, where rainfall isotopic data was available for several years. The study area is characterised by a slightly undulating topography over the weathered granite with a marked drop in altitude to more level sandstone terrain to the west. Significant geographical control is seen on the steeper slopes of the Blouberg, where the most negative values are found, as are the lightest $\delta^{13}\text{C}$ values, whilst the heaviest, with an evaporation signal, are on fairly level terrain on the granite-gneisses.

Overall, the different values are interpreted as being established by rainfall selectivity produced by variable *local* recharge conditions, and surface evaporation losses before infiltration. These are likely to mask any altitude effect in rainfall over a maximum rise in altitude of sampling points of some 150m, or some -0.3 ‰ in $\delta^{18}\text{O}$ in these semi-arid conditions (Clarke and Fritz 1997). This may reflect a local rainfall regime characterised by a local meteoric water line

(LMWL), as was inferred for the Taaibosch area, where rainfall isotopic data was available for several years.

The Bochum stable isotope data therefore does not clearly reflect significant surface evaporative losses due to ponding of rainwater. The spread of data points does not suggest any particular difference in rainfall selectivity between the two main geological/physiographic terrains and do not identify a particular “recharge area”, which is corroborated by the ^3H and ^{14}C data.

6.7 The relationship between NO_3 and groundwater residence time

Generally, the concentration of tritium in groundwater is an indication of the extent of local recharge, or recharge/storage ratio. The inverse of this relationship is a measure of mean residence time. Radiocarbon gives the same type of information, but on a longer time scale. The relationship between the concentration of NO_3 and respectively ^3H and ^{14}C is shown on figure 14. For both the longer (^{14}C) and shorter (^3H) time scales, there is a trend of nitrate concentrations to increase with increasing groundwater residence time. This trend may be seen as a build-up of nitrate with increasing storage and/or depth. There is no discernible dependence of nitrate on overall groundwater mineralisation, expressed as EC.

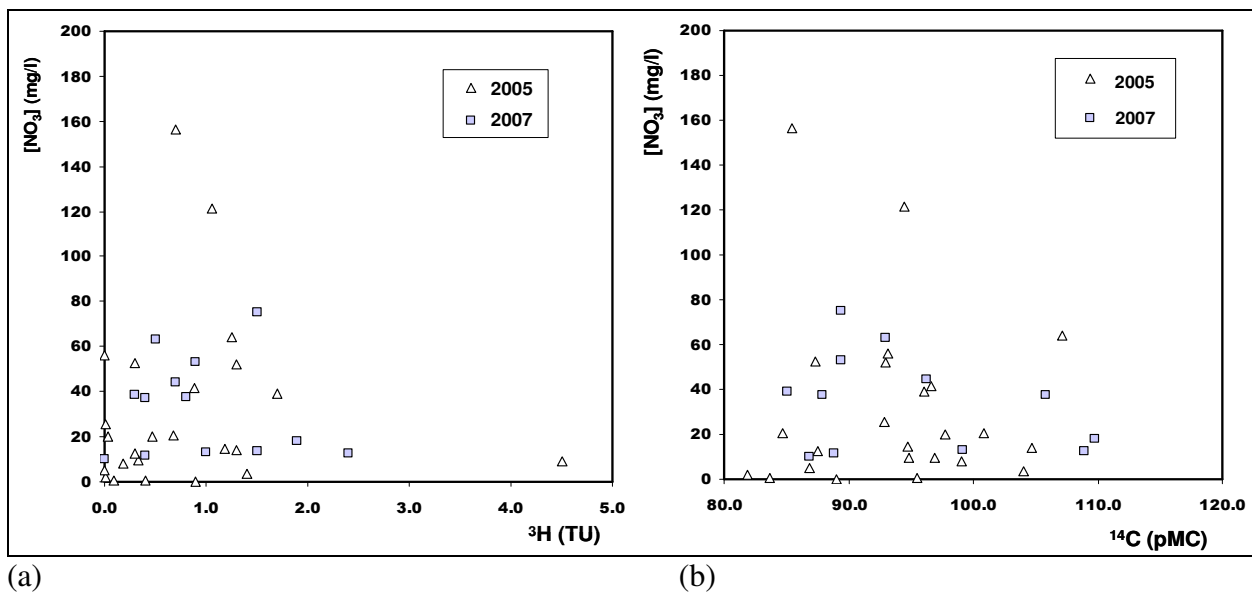


Figure 14. X-Y plots of nitrate concentrations as a function of (a) tritium and (b) radiocarbon values

The primary natural source of groundwater nitrate is taken to be the soil (Heaton 1984). In areas of thicker soil cover, the recharge rate would be lower due to evapotranspirative losses, with a concomitant increase in chloride. In areas of thinner soil cover, mainly over the gneisses, with their numerous exposures on raised terrain, rain runoff is probably higher. It is possible that at least part of the nitrate build-up with time is the result of the production of nitrate at depth. This conclusion is supported by the observed higher Si associated with higher NO_3 , characteristic also of Taaibosch ground water.

6.8 Nitrogen-15 as a function of nitrate concentration

The value of $\delta^{15}\text{N}_{\text{NO}_3}$ may act as an indicator of the source of nitrate in groundwater (e.g. Kreitler, 1975; Heaton, 1984). Values $\delta^{15}\text{N} < 10 \text{ ‰}$ are generally taken as indicating natural sources as well as nitrate derived from artificial fertilizers. Values $> +10 \text{ ‰}$, especially with attendant high nitrate concentrations, may indicate nitrate derived from animal and human waste.

Figure 15 shows no clear overall relationship between nitrate $\delta^{15}\text{N}$ and nitrate concentration in Bochum ground water. The $\text{NO}_3\text{-N}$ concentrations of only a few points lie below the potable limit of 10 mg/l. Two points with higher nitrate concentration show “natural” $\delta^{15}\text{N}$ values. The remainder show a wide range $\delta^{15}\text{N}$ values, ranging from -3 ‰ to a high of $+13.3 \text{ ‰}$ which could be regarded as sewage/animal waste associated with a trend of higher $\delta^{15}\text{N}$ for higher $\text{NO}_3\text{-N}$ values.

High nitrate concentrations therefore appear to be generated not only by sources such as pit latrines, septic tanks or livestock concentrations in areas of active recharge or near boreholes with leaky collars. Nitrate input from tillage as well as the natural process such as identified in the Taaibosch study could also contribute.

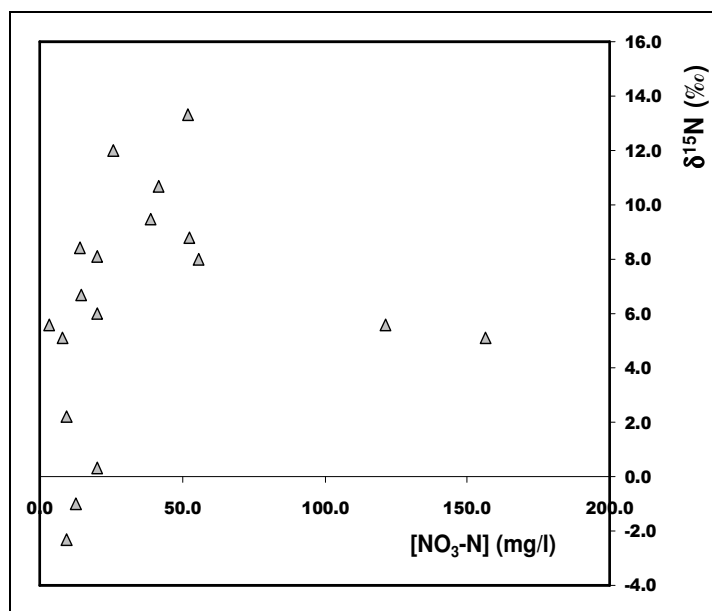


Figure 15. Plot of $\delta^{15}\text{N}$ values against nitrate concentrations for 2005 data set

6.9 Denitrification

High $\delta^{15}\text{N}$ values are generated in the process of nitrate isotope fractionation during anaerobic fermentation of nitrogen-containing organic materials, e.g. proteins. The separation of a volatile component (NH_3) that is highly depleted in the heavy ^{15}N isotope leaves the solid/dissolved residue correspondingly enriched (Heaton 1984; Clark and Fritz 1997). Subsequent mineralisation under oxic conditions generates nitrate carrying this high $\delta^{15}\text{N}$ signature. Where conditions subsequently introduce more dissolved organic material into groundwater and dissolved oxygen values drop, nitrate in its turn is subjected to anaerobic bacterial breakdown, down to NO and finally N_2 gas. In this denitrification process, with the generation of a volatile end-product, $\delta^{15}\text{N}$ values of the remaining nitrate will increase. As discussed under 2.4, a concomitant increase in $(\delta^{18}\text{O})_{\text{NO}_3}$ can be taken as a definite indication of denitrification; measurement of this parameter was not possible in this study.

Other than the plot of $\delta^{15}\text{N}$ against nitrate concentration (Figure 15) no meaningful relationship of $\delta^{15}\text{N}$ with any other measured parameter was found except for the significant inverse relationship between nitrate $\delta^{15}\text{N}$ values and dissolved oxygen levels in individual groundwater samples taken in 2005 (Figure 16). It should be pointed out that dissolved oxygen measurements were conducted at the well head whilst sampling and that samples for nitrogen isotope analysis

were immediately frozen and only thawed immediately before analysis. The relationship suggests a process of denitrification under increasingly anoxic conditions of dissolved nitrate, itself formed by mineralisation under oxic conditions, may to a considerable extent be responsible for the high nitrate $\delta^{15}\text{N}$ values observed.

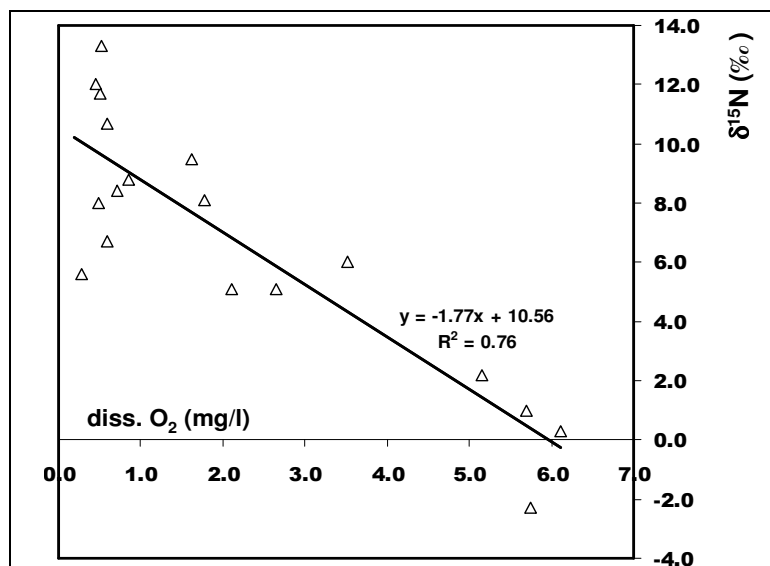


Figure 16. *The relationship between $\delta^{15}\text{N}$ and dissolved oxygen concentrations for the 2005 sample set*

The points with dissolved oxygen below 1.0 mg/l are all from boreholes at relatively densely inhabited villages. The large range of $\delta^{15}\text{N}$ values in this group appears to be independent of dissolved oxygen content and may suggest the presence of variable concentrations of organic solutes, or dissolved organic carbon (DOC) in the groundwater. This is a potability factor possibly overlooked up to now and may require further investigation. The remaining points show a marked inverse correlation of $\delta^{15}\text{N}$ with dissolved oxygen which suggests denitrification. As the sampling points are widely distributed and reflect local conditions e.g. Koekoek 1 and Miltonduff (See 6.10,11 below), it is not possible to distinguish between the primary process of denitrification, which should show an exponential relationship and mixing between differently de-nitrified end-members, a linear relationship (Kendall, 1998)

6.10 Pollution Case 1: The Miltonduff borehole

The Miltonduff borehole is situated close to the sandstone/granite-gneiss contact on the level terrain with low outcrops of sandstone nearby, on the outskirts of a village and in close proximity of cattle pens.

Major ion analysis in 2005 data (TN 50) showed fairly high mineralisation with a TDS of 5210 $\mu\text{s/cm}$, and a nitrate concentration 5 times the limit for portable water. The value $\delta^{15}\text{N} = +13.3\text{‰}$ suggests that although denitrification could occur at dissolved oxygen values of 0.5mg/l, the size of the remaining pool of nitrate argues against its isotope signatures having changed significantly by this process. Therefore it is assumed that it reflects animal excreta as the source.

The mineralisation of the 2007 data (TN 73) was found to have increased significantly by some 20%. As is confirmed by the Piper plots (Figure 7 and 8), the ionic ratios remained essentially the same, suggesting either a non-fractionating enrichment or, more likely, a greater ingress from the same pollution source. However, the nitrate concentrations had increased by some 250%. Unfortunately, the $\delta^{15}\text{N}$ value is not available.

Wellhead observation gave no indication of organic contamination in this borehole. It is therefore concluded that surface and shallow soil accumulation of animal excreta occurs which mostly dries out. Intense rainfall could mobilize the mineral content of these deposits and flush it into the aquifer.

6.11 Pollution case 2: The Koekoek 1 borehole

This borehole is situated some 30m from a dwelling house next to a sheep enclosure on sloping terrain on the edge of a granite outcrop with thin soil cover. It was being used as a drinking water supply when sampled (TN 61) in 2005, although at that stage the $\text{NO}_3\text{-N}$ concentration was 20 mg/l, i.e. well above the potable range. The $\delta^{15}\text{N}$ value was +8.1‰ and the dissolved oxygen 1.8 mg/l. These figures did not suggest major anthropogenic impact. When the borehole was revisited in late 2007 (TN 75), it was being used for garden irrigation only. Two pit latrines had been installed some 30m up-slope from the borehole. They had been excavated partially by

blasting into solid rock a year before. The borehole water had an unpleasant smell and appearance. As a result, no wellhead observations were made and a sample was taken for chemical and bacteriological analysis only.

The major ion analyses for 2005 and 2007 are compared in Table 4. There was no measurable NO_3 in the 2007 sample. Most other major ion concentrations had increased, the most marked being TAlk. Si had remained unchanged suggesting strongly that the chemical changes were not associated with water/rock interactions. A bacteriological analysis showed a total coliform bacteria count of 26000/100ml and faecal coliform at 300/100ml. The deterioration of water quality therefore can be linked directly to sewage pollution that resulted in increased dissolved organic carbon probably leading to anoxic conditions and complete denitrification of NO_3 . This may be a telling example of how a low concentration of NO_3 , or its absence, may not necessarily indicate the absence of sewage pollution.

Table 4. *Comparison of major ion chemistry of Koekoek 1 borehole as measured in 2005 and 2007. Concentrations in mg/l.*

year	pH	$\text{NO}_3\text{-N}$	F	TAlk	Na	Mg	Si	SO_4	Cl	K	Ca	EC
2005	7.99	20.3	0.21	360.3	191.6	70.1	37.5	45.0	306.2	11.7	88.4	192
2007		0.0	0.1	537.0	200	88.3	37.4	48.8	435.1	15	115	

6.12 Comparison between pollution cases 1 and 2

In contrasting the pollution trends in Miltonduff and Koekoek 1 boreholes. It is noted that at neither was there any on-site evidence that pollution could gain direct (surface) access to the borehole itself. It appears that both cases clearly represent fairly rapidly turned-over groundwater moving through the formation, and affected by pollution sources. In 2005, Koekoek borehole was in use, even provided water for other villagers and produced an unremarkable chemical analysis with slightly elevated nitrate. The 2007 analysis showed some increase in some ionic species, but the nitrate value had dropped to 0 and the water was foul-smelling. This is ascribed to dissolved organic material derived from the newly-installed pit latrines producing complete denitrification. In the case of Miltonduff, the changes were due to a large increase in overall mineralisation without a significant organic component.

CHAPTER 7: CONCLUSIONS

The spatial distributions show that major ion concentrations and environmental isotope values obtained in this study, with the exception of the steeper southern slopes of the Blouberg, with its higher groundwater mobility, are not significantly influenced by the observed regional piezometric gradients and inferred groundwater flow. Local turnover of water (recharge vs. evapotranspiration and other losses) seem to dominate the geo-hydrology of the region. No particular “recharge area” is evident from the isotope data.

Scrutinising the isotope and other analytical data presented above has thrown some light on the groundwater hydrology and hydrochemistry of the Bochum area. In particular, isotope data was able to illuminate certain aspects of the systematics of nitrate production. Animal and human waste contamination is probably only one source of medium to high nitrate levels. This is borne out by the fact that high nitrate concentrations tend to be found away from settlements. On the other hand the evidence of possible denitrification suggests a fairly general presence of dissolved organic material in groundwater that might indicate diffuse pollution. It suggests further that nitrate concentration may not, in itself, be a useful or reliable measure of anthropogenic pollution of groundwater.

Results from the Taaibosch study (Verhagen et al. 2004a,b) in a very different hydrogeological setting, and a similar incidence of high nitrate concentrations, showed quite conclusively that many of these cases were of non-anthropogenic origin. The outlines of a possible regional approach to the problem of ubiquitous high nitrate values in Limpopo Province can possibly be detected in the results of both Taaibosch and Bochum studies.

The present (Bochum) study has shown that a combination of hydrochemistry and environmental isotope analysis can contribute significantly to an understanding of the genesis of nitrate in groundwater in the context of its hydrology and hydrochemistry. The very limited number of nitrogen isotope analyses that could be produced has demonstrated that $\delta^{15}\text{N}$ data are fundamental to this, when interpreted in the framework of the overall hydrological and hydrochemical information.

In comparing the results from the Bochum study with those obtained at Taaibosch, the following may be observed.

- I. The category of high ^{14}C /low ^3H (“forbidden”) values that was ascribed to the transport of recent biogenic carbon to the water table by phreatophyte roots at Taaibosch is much less prominent in Bochum.
- II. The category of $^{14}\text{C}/^3\text{H}$ values that plots well below the exponential model curves fitted to the Taaibosch data set, interpreted as a mixture of distinct water types, is totally absent at Bochum.
- III. There is a similar striking number of cases showing a concurrence between high NO_3 and high dissolved silicon concentrations such as observed at Taaibosch. This feature therefore appears not to be unique to the basalt aquifer and may be a useful parameter for nitrate investigations in other (hydro-) geological environments. In none of the literature reviewed here has this phenomenon been reported. The mechanisms underlying the model as proposed by Verhagen et al.(2004a,b; 2005) should be investigated further.
- IV. The significant inverse correlation between $\delta^{15}\text{N}$ and dissolved oxygen, taken as a measure of de-nitrification at Bochum, was not observed at Taaibosch. Lower DOC values at the latter may be the controlling factor.
- V. The differences referred to above are ascribed to differences in vegetation distribution as well as hydrogeology, the most fundamental being the absence in Bochum of the basalt aquifer that overlies what has been shown to be highly productive deeper Karoo sandstone which appears to control the hydraulics at Taaibosch. A further factor may be the differences in the pattern of settlements in the two areas which, as stated above, may characterise differences DOC values distributions.

In the reviewed literature, both international and southern African, only in the work of Stadler (2006) has there been a similar attempt to combine the various inputs of hydrogeology, isotope hydrology, major ion and nitrogen isotope hydrochemistry in

unraveling questions surrounding the anthropogenic and natural generation of (high) nitrate concentrations in groundwater.

This study therefore suggests a need for and recommends further investigations, such as ongoing monitoring of nitrate levels, in areas of suspected pollution as well as areas where natural processes seem to operate. Further defined areas with high groundwater nitrate occurrence should be subjected to intensive, multi-parameter studies such as has been outlined here.

Due to a variety of factors, a reliable, routine analytical facility for $\delta^{15}\text{N}$ measurements is no longer available in South Africa. An initiative to re-establish such a facility would provide invaluable support to such investigations.

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APPENDIX

NORMALISING ^2H AND ^{18}O DATA (all δ values are in ‰ SMOW)*	
Calibration standards used:	
V-SMOW _{reference} :	$\delta^2\text{H} = 0.0$
(Standard Mean Ocean Water)	$\delta^{18}\text{O} = 0.0$
V-SLAP _{reference} :	$\delta^2\text{H} = -428.0$
(Standard Light Antarctic Precipitation)	$\delta^{18}\text{O} = -55.5$
Normalising Equation:	
$X_{\text{normalised}} = (X - \text{SMOW})_{\text{measured}} * (\text{SMOW} - \text{SLAP})_{\text{reference}} / (\text{SMOW} - \text{SLAP})_{\text{measured}}$	
To check normalising slope:	
V-GISP _{reference} :	$\delta^2\text{H} = -189.73$
	$\delta^{18}\text{O} = -24.78$
Internal Standards:	
high : $\delta^2\text{H} = -4.8$ ($\sigma = 0.32$); $\delta^{18}\text{O} = -1.11$ ($\sigma = 0.03$)	
low : $\delta^2\text{H} = -21.5$ ($\sigma = 0.28$); $\delta^{18}\text{O} = -4.89$ ($\sigma = 0.03$)	

* Procedure used in Environmental Isotope Laboratory, iThemba LABS (Gauteng). (M.J.Butler pers. comm.)