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# Development of a local sampling and monitoring Protocol for radioactive elements in fractured rock Aquifers in South Africa using a case study in Beaufort West

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By

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I, Gaathier Mahed, declare that the work, Development of a local sampling and monitoring protocol for radioactive elements in fractured rock aquifers in South Africa using a case study in Beaufort West, is my own. Furthermore all related works have been cited and referenced appropriately.

Signature 30th November 2009

*‘To my late grandfather, Sheikh Aburazak Najjaar, who always supported the pursuit of knowledge ’*

## Acknowledgements

Firstly I must thank my creator for placing me on this Earth with a purpose, this is not entirely clear to me but hopefully it will unfold as I move through this world

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## Abstract

**Keywords:** Groundwater sampling, radioactivity, fractured rock aquifers, uranium, radon, groundwater monitoring, protocol,

The aim of this study was to test whether one could use the same methods as used for sampling heavy metals and apply them to radioactive elements. Furthermore a sampling protocol was developed, the first of its kind, for the sampling of radioactive elements in fractured rock aquifers. This was achieved by initially examining local as well as international manuals and methods. The aforementioned was done in conjunction with a literature review of the movement of radioactive elements in these fractured rock aquifers.

Beaufort West was utilised as a study area and the geology, hydrogeology and topography was outlined. Background radioactivity was generally acceptable except for two samples which were anomalously high. Taking cognisance of the methods used, as well as those previously applied in the area and abroad, a sampling protocol for radioactive elements in fractured rock aquifers was developed and attached as an appendix.

In conclusion it was suggested that multiple methods be tested on one well in order to check whether similar results would occur. This would thus determine the best applicable methods. Also it was proposed that a new method, called DGT sampling, be applied in order to gain a time weighted average of the heavy metals and radioactive elements in groundwater. It could also be clearly seen, by comparing historical data and the current data, that the methods used for sampling heavy metal can be applied to radioactivity.

## Abbreviations:

DGT-Diffusive Gradient Thin Films

DOE-Department of Energy

DME-Department of Minerals and Energy

DWAF-Department of water affairs and Forestry

EPA- Environmental Protection Agency

HDPE- High Density Poly-ethylene

IAEA- International Atomic Energy Agency

$\mu$ - micron

mBq/l- milli Becquerel per litre

mg/l- milligrams per litre

ml/min- millilitres per minute

L/min- Litres per minute

QA/QC-Quality control/ Quality assurance

NECSA- Nuclear Energy Corporation of South Africa

USACE- United States Army Corps of Engineers

USGS- United States Geological Survey

W.R.C-Water Research Commission

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# Chapter 1 Introduction

## *1.1 Background*

Potable water is becoming increasingly important due to population growth. More importantly, groundwater is the most abundantly available fresh water resource (Miller, 2002). Both groundwater quantity and quality are critical for the development of communities who are solely dependant upon groundwater. Under a natural environment, the factors affecting groundwater quality mainly include the rocks involved in an aquifer, recharge sources feeding the aquifer, time of subsurface water circulation, and so forth. Radioactive elements such as Uranium and most of its daughter products usually pose a negative impact on groundwater quality because they can be dissolved in and transported by groundwater during the process of Uranium-rich rock and water interaction, especially under an oxidized environment.



Due to the increase in the price of Uranium (Fox, 2007), which has stemmed from an increase in demand and limited supply, inevitably there will be an increase in the volumes of waste. Mudd (2000) has shown the devastating impacts which Uranium mining has on the environment, specifically groundwater, where the uranium-rich rocks are extensively exposed to air and water under an oxidized environment. Also the effect of nuclear waste is still felt today in the vicinity of Chernobyl, Hiroshima and Nagasaki. Therefore being able to effectively monitor radioactivity is critical for the health of humanity and the advancement of the human race.

To effectively monitor and assess the radioactivity of Uranium and its daughter elements in groundwater, concentration analysis in laboratory is often employed. This method requests an appropriate in situ groundwater sampling which can be influenced by device, selection of sampling network, quality and quantity of water sampled, and so forth. Unfortunately, there is yet not a uniform groundwater sampling guideline which can be applied to the areas dominated by fractured rocks. Particularly, not a single sampling manual and monitoring protocol is available for the research of radioactive elements in fractured rocks (Jousma and Roelofsen, 2003).

The project for the development of a sampling and monitoring protocol for fractured rock aquifers was commissioned by the W.R.C. A consortium of researchers worked in conjunction with scholars in the field in order to produce the protocol, with special focus placed on radioactive elements. Furthermore these aforementioned fractured rock aquifers underlie an extensive area of the country. Due to their highly heterogenous nature, as well as their ability to yield water, we find a substantial amount of research is being carried out in an attempt to understand these saturated geological units. Lastly the health impacts relating to radioactivity are not the focus of this study and the reader is referred to various other texts dealing with the subject matter.



## *1.2 Aims and Objectives:*

In relatively recent times, various studies have characterized the extent to which natural radioactive contamination is occurring within groundwater (Hainberger et al, 1974, Horvath, 2000, Godoy and Godoy, 2004, Ilani et al, 2005). Unfortunately there is no standard sampling or monitoring protocol available for the radionuclides within secondary aquifers. Although it has been suggested that radioactively contaminated groundwater should be sampled using the same protocol as for heavy metals (Wilde et al, 1998; Smedley et al, 2006; Weaver et al, 2007), very few researchers eventually investigate the effectiveness of these methods applied to the secondary aquifers that are different from primary ones.

Groundwater contamination from radioactivity causes extensive problems (Fetter, 2001). These impacts are long lasting due to the half lives of the radionuclides. Also the fundamental characteristic of fractured rock aquifers is extreme spatial variability in hydraulic conductivity (Cook, 2003).

It is also important to note that Uranium and its daughter products have adverse effects on human health. In order to minimise these impacts the monitoring of these radio-nuclides has to be done in an effective standardized manner.

Thus the aim of this work is to ascertain the applicability of the sampling methodology for radioactive elements, as outlined by Wilde et al (1998), Smedley et al (2006) and Weaver et al (2007).

This goal would be achieved by sampling, as well as carefully examining international best practices and adapting them in order to suit the nature of radioactive elements in fractured rock aquifers.



### *1.3 Radioactive contamination of groundwater:*

Radioactive contamination has devastating impacts on the environment. This problem is escalated when the groundwater is contaminated due to the fact that it is extremely difficult to remediate.

Mudd(2002) reviewed contamination from Uranium mill tailings in Australia. The Ranger project, which was one of the case studies, highlighted the fact that fractures are able to act as conduits for contamination. White and Gainer(1985) drew similar conclusions, relating to contaminant movement. Factors such as fracture density, width, aperture and length would be the main determinants in mass transport. Thus if the flow of water is faster, the time allowed for interaction with the surface of particles or fracture walls within the aquifer is limited. This has to be looked at in conjunction with the chemistry of the radionuclides in order to determine their movement within the saturated zone (Figure 1). The rapid movement along the preferential pathways led to contamination of a world heritage site in the vicinity of the Ranger mine. One would deduce that the highly acidic contaminant would aid in the dissolution of the carbonate fractured media as well as mobilize heavy metals in the subsurface, as shown by Mudd(2000). Unfortunately the hydrogeochemistry was not reviewed.

Mudd (2000) has also examined the effects which In situ Leaching (ISL) mining has on the environment. ISL mining is a most common method of extracting Uranium from its ore. A slightly acidic and heavily oxygenated solution is circulated through boreholes and the Uranium is extracted at the surface by an ion exchange process (Lacy, 2003). Upon precipitation the Uranium or "yellowcake", as it is more commonly known, is packed into drums ready to be shipped.



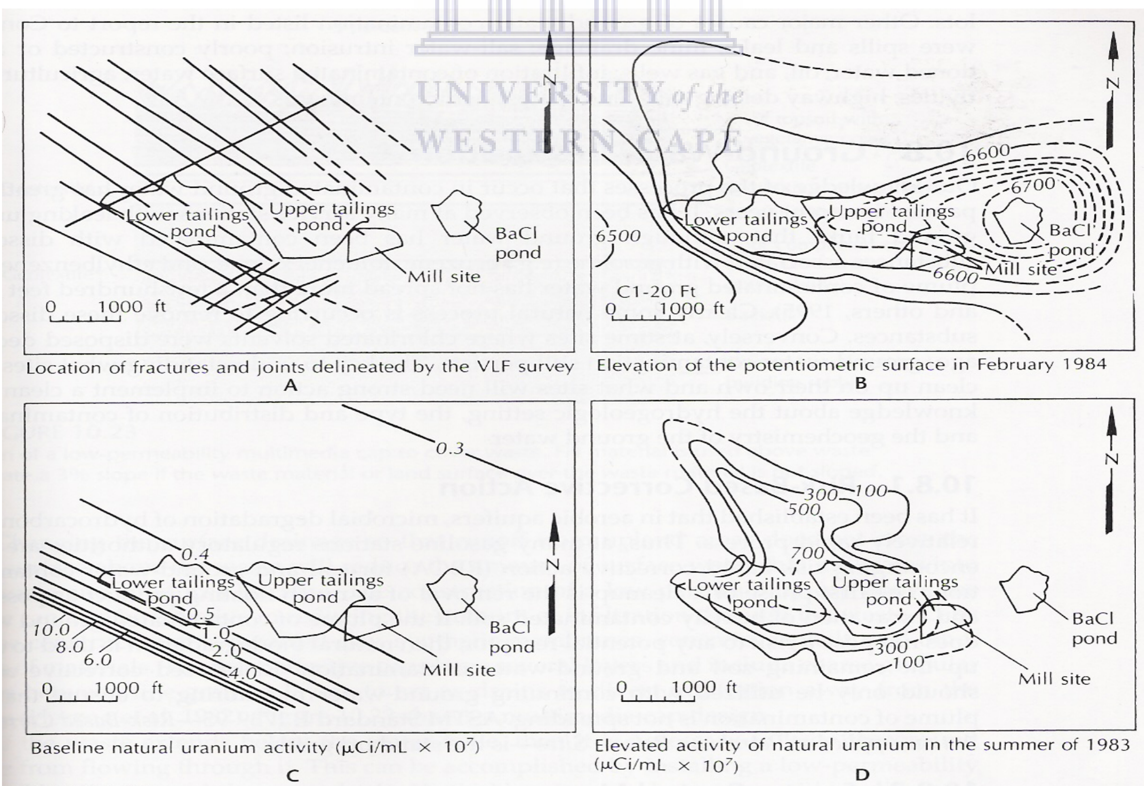



**Figure 1:** The seepage of Uranium from a tailings pond (White and Gainer-1985).

This method of mining method significantly alters the groundwater quality in the region (Mudd, 2000).This is due to the fact that extraction methods liberate the Uranium and thus allow it to seep into the aquifers, if the liquid is not transported to the surface. A comparison before and after ISL mining can clearly be seen in Table 1 and one can deduce the aforementioned devastating impacts. An extensive review of work completed, relating to ISL, in the former Soviet Union as well as Asia has been compiled by Mudd (2000). The author looked specifically at groundwater quality and it was determined that desperate measures need to be taken for remediation. This is important due to the fact that a public water supply was in close vicinity to the contamination area. Mudd (2001) also drew similar conclusions with regards to ISL mining in America and Europe.



| | pH | TDS | $SO_4^{-2}$ | $NO_3^-$ | F | U | Ra |
|---|---|---|---|---|---|---|---|
| | units | g/L | g/L | mg/L | mg/L | mg/L | Bq/L |
| Cenomanian Aquifer-confined (Before) | 6.7 | 0.14 | 0.033 | <1 | <1 | 0.02 | 8.74 |
| Cenomanian Aquifer (After) | 1.8-2.8 | 5-20 | 3.3-13 | 5-100 | 5-50 | 0-15 | 30-70 |
| Turonian aquifer-unconfined(Before) | 6.7 | 0.1 | 0.035 | 5.2 | <1 | 0.01 | 0.07 |
| Turonian aquifer(After) | 2.5-7.0 | 0.5-5.5 | 0.05-3.3 | 5-1000 | 0.5-25 | <1 | 0.1-1 |

**Table 1**: A comparison of average groundwater quality before and after ISL mining in the Czech Republic (Mudd, 2000)

A more intensive study was completed by Gomez et al (2006). The geology of the area was critically analysed and this included a model for the fault architecture. This abandoned mine, on the Iberian peninsula, was located within granitic pluton which hosts a Uranium deposit. The secondary mineralisation of the Uranium deposits meant that the deposits would occur in the vicinity of fracture zones. Interestingly enough a generic sequence, in terms of Uranium deposits has been established with depth: pitchblende, parapitchblende, sooty pitchblende, coffinite, black, orange and yellow gummites and uranyl phosphates (Gomez, 2006). Equilibrium modeling, which closely correlated to the actual results of the sampling, proved that the uranyl carbonate complexes dominated the aqueous phase. The authors extensively sampled and analysed the groundwater in order to gain a fully representative sample. This excellent study epitomizes the manner in which sampling for Uranium should be carried out. The knowledge of geology and hydrogeological parameters aided the understanding of hydrogeochemistry.

The aforementioned secondary mineralisation phenomena could be explained by the precipitation of radioactive elements along fracture walls (Durrani and Ilic, 1997). This means that one would find a higher concentration of the mineral in the fracture than the rock matrix (Figure 2). Therefore specific areas, within fractured rock aquifers, would have anomalously high Radon emissions. Furthermore the short half life of the radionuclides would mean that it cannot be transported great distances, due to the fact that it would completely decay. Thus when the Radon is detected it would be indicative of Radium being at or near the rock water interface (Wood et al, 2004). The parent material, Uranium, would also be liberated by means of alpha recoil (Ivanovich and Harmon-1982).

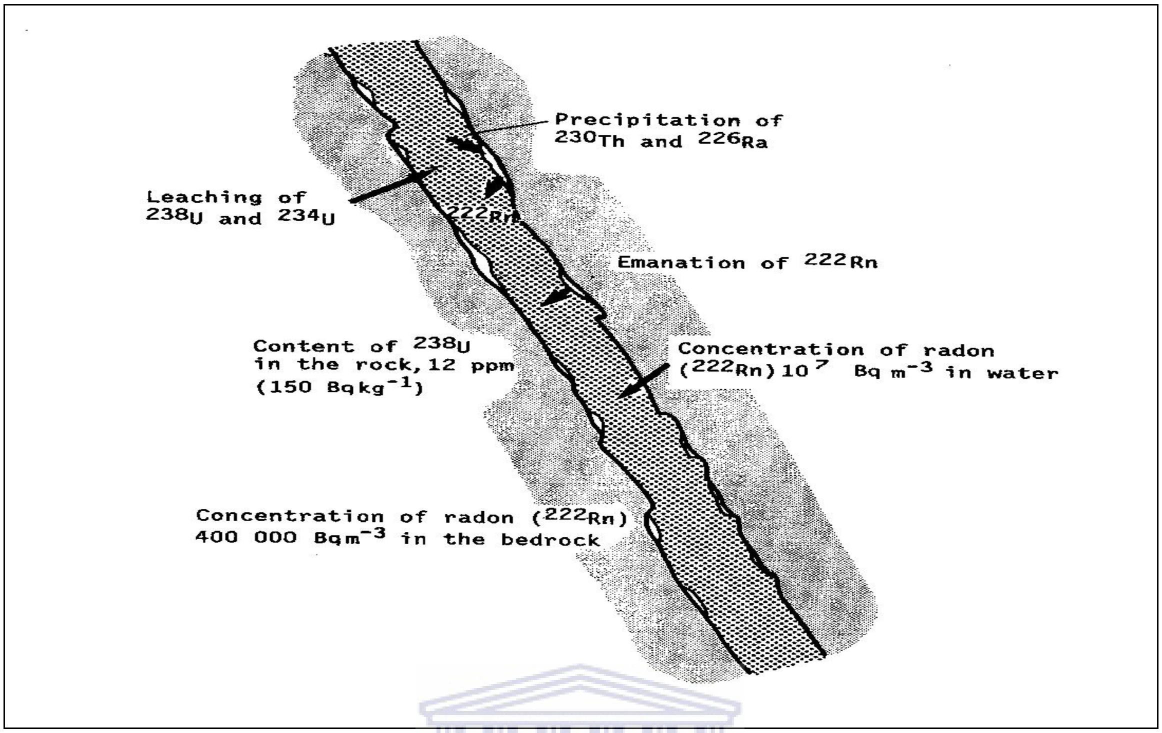



**Figure 2**: Increase concentration of Radon in fractures due to precipitation of parent elements (Durrani and Ilic, 1997)



On a local scale, in South Africa, we find that most of the radioactivity related to mining stems from Gold mines in the Witwatersrand basin( Rosner et al, 2001) Scholtz (2003) has also shown that a considerable amount of radioactivity has scarred the areas in the vicinity of Uranium trial mines near Beaufort West. When one compares this to the devastating impacts which Uranium mining has had on a global scale, we can clearly see that our environment is in for a terrible shock.

Winde and Van der Walt (2004) have examined the contamination stemming from gold mine tailings dams in the Witwatersrand basin. The authors have shown that the alluvial aquifers act as a conduit for the contaminated tailings, which migrate into surface water supplies. Once present in streams, this radioactive liquid mobilises other metals and adsorbs to sediment, thus slowly decaying and constantly releasing daughter products. (Wade et al, 2002)

The impacts of these mines are long lasting and they continue to contaminate the groundwater even after closure (Hodgson et al, 2001). Rosner et al (2001) examined multiple mine reclamation sites within the Witwatersrand area. Pedological profiles and soil samples within the reclaimed tailings dams were taken. These were shown to contain elevated levels of heavy metals and Uranium. Only certain sites allowed a shallow groundwater sample to be taken and these were unfit for human consumption due to displaying similar characteristics to the soil. Thus one can deduce that the conditions of the environment, specefically groundwater, prior to mining cannot be attained by means of reclamation due to the alteration of the natural state of the landscape.

# Chapter 2 Literature review

## *2.1 Physio chemical properties of Uranium:*

Uranium is the last naturally occurring element on the periodic table. It has three naturally occurring radioactive isotopes, which are $^{238}U$,$^{235}U$ and $^{234}U$ These isotopes have a natural relative abundance of 99.27%, 0.72% and 0.0055% respectively. This actinide, which forms part of any of a series of radioactive elements with atomic numbers 89 through 103, also forms the parent material for two decay series (Appendix A & B) When purified it forms a silvery white material with a density of 18.95 at melting point of 1132˚C and boiling point of 3818˚C. Martin Klaproth, a German chemist, was the first scientist to discover Uranium and do research on its chemical composition. He came across the element in samples of the mineral pitchblende.



By inferring from Table 2 and Figure 3 it can clearly be seen that in natural water Uranium would occur as urananite and rutherfordine, rendering both compounds as insoluble. At low pH and in reducing environments we find the possibility of a soluble species of Uranium in the form of $U^{4+}$. Also at high pH and oxidising conditions the Uranyl dicarbonate and tricarbonate species are dominant
(Figure 4).

| Compound | Valence | Dissolved state | Remarks |
|---|---|---|---|
| $U^{3+}$ | +3 | Soluble | |
| $UO_2$ | +4 | Insoluble | Urananite |
| $U^{4+}$ | +4 | Soluble | |
| $UOH^{3+}$ | +4 | Soluble | |
| $U^{5+}$ | +5 | Soluble | Laboratory conditions |
| $UO_2^{+}$ | +5 | Soluble | Laboratory conditions |
| $UO_2CO_3$ | +6 | Insoluble | Schoepite |
| $UO_2^{2+}$ | +6 | Insoluble | Rutherfordine |
| $UO_2OH^{+}$ | +6 | Soluble | |
| $UO_2(CO_3)_22H_2O^{2-}$ | +6 | Soluble | Uranyl dicarbonate |
| $UO2(CO_3)_3^{4-}$ | +6 | Soluble | Uranyl tricarbonate |

**Table 2**: Uranium compounds to be found in natural water (Johnson 1994).

Hem (1986) suggests that Uranium is present in most natural water in concentrations between 0.1 and 10µg/l. This natural occurrence would occur alongside other ions and compounds, thus altering the phase diagram due to the fact that the water would not be pure. Ilani et al(2005), on the other hand, allude to the fact that Uranium does not occur in the aqueous phase in an anoxic environment. The geothermal brine, which formed part of their study, bears testimony to this point. Taking into consideration this fact, as well as Figure 3, it can be concluded that groundwater in a reducing environment would not contain Uranium.

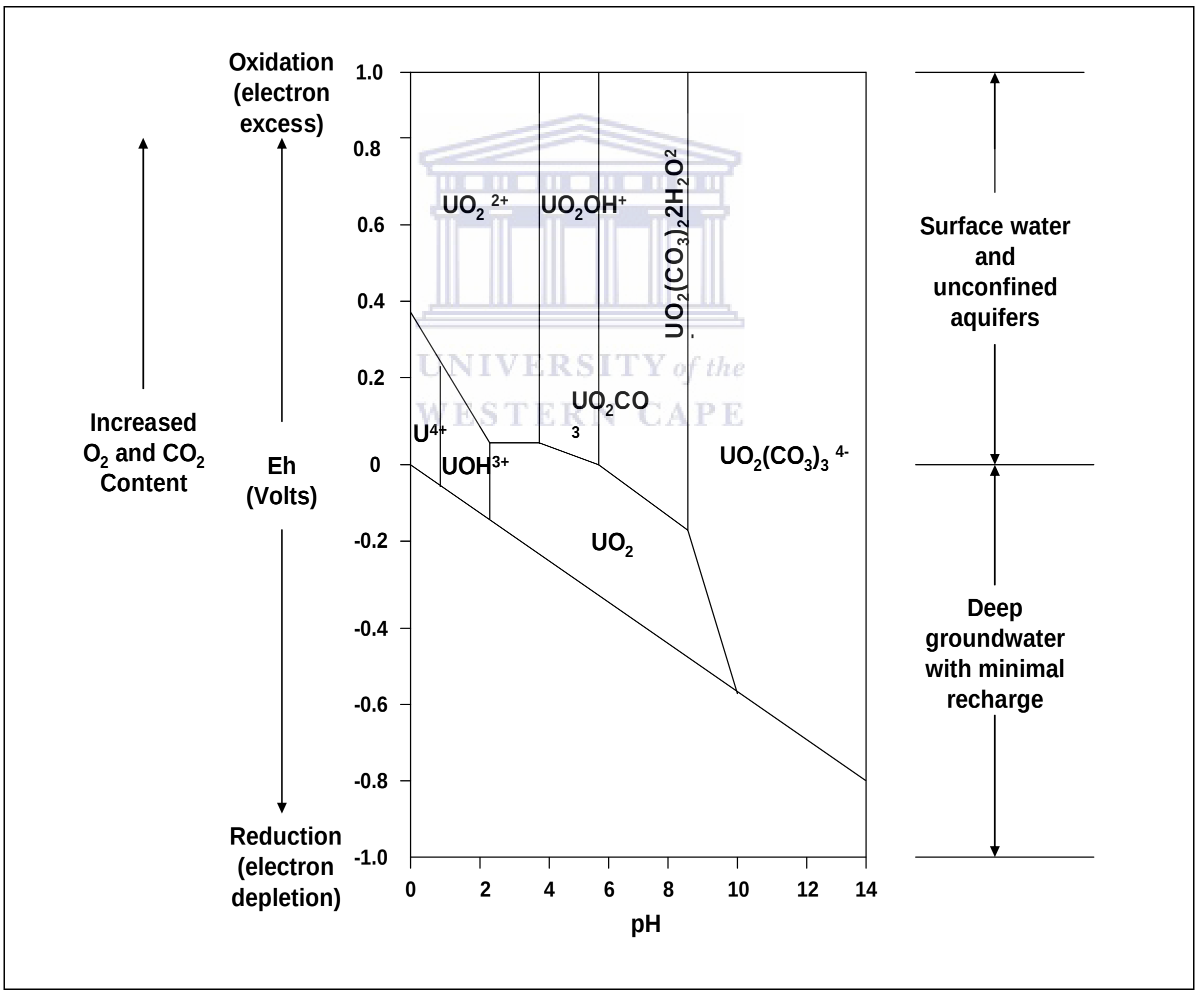




**Figure 3**: Phase diagram of Uranium speciation in water (Grainger, 1958)

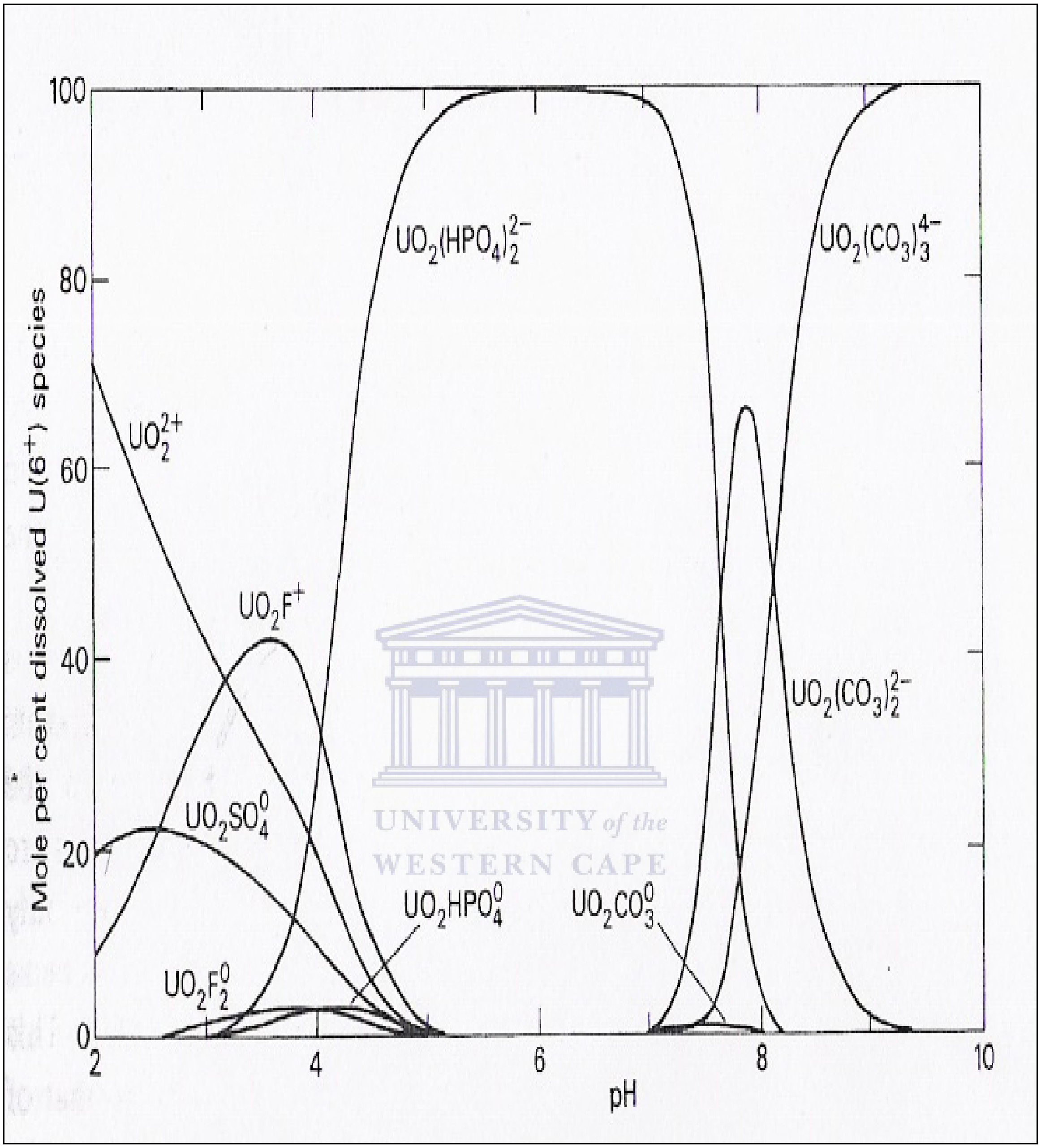



**Figure 4:** Distribution of uranyl complexes plotted against pH at 25˚C for a total U concentration of $10^{-8}$ M in the presence of other ions: F=0.3ppm, Cl=10ppm, $SO_4$=100ppm, $PO_4$= 0.1ppm and $SiO_2$= 30ppm (Ivanovich and Harmon, 1983).

Fetter (1999) stated that Radium is more soluble than both Uranium and thorium and can be bio-concentrated in plants. Ivanovich and Harmon(1983) on the other hand disagree, and have shown that Uranium is much more soluble (Figure 5) Hem(1985) suggests that the Radium behaves somewhat like barium, due to the fact that they both belong to the alkaline earth metals. It seems though that solubility is dependant on multiple factors, as previously shown.

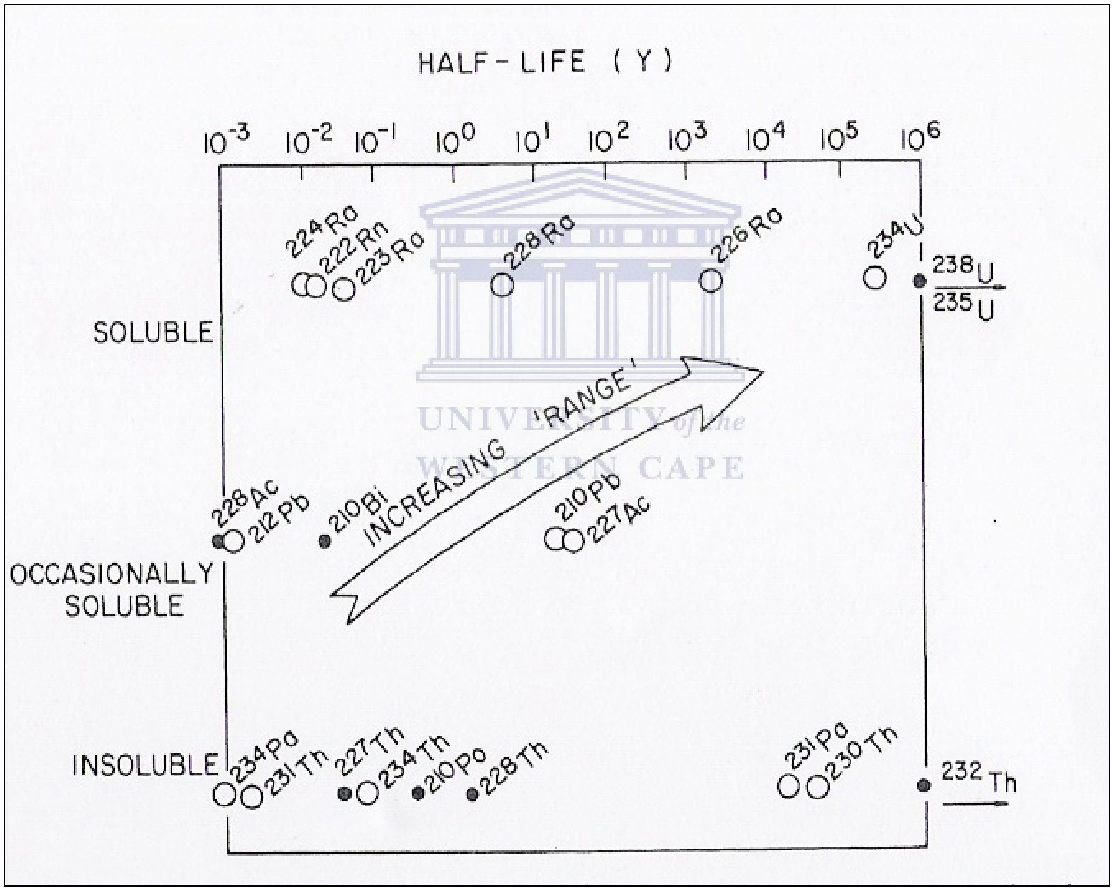



**Figure 5**: Solubility of some of the major radionuclides in relation to their half-lifes. (Ivanovich and Harmon, 1983).

## *2.2 South African Water Quality guidelines for Radioactivity:*

DWAF(2002) has classified water quality in relation to radioactivity(Table 3). Chemical as well as radiological indicators were used as parameters for quality determination. A study using these standards as a benchmark was carried out in the Klip River Catchment, Gauteng(D.W.A.F, 2003). In this specific study groundwater as well as surface water was monitored for radioactivity. It was recommended that discharge by mines should be kept at a minimum in order to maintain the water quality at the time. It was also concluded that if water quality should deteriorate then it would be unfit for human consumption.

A similar monitoring programme was conducted in the Northern Cape(D.W.A.F, 2005) From this study it was determined that the water at only one borehole was unfit for human consumption and household use. The majority of the water had some trace of radioactivity but it was still potable in terms of D.W.A.F(2002). The source of the radioactivity is most probably the underlying geology.



Horvath et al(2000) consider Radon to be the primary cause of health damage among the radionuclides. Furthermore the authors state that Radium is also a major health hazard due to its ability to be built into bones. Wade et al (2002) also extensively examine the health impacts of radioactivity, specifically in surface water.

On the other hand Przylibski et al(2004) suggest that some radioactivity could be conducive towards an individuals well-being. The authors' argument lies in the fact that spring waters in Poland, with an elevated Radon content, are used for balneatic purposes. Springs are frequented by individuals and are believed to alleviate certain disorders and just generally relax those who bathe in their waters. Therefore it can be deduced that some threshold does exist relating to radiation levels as well as the period of exposure. Thus understanding the migration of the radionuclides in groundwater is of the utmost importance

| *Class /Colour* | *Dose range; mSv/a* | *Health Effects and Typical Exposure Scenarios* | *Intervention Decision Time Frames* |
|---|---|---|---|
| **Class 0** (Blue - Ideal water quality) | 0.01 – 0.10 | • There are no observable health effects.<br>• This is the range of exposure from ideal quality water sources.<br>• Most treated water falls in this water quality range.<br>• Additional doses that result from human activities that fall within this range are difficult or impossible to determine and/or to distinguish from variations in background doses with sufficient confidence. | Intervention not applicable for this class of water. |
| **Class 1** (Green - Good water quality) | > 0.10 – 1 | • There are no observable health effects.<br>• It is the range of exposure from some natural and untreated water sources (e.g. ground water / wells) as well as water sources that could be influenced by mining and mineral processing activities.<br>• A dose between 0.2 to 0.8 mSv/a is the typical worldwide range of ingestion radiation dose resulting from water as well as food.<br>• A dose equal to 1 mSv/a corresponds to the regulatory public dose limit for human activities involving radioactive material. | No intervention is required although ALARA principles apply. |
| **Class 2** (Yellow - Marginal water quality) | > 1 – 10 | • A small increase in fatal cancer risk associated with this dose range.<br>• Probably only a small number of natural water sources of this quality exist, resulting from exceptional geological conditions.<br>• Abnormal operating conditions at some nuclear certified mineral and mining processes may result in a dose in this range when a person drinks the untreated water. Intervention will most likely be required to improve the quality of water that is released into the public domain.<br>• The total natural background radiation from all exposure pathways, not only water, falls in this range. | Intervention considerations within 2 years. |
| **Class 3** (Red - Poor water quality) | > 10 – 100 | • Health effects are statistically detectable in very large population groups.<br>• This range represents excessive exposure.<br>• It is highly unlikely to find water of this poor quality in the natural environment. | Intervention is required in less than 1 year. |
| **Class 4** (Purple - Unacceptable water quality) | > 100 | • Health effects may be clinically detectable and a significant increase in the fatal cancer risk (greater than one in a thousand).<br>• A dose greater than 100 mSv can usually only occur during a major accident at a nuclear facility. These facilities have to demonstrate that such an accident cannot happen with a frequency of more than once in a million years. | Immediate intervention is required. |

**Table 3**: Classification of water quality according to radioactivity (D.W.A.F, 2002)

## *2.3 Existing sampling and monitoring protocol:*

### *2.3.1 Local*

The most comprehensive groundwater sampling guide, in South Africa at the moment, would have to be the second edition of “Groundwater sampling”(Weaver et al, 2007). This manual outlines every aspect of sampling and even highlights what could go wrong.

Weaver et al (2007) have shown that prior to sampling it is necessary to liase with the laboratory in order to ascertain which containers, preservatives and reagents are to be used when sampling for radionuclides. Levin (1983), who also developed a local sampling manual, states that sample bottles should be thoroughly rinsed with 10% HCl and then emptied and rinsed thrice with de-ionised water. Levin (1983) also states that the samples should be taken as follows:



- 2 l for the determination of the trace elements such as Al, As, Be, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Ti, Si, Zn

- 500ml for the determination of U, V and $NO_3^-$

- 250 ml for the determination of the major components $SO_4^{2-}$, $Cl^-$, $F^-$, $Na^+$, $K^+$, $Ca^{2+}$ and $Mg^{2+}$

The authors definitely took cognizance of the fact that the trace metal content of water could be altered in storage. Therefore the use of acid has been recommended in order to reduce the possibility of precipitation of heavy metals, which includes radioactive elements.

Taking cognizance of the fact that radioactive elements are heavy metals one then has to filter the sample, once it has been extracted from the aquifer (Levin, 1983). Typically a 0.45µm filter paper is utilized. Levin (1983), also suggests that the filter paper should be kept, if the suspended particles are to be analysed. This is important, taking into consideration that Radium precipitates under oxidizing conditions (Ilani et al, 2005). Other than these specific methods, relating to sampling for radioactivity, we find that all other aspects are generally generic within these two locally developed manuals

Weaver et al (2007) advise that approximately two well volumes should be purged in order to remove stagnant water. Levin (1983) on the other hand says that the pump should be run for 10 minutes before a sample is taken. Prior to this a water level should be measured. Furthermore it is suggested that field parameters be measured in-situ (Weaver et al, 2007 and Levin 1983). These include temperature, total dissolved solutes, Electrical Conductivity, pH, Eh and oxidation reduction potential. This is done for the following reasons (Weaver et al, 2007):



- to check the efficiency of purging
- to obtain reliable values of those determinands that will change in the bottles during transport to the laboratory
- to obtain some values that may be needed to decide on the procedure or sampling sequence immediately during the sampling run

Weaver et al (2007) also advise the use of a flow through cell in order to maintain the in situ condition of the sample and thus gain an actual representation of the conditions in the subsurface.

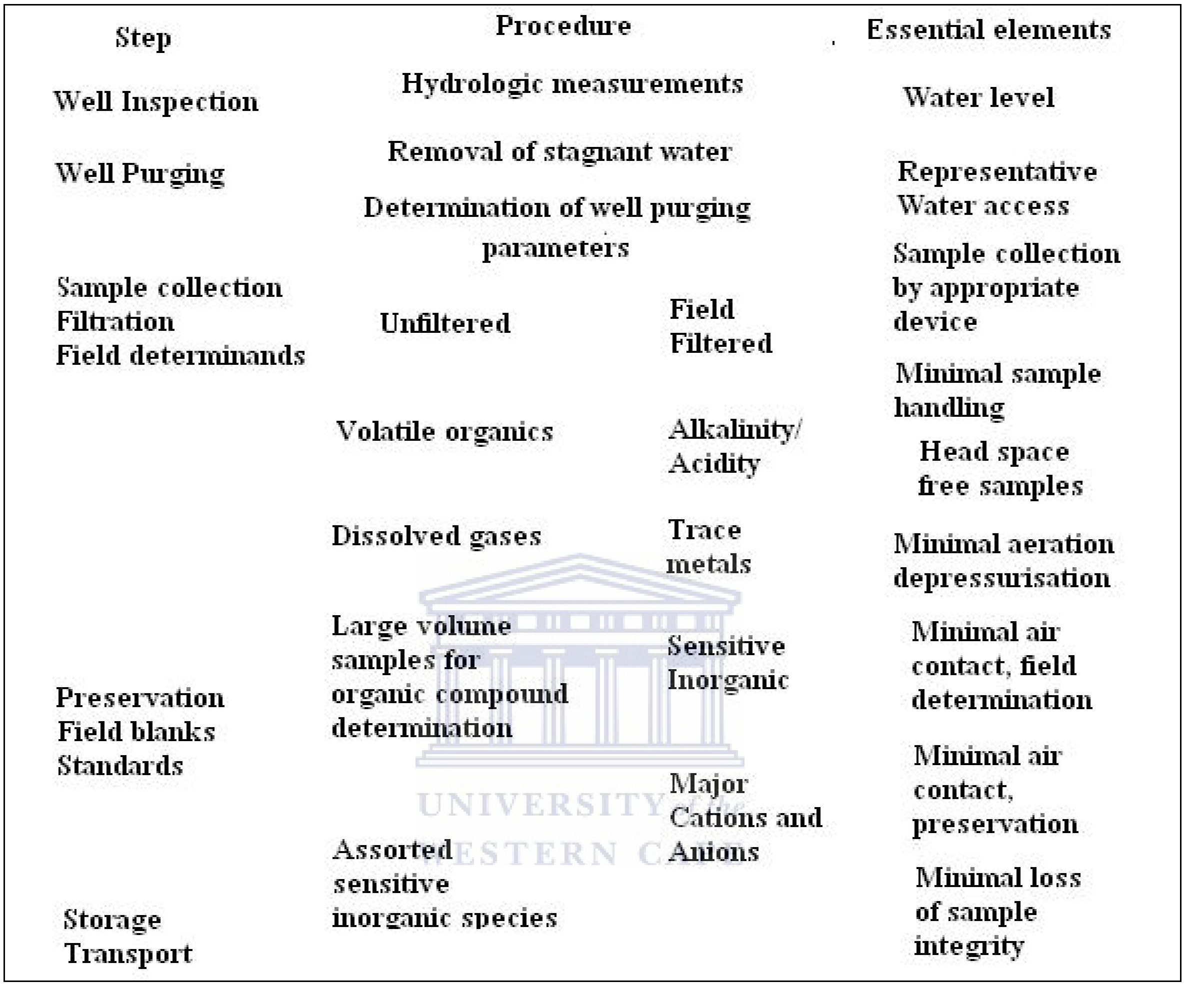
Vogel et al (1980) were visionary in their use of packers for sampling in the Beaufort West area. Even though their study is not strictly classified as a protocol, it is interesting to take note of the methods used. A submersible pump mounted between two inflatable rubber packers, approximately 1.8 metres apart was utilized (Vogel et al,1980). This equipment allowed multi level sampling within boreholes. At the depth of interest the packers were inflated with nitrogen and the pump then delivered water to the surface from the aforementioned fracture.

### *2.3.2 International*

Jousma and Roelofson (2003) have reviewed approximately 400 documents relating to sampling and monitoring groundwater and related aspects. The authors have not found a single document relating to radioactivity sampling in fractured rock aquifers. Furthermore it was recommended that more research in hard rock aquifers is required (Jousma and Roelofson, 2003)



Despite the aforementioned point the IAEA (2004), have developed a manual specifically for radioactive monitoring of near surface waste facilities. Unfortunately the manual does not deal with the intricacies of sampling but instead refers the reader to various other manuals. One of these manuals was most probably the first groundwater sampling manual and was developed by Barcelona et al (1985). This document outlines a specific route to follow when sampling (Figure 6)



| Step | Procedure | | Essential elements |
|---|---|---|---|
| Well Inspection | Hydrologic measurements | | Water level |
| Well Purging | Removal of stagnant water<br>Determination of well purging parameters | | Representative Water access |
| Sample collection<br>Filtration<br>Field determinands | Unfiltered | Field Filtered | Sample collection by appropriate device<br>Minimal sample handling |
| | Volatile organics | Alkalinity/ Acidity | Head space free samples |
| | Dissolved gases | Trace metals | Minimal aeration depressurisation |
| Preservation<br>Field blanks<br>Standards | Large volume samples for organic compound determination | Sensitive Inorganic | Minimal air contact, field determination |
| | | Major Cations and Anions | Minimal air contact, preservation |
| Storage<br>Transport | Assorted sensitive inorganic species | | Minimal loss of sample integrity |



**Figure 6** : General guideline for groundwater sampling (adapted from Barcelona et al, 1985)

Radioactivity, Uranium as well as Radon are unfortunately not mentioned in the document. Nevertheless it is still used as reference point for many studies and manuals which have utilized other aspects of the text. These aspects include monitoring well design and completion as well as sampling mechanisms and materials. In the manual, Barcelona et al (1985) mention the important characteristics of a sampling device:

- The device should be simple to operate to minimize the possibility of operator error.

- The device should be rugged, portable, cleanable and repairable in the field.

- The device should have good flow controllability to permit low flow rates (= 100 mL/min) for sampling volatile chemical constituents, as well as high flow rates (> 1 L/min) for large-volume samples and for purging stored water from monitoring wells

- The mechanism should minimize the physical and chemical disturbance of ground-water solution composition in order to avoid bias or imprecision in analytical results.



Freyer et al (1997), concur with the aforementioned facts. The authors have also shown that the low flow sampling devices, which are used for Radon sampling, do not greatly affect the Radon concentration (Figure 7). Thus these devices are all aptly suited for sampling and fit the criteria previously mentioned by Barcelona et al (1985).

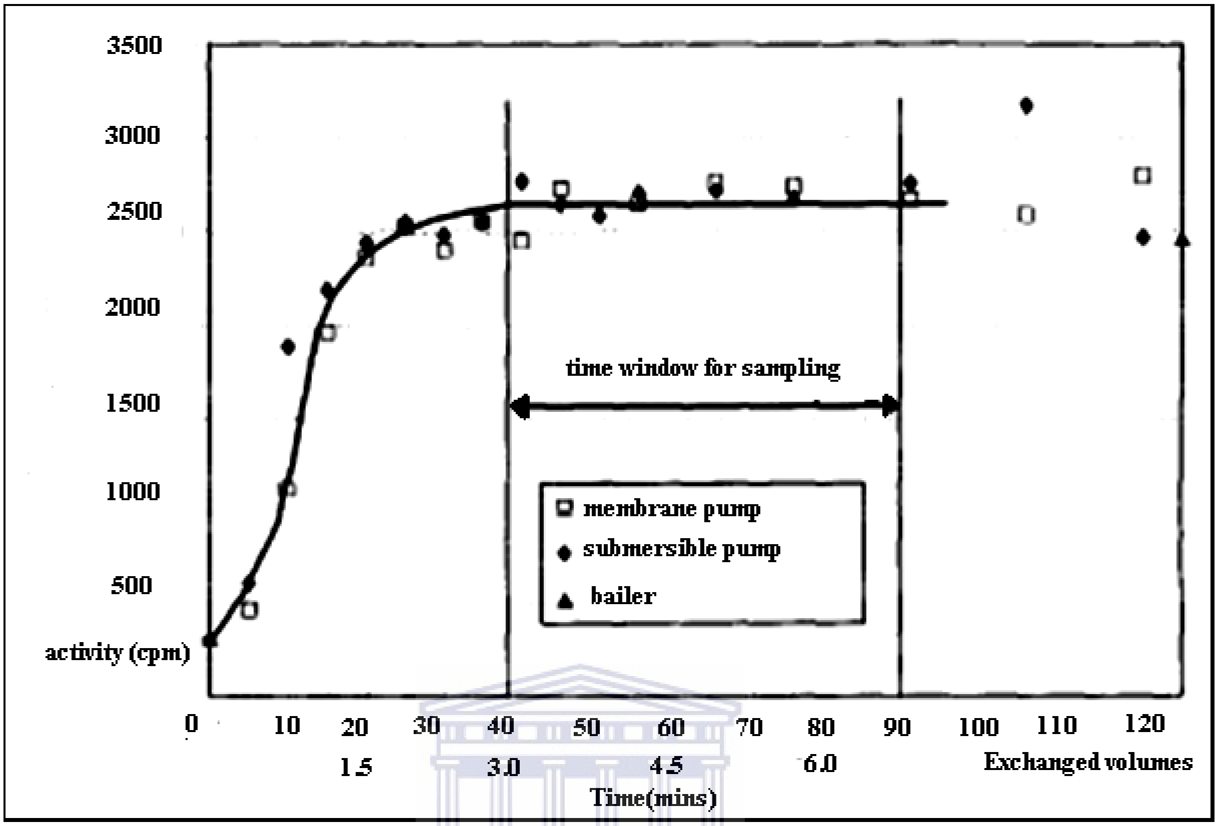



**Figure 7**: A comparison of various sampling techniques and the Radon concentrations acquired from each one (adapted from Freyer et al, 1997)



Furthermore Barcelona et al (1985) systematically outline a general sampling protocol which could be used for any analyte which may be of major concern. The steps, goals and recommendations are shown in a tabular format in order to minimize confusion and simply explain the specifics relating to each systematic step (Table 4).

| Step | Goal | Recommendations |
|---|---|---|
| Hydrologic measurements | Establishment of Static water level | Measure water level to approximately 0.3 cm (0.1 ft) |
| Well Purging | Removal of stagnant water which would otherwise bias representative sample | Pump water until well purging parameters (eg pH, T, Eh) stabilize to approximately 10% over at least two successive well volumes pumped |
| Sample collection | Collection of samples at land surface and or in well-bore with minimal disturbance of sample chemistry | Pumping rates should be limited about 100ml/min for volatile organics and gas sensitive parameters |
| Filtration/Preservation | Filtration permits determination of soluble constituents and is a form of preservation. It should be done in the filed as soon as possible after collection | Filter trace metals, inorganic anions/cations, Do not filter: TOC, TOX, volatile organic compound samples. Filter other organic compounds samples only when required |
| Field Determinands | Field analysis of samples will effectively avoid bias in determination for parameters/constituents which do not store well eg gases, alkalinity pH etc | Samples for determination of gases, alkalinity and pH should be analysed in the field if it all possible |
| Field Blanks | These blanks and standards and will permit the correction of analytical results for changes which may occur after sample collection, preservation and storage | At least one blank and one standard for each sensitive parameter should be made in the field on each day of sampling. Spiked samples are also recommended for good QA/ QC |
| Sample Storage | Refrigeration and protection of samples should minimize the chemical alteration of samples prior to analysis | Observe maximum sample holding or storage periods recommended by the Agency. Documentation of actual holding periods should be carefully performed |

**Table 4**: Generalised groundwater sampling protocol (adapted from Barcelona et al, 1985)

The EPA (1992) also penned a protocol in a similar fashion to that of Barcelona et al (1985). The greatest attention was afforded to the physical aspects of groundwater flow and monitoring well design. Interestingly enough the use of packers is advocated in order to isolate a specific area of interest within the subsurface (EPA, 1992). These inflatable devices are placed above and below the fracture of interest, in order to isolate the area (Figure 8). Prior to this a pump is isolated within the structure. USGS (2001) have designed the BAT$^3$ (Bedrock Aquifer Transportable Testing Tool) specifically for sampling in fractured rock aquifers. Besides having packers and a pump it is also installed with three pressure transducers. One is located above the packers, the between the packers and the last one is below the packers. These are utilized in order to monitor fluid pressure and correctly ensure that the packers are properly isolating the fracture of interest (USGS, 2001)

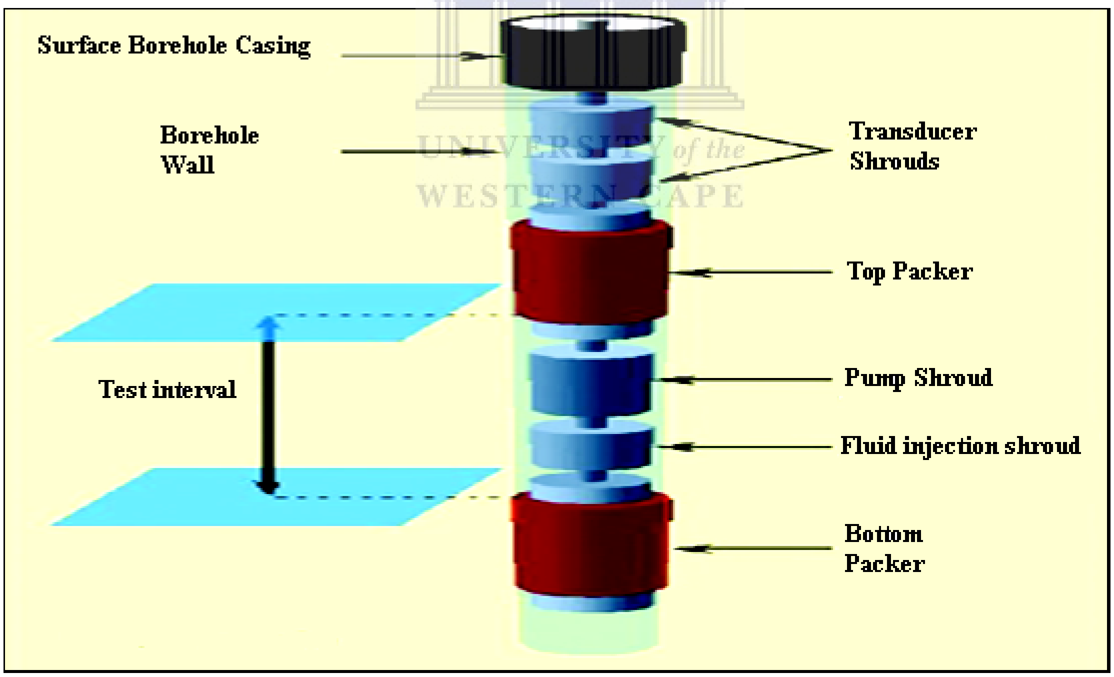



**Figure 8**: Multifunction BAT$^3$ in a bedrock borehole with borehole packers inflated to seal against the borehole wall (adapted from USGS, 2001).

Puls and Barcelona (1996) strongly recommend that low flow sampling, in conjunction with packers, should be done in fractured rock aquifers. This approach should only be attempted after identifying the water bearing fractures and thus the sampling zone can be isolated.

EPA (1992) promotes the hourly sampling of fractured aquifers for field determinands. This protocol was developed specifically for nuclear waste facilities and the parameters which would be measured on an hourly basis would include those which a data logger could determine. These include temperature, TDS and water level. This would aid in determining whether leakage has occurred from the storage facility and also aid in determining anomalous inflows of contaminants in groundwater, in a natural setting. The aforementioned could be inferred from an increase in TDS, pH and temperature. It is an effective monitoring strategy and the aforementioned parameters would act as indicators for the contamination of groundwater

OHIO EPA (1995) have also developed a document specifically for groundwater sampling and monitoring. Once again there is not much difference between this technical manual and that of Barcelona et al (1985) and EPA (1992). An interesting component is the description of the use of statistics in order to assimilate data into information. Helsel and Hirsch(2002) have also shown the importance of utilizing statistics as a tool for the interpretation of data. The document acts as a reference tool for hydrologists in the USGS and provides the basic, as well as advanced, statistical methods applicable to the hydrological sciences (Helsel and Hirsch, 2002).

OHIO EPA (1995) have made the concerted effort to update their document, unlike Barcelona et al (1985) and EPA (1992). Specefic chapters have been modified and or added in order to make the manual more relevant. An extensive examination of sampling methodology was revisited and could prove to be useful especially for the novice, due to its simplicity and applicability. Unfortunately radioactivity is not focused upon and thus sampling protocol for radioactive elements is not covered. This must be due to the fact that OHIO EPA (2006) was heading for a more generic sampling methodology and nothing specific in this updated version.

The USACE (1998) has developed an engineering and design manual entitled 'Monitoring Well Design, Installation, and Documentation at Hazardous, Toxic, and Radioactive Waste Sites'. The manual unfortunately does not cover aspects of groundwater sampling. Once again this is not in line with the purpose of the document. Instead the purpose of the Engineer Manual is to provide the minimum elements for consideration in the design, installation, and documentation of monitoring well placement and other geotechnical activities at projects known or suspected to contain chemically hazardous, toxic, and/or radioactive waste (USACE, 1998).

Wilde et al (1998) on the other hand have turned some attention towards the sampling of radioactivity. They suggest that radioactive elements should be sampled in a similar manner to heavy metals. This is a view shared by Weaver et al (2007) as well as Smedley et al (2006).Wilde et al (1998) suggest that a 1 litre polyethelyne bottle be acid rinsed and then the sample should be preserved to pH<2 using $HNO_3$. It would also mean filtering the sample in order to remove suspended particles which could possibly lead to the precipitation of metals onto its surface. This manual is a major step forward, in terms of radioactivity sampling. We also find that each chapter of the manual is published separately and updated on a periodic basis (Wilde et al, 1998).Furthermore corrections are posted on the website and these additions should be made to the respective chapters. This USGS manual is also quite generic and provides methods for surface as well as groundwater sampling.

Yeskis and Zavala (2002) tackled methods of sampling as well as equipment and recommend low flow sampling, just like Puls and Barcelona (1996). This approach is justified because samples with elevated levels of turbidity are collected by high speed pumping. This results in the inclusion of otherwise immobile particles which cause an overestimation of specefic analytes of interest (Puls and Barcelona, 1996). Furthermore, with regards to radioactivity, we find that once there is a change in chemical environment there is also an alteration in the dominant radionuclide in the aqueous phase (Ilani, 2006). A good example of this is the fact that Uranium dominates under oxidizing conditions whereas Radium prefers a reducing environment (Ivanovich and Harmon, 1982). Thus Yeskis and Zavala (2002) also advocate filtering, in order to differentiate between dissolved and non-dissolved species, therefore eliminating adsorbed radioactive particles.

DOE (2004) as well as IAEA (2004) developed a monitoring protocol for radioactive waste facilities. Aspects of monitoring network design, well placement and data management are examined (DOE, 2004). IAEA (2004) instead look at the monitoring of general environmental conditions, which includes soil, air, hydrology and hydrogeology. Both manuals are geared towards facilities management and DOE (2004) provides a good systematic monitoring protocol. IAEA (2004) on the other hand make many references to various other documents and is not as user friendly as DOE (2004).

Thus we see the natural progression of sampling manuals. This evolution involved a step towards the intensive examination of the physio-chemical parameters, as shown by Weaver et al (2007). Furthermore we find specefic manuals becoming all encompassing guides and thus the need to constantly update as the knowledge base is widened, as in the case of Wilde et al(1998) and OHIO EPA (1995). It can also be seen that certain manuals, such as Jousma's (2006) Guideline on Groundwater monitoring for general reference purposes, are very specific in their subject matter. Therefore a simple comparison of the manuals examined in this review has been completed (Table 5). This was based on headings or sections in the document. Therefore if no section or subsection on the topic was present then the topic was regarded to be insufficiently covered or omitted.

| | Topic covered in document | | | | | | |
|---|---|---|---|---|---|---|---|
| Document | General Sampling Protocol | General Sampling Methods | General Sampling treatment | Monitoring protocol | Monitoring well design | Sampling frequency | Radioactivity sampling |
| Barcelona et al (1985) | ✓ | ✓ | ✓ | | ✓ | ✓ | |
| EPA (1992) | ✓ | ✓ | | | ✓ | ✓ | |
| OHIO EPA (1995) | ✓ | ✓ | ✓ | | ✓ | | |
| Wilde et al (1998) | ✓ | ✓ | ✓ | | | | ✓ |
| USACE (1998) | | ✓ | | | ✓ | ✓ | |
| Yeskis and Zavala (2002) | ✓ | ✓ | ✓ | | | | |
| IAEA (2004) | | | | ✓ | | | ✓ |
| DOE (2004) | | | | ✓ | | | |
| Jousma (2006) | | | | ✓ | | ✓ | |
| Weaver et al (2007) | ✓ | ✓ | ✓ | | | | ✓ |



✓ - indicates that the topic is covered in the document

a blank cell shows that the topic was omitted from the document

**Table 5**: Comparison between sampling manuals and their relevance to radioactivity sampling

It can clearly be seen that no one manual is able to cover all the topics required for sampling and monitoring of radioactive elements in fractured rock aquifers. Furthermore other useful documents, such as Cook (2003), are also quite relevant and applicable. Similarly NCA (1996) could be utilized specifically for fractured rock studies.

Thus it is suggested that multiple applicable manuals are utilized for sampling and monitoring at a site. These documents should be applicable and relevant to the context within which they are being applied.

## *2.4 Relevance to the South African Situation:*

It seems as if Weaver et al (2007) is quite applicable to the local context. This is due to the fact that the document was developed for South Africans by South Africans. Furthermore it serves as an excellent all round sampling guide covering various aspects of the sampling process. A monitoring guide, such as Jousma (2006), could be used in conjunction with Weaver et al (2007). This is due to the fact that Jousma (2006) is quite generic and can be broadly applied to any situation. Similarly the manual of Barcelona et al (1985) outlines numerous aspects of sampling in a generic manner. The methods used by Vogel et al (1980), as previously outlined, are also quite relevant to local conditions. Furthermore Vogel et al (1980) adapted their methodology, which is important for varying situations.



Cook(2003), which could also be applied to a local context, has compared sampling prior to purging as well as post purging(Figure 9). The author has concluded that the Radon concentration within the well varies greatly due to the ability of the gas to diffuse. Other methods used by Cook(2003), as well as NCA (1996), could be readily applied to a South African context. These include fracture detection, fracture characterization and numerous case studies where useful applications could be learnt.

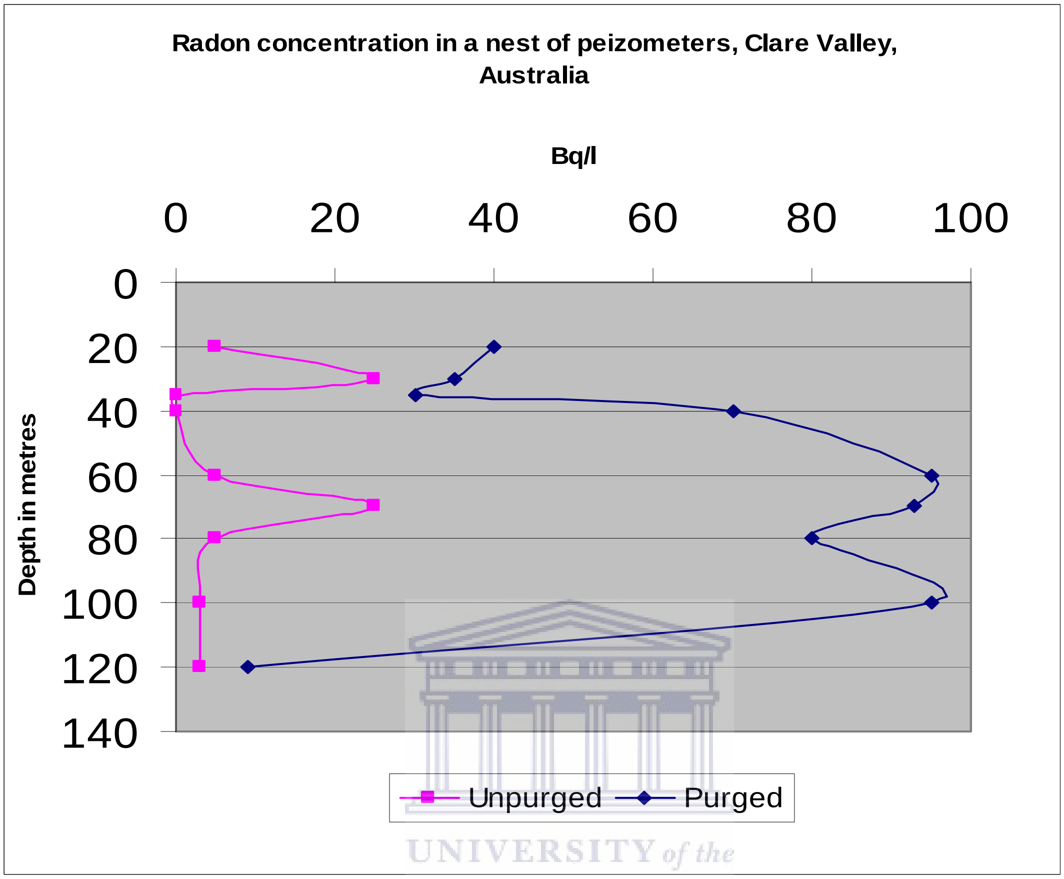





**Figure 9** : A comparison between the Radon concentrations before purging (pink) as well as after purging two well volumes (blue) (Cook, 2003)

# Chapter 3 Methodology

## *3.1 Purpose of sampling and monitoring:*

Groundwater monitoring can be defined as the scientifically-designed, continuing measurement and observation of the groundwater situation (Jousma and Roelofsen, 2003). Ideally the design of network density and sampling frequency would be based on an optimization of the cost of monitoring and of the accuracy of collected and derived data related to the objectives of the network(Kovalevsky et al, 2004). In line with this. Netili et al (2007) further propose that groundwater monitoring and sampling sites should be selected to be representative of geographic distribution, geology, groundwater use, land-use and groundwater flow regimes amongst other factors.

Thus we can see that ideally the sampling programme for a groundwater investigation will collect the minimum number of samples required to have adequate three-dimensional spatial and stratigraphic coverage of the area being investigated and thus the fundamental task is to obtain samples that are representative, diagnostic, and characteristic of the aquifer and to analyse them with minimal change in composition (Kovalevsky et al, 2004). The data stemming from this knowledge should in turn lead to better groundwater management practices.

### *3.2 Existing datasets:*

These data sets aided greatly in understanding applicable methodologies for sampling radioactivity in fractured rock aquifers. The methods used to generate this historic data also contributed towards the development of the protocol.

Brunke (1977) conducted the initial work relating to the hydrogeochemistry within the vicinity of the Uranium channels of Beaufort West. The aim of the study was to investigate the possible relationship between Uranium and other trace elements in groundwater in the region. (Brunke 1977) suggested that the water quality is mainly a function of residence time and extent of rock/water interaction. It was further observed that waters with higher salinity values were enriched in $SO_4$ and Cl. The subsurface waters were generally well aerated and had a positive Eh. These conditions favoured the leaching of Uranium, which also had a positive correlation with TDS.



Scholtz (2003) assessed the potential toxic influence of Uranium trail mining in the Karoo Uranium Province. The study revealed localised elevated values for U, Mo, Pb, Cu, As and Fe in surface - and ground water, soils, sediment and crops. Scholtz (2003) concluded that the U concentration in the groundwater was acceptable. Unfortunately the author did not purge the wells and thus sampled stagnant groundwater. Purging is essential in order to gain a sample which is representative of the in-situ conditons, especially in fractured rock aquifers (Cook, 2003)

Sami and Druzynski (2003) looked at the predicted spatial distribution of Uranium, Arsenic and Selenium within the borders of South Africa. This report yielded numerous maps for the occurrences of the aforementioned elements in groundwater throughout the country (Figure 10). An explanation of Figure 10 can be found in Appendix C. The authors also extensively examined the health hazards, geology, physio-chemical properties as well as sources of Uranium. This is an excellent study for understanding the migration of Uranium as well as deposition of the aforementioned elements.

Pietersen and Kruger (2007) have thoroughly examined all the data relating to the occurrence of radioactivity within the Karoo. The authors have concluded that the overall water quality is poor, with most of the datasets showing TDS concentrations above the allowable limit of 450 mg/l. Despite this fact it has been shown, by means of historic data sets, that the levels of Uranium in the groundwater were generally acceptable (Pietersen and Kruger, 2007). Uramin (2008) display similar sentiments and this is surprising due to the fact that their study was in the immediate vicinity of the Rystkuil channel. Furthermore extensive mine dewatering was undertaken before sampling was carried out and similar results to previous studies were generated.

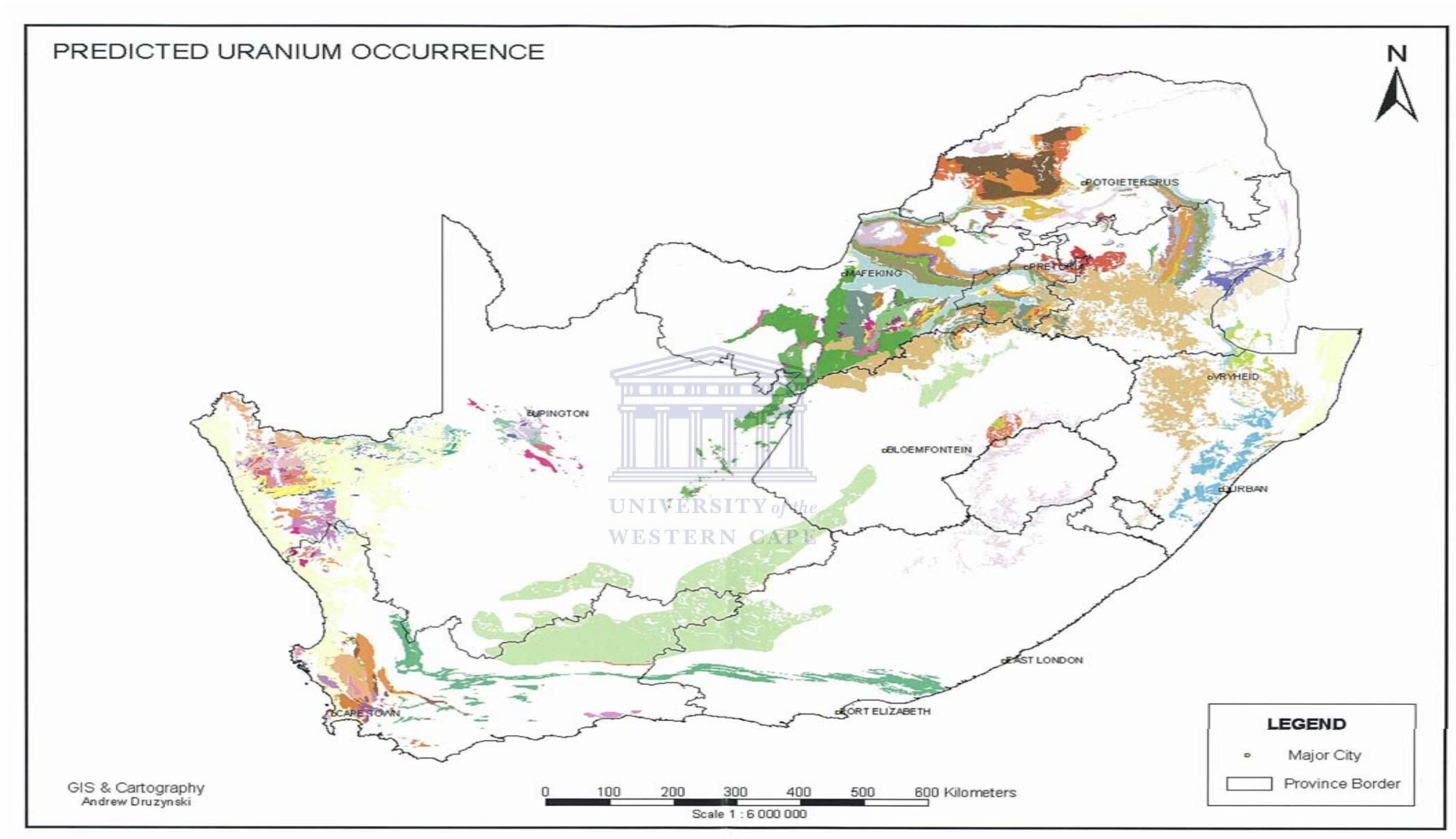




**Figure 10**: The predicted spatial distribution of Uranium in South Africa (Sami and Druzynski, 2003)

## 3.3 Field work design

Previous reports as well as maps of the area were consulted in order to determine the boundaries of the study area. The geology and hydrogeology were carefully examined to properly understand groundwater flow. Lastly boreholes in the vicinity of known Uranium deposits were earmarked for radioactivity sampling.

## 3.4 Sampling design:

The sites, which are located within the vicinity of the town of Beaufort West, were visited in order to carry out a groundwater sampling exercise. The proposed methodology for sampling radioactive elements was in line with that of heavy metals (Weaver et al,2007).

In the case of windmills the sample was taken as close to the outlet pipe as possible. Furthermore it was assumed that the hole was purged due to the fact that the wind powered pump ran whole day. With the pumps on the other hand we find that they are permanently installed, thus making it difficult to determine the depth of the hole as well as static water level. Therefore these pumps were allowed to run for a few minutes before being sampled. In many cases the pumps were ran prior to the arrival of the team on-site.

The samples were then filtered through 0.45 $\mu$ filter paper and placed in HDPE sample bottles. The sample which was to be analysed for heavy metals, was filtered into a 250ml plastic bottle and spiked with 10% $HNO_3$ in order to prevent the heavy metals from precipitation. The radioactivity sample, which was filtered into a 5 litre bottle, was also spiked with 10% $HNO_3$. These radioactive samples were then placed in a cooler box and soon sent to the laboratory at NECSA for analysis.

### 3.5 Data analysis:

The chemistry data was examined and processed by means of Aquachem™ by Schlumberger. Piper plots were constructed in order to compare the macro chemistry of the groundwater in and around the study area. Furthermore the major cations and anions distribution was spatially examined. These results were all graphically plotted and then analysed in order to gain a better understanding of the hydrogeochemistry in the area.

### 3.6 Protocol development:

Prior to venturing into the field for sampling, a draft sampling protocol was developed in order to fully understand processes and applications which should be implemented for sampling. This process was completed by assessing all the best practices from across the globe, as well as in South Africa, and outlining possible options.



Upon returning from the field, an entire new outlook was required due to the fact that certain applications were not suited for local conditions. Therefore the protocol was re-evaluated and then refined in order to be more locally applicable and relevant. A new section on monitoring was also included in order to meet the requirements of the W.R.C project. This sampling and monitoring protocol for radioactive elements in fractured rock aquifers is attached as Appendix E

# Chapter 4 Study Area

## *4.1 Climate and Topography*

The study area is located in the vicinity of the town of Beaufort West (Figure 11), which lies at approximately 930 metres above sea level (Spies and Du plessis, 1976). At this altitude the majority of the precipitation occurs during the summer months due to a high pressure system dominating the inflow of moisture filled air into the escarpment (Tyson and Preston-Whyte, 2000). Average precipitation in the vicinity of the town is 235 mm per annum (Kotze et al, 1997)

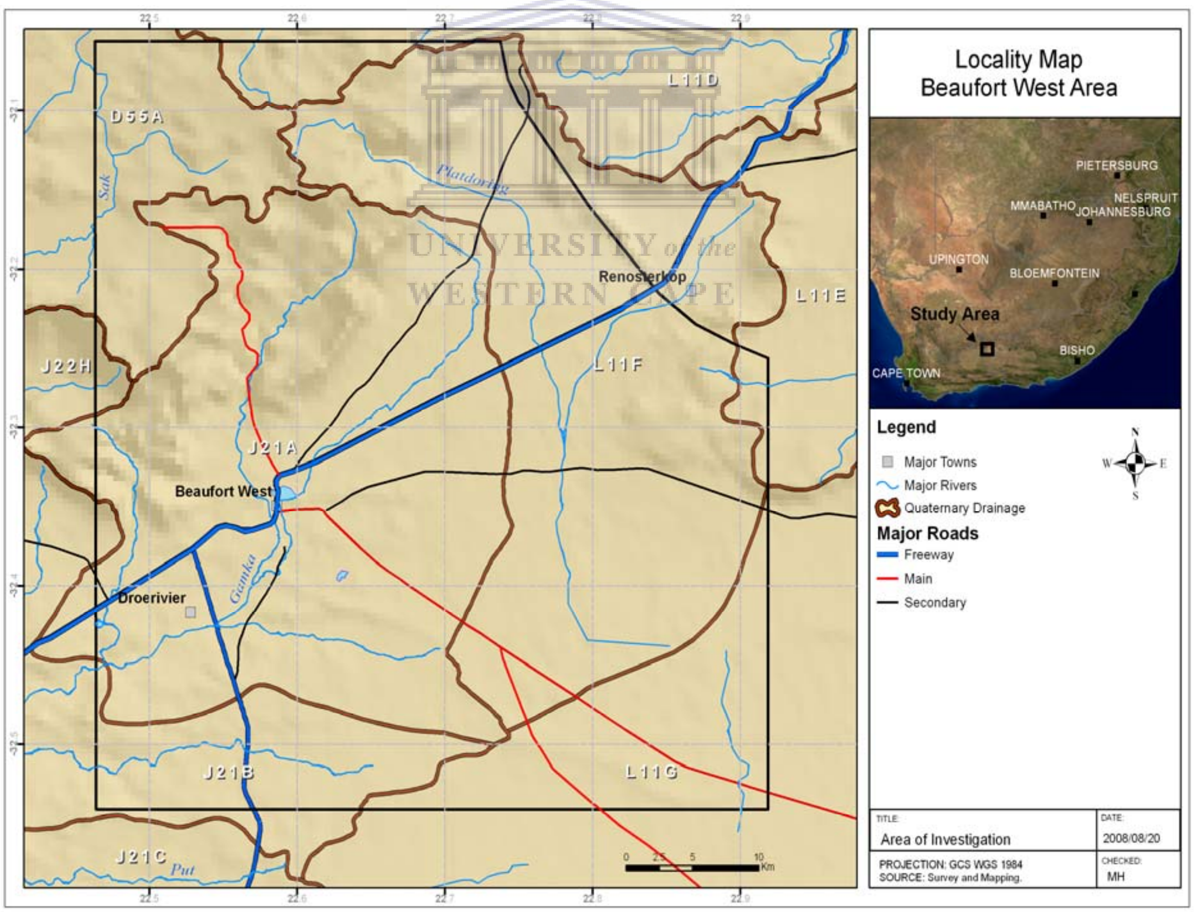



**Figure 11** : The study area, which includes surface flow systems near the town of Beaufort West

The area itself is fairly flat with scattered mesa’s and butte’s predominating as one draws closer to the Nuweveld mountains in the north which basically controls groundwater recharge in the area. The major veld types populating the barren soils have been classified by Acocks (1988) as being False Karoo and Karroid Bushveld. Furthermore, cattle farming seems to be the dominant agricultural activity with sheep and cows being the major livestock. Rose and Conrad (2007) have pointed out, by means of satellite imagery, that certain plots of land are also being cultivated along the Gamka, Hans and Kwagga rivers to the south of Beaufort West. The Game reserve, which is located in close proximity to the town, also houses varieties of buck and wildlife.

## *4.2 Geological framework*



The Karoo Basin extends over a large area of South Africa. The basin came into existence during the early Carboneforous period (Visser, 1990) and its formation according to Woodford and Chevallier (2002), was controlled by four major geodynamic events:

- Deposition of the Karoo Supergroup sediments in a foreland basin during the uplift of the Cape Fold Belt (~260 Ma to 190 Ma).
- The break-up of Gondwanaland with the intrusion of the Karoo dolerite and extrusion of the Drakensburg basalts(~190 to 180 Ma).
- Intra-plate mantle upwelling and emplacement of kimberlite pipes and fissures accompanied by the intrusion of carbonatite plugs(~170 to 60 Ma).
- Weak tectonic activity associated with uplifting, geomorphological, changes, erosion, modern river system and joint development (~30 Ma to present time).

The first depositional event was glacial and as the ice sheets disappeared we find the fluviodeltaic sands accumulated in the northern part of the basin. At the same time muds overlaid by turbid sands and silts were deposited in the deeper trough in the south because of the increasing influence of orogenic activity (Visser, 1998). This was followed by the extrusion of dolerites, which still scar the landscape today

The occurrence of Uranium in the Karoo Basin is mainly in the Teekloof formation, which forms part of the Adelaide Sub-group and this in turn forms part of the Beaufort group (Cole, 1998). The aforementioned succession flows from the lowest level of geological classification to the broadest and most inclusive. (Table 6). This Karoo Uranium province extends across the Western, Eastern and Northern Cape and even into the Free State as far north as Bloemfontein.

Furthermore specific deposits have been earmarked for their economic viability. These include the Rystkuil and Rietkuil channels (Figure 12). Cole (2007) states that the sandstone hosted deposits can be seen as epigenetic concentrations of Uranium minerals occurring as uneven impregnations that were deposited in fluvial, lacustrine and deltaic paleoenvironments. Hobday and Galloway (1999) are of the opinion that these type of deposits were produced by meteoric groundwater flow along burial of the host's depositional system. In line with this Cole (2007) further classifies the deposits within the Karoo as either roll front or tabular deposits. According to our field investigation to previous and currently exploration boreholes, the depth of these holes mostly hit to a maximum of 150 m, which means that the extension of uranium ores is merely confined to a relatively shallow zones. This might suggests that the contamination of groundwater of uranium and is daughter elements due to the mining activity in this area would likely take place in a shallow zone, particularly tailing seepage into the surface water system.

| Group | Sub-Group | Formation | Area | Lithology | Thickness(m) |
|---|---|---|---|---|---|
| Beaufort | Adelaide | Balfour | Southern and Central Karoo Basin | Mudrocks and sandstones | 2150 thins northwards |
| | | Middleton | | | 1500 thins northwards |
| | | Konaap | | | 1300 thins northwards |
| | | Teekloof | South Western Karoo Basin | Mudrocks and sandstones with Uranium present | 1000 thins northwards |
| | | Abrahamskraal | | | 1400 thins northwards |

**Table 6** : Stratigraphy of the Beaufort group, which hosts Uranium deposits within the Teekloof and Abrahamskraal formations (Brink, 1985)

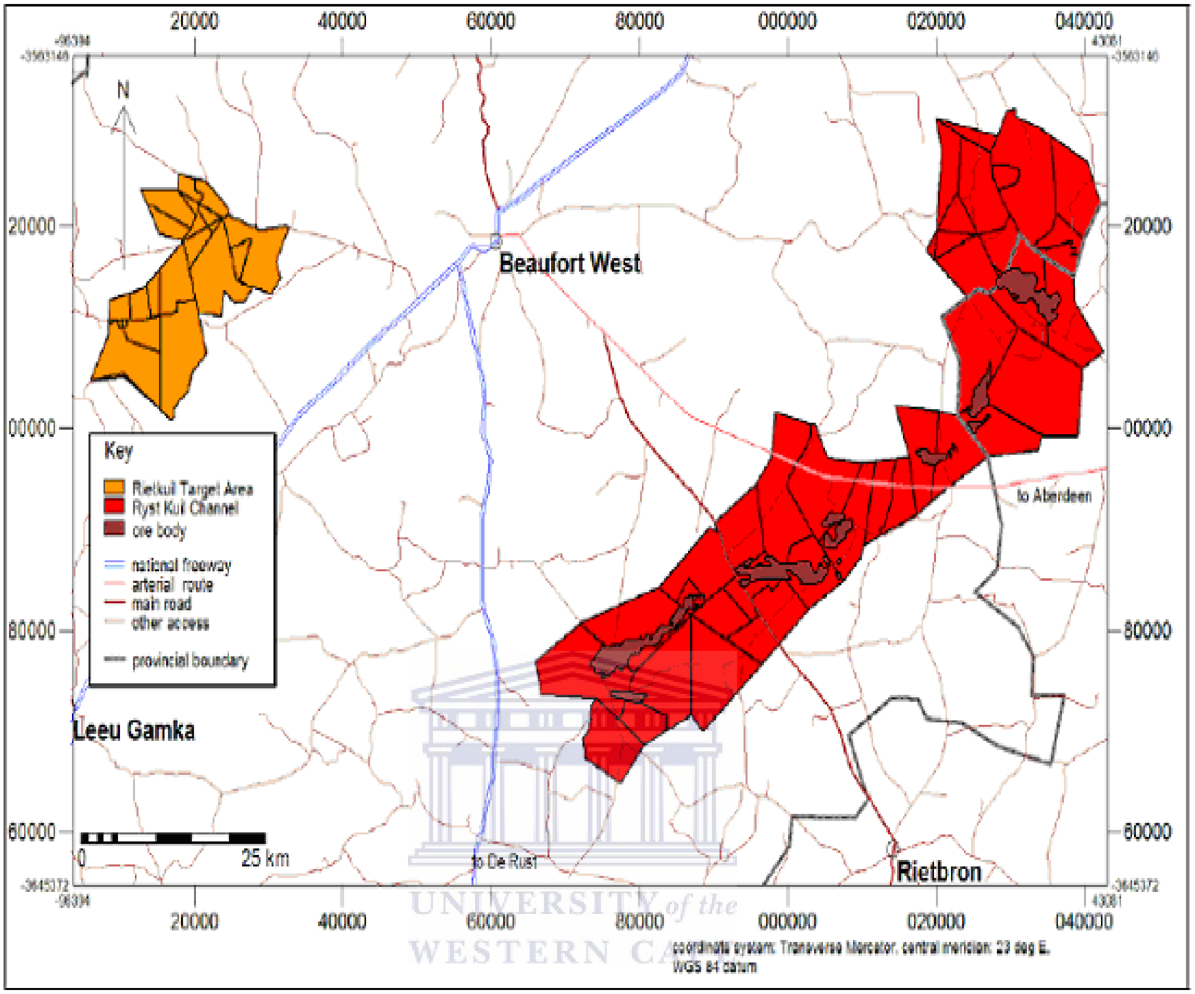



**Figure 12**: The two major target areas for Uranium mining in the vicinity of Beaufort West (Turgis Consulting, 2007)

### *4.3 Hydrogeology*

Woodford and Chevallier (2002(a)) have extensively examined the hydrogeology in the vicinity of the study area, on a macro scale by means of GIS. A compendium of the studies conducted relating to the hydrogeology of the entire karoo basin has also been compiled (Woodford and Chevallier, 2002(b)).

With regards to the town of Beaufort West we find numerous hydrogeological reports assessing the wellfields, which are located north of the town (Figure 13), for municipal supply. Those reports up until 1980 have been compiled and assessed by Kok (1982). Kotze et al (1997) have utilized this data and shown short term water level fluctuations in the municipal well fields, but there is a definite decline in water levels in general (Gilbert and Kotze, 2000). This is the reason for exploration work to the south of the town (Figure 13), which has been commissioned by the municipality and undertaken by Rose and Conrad (2007).

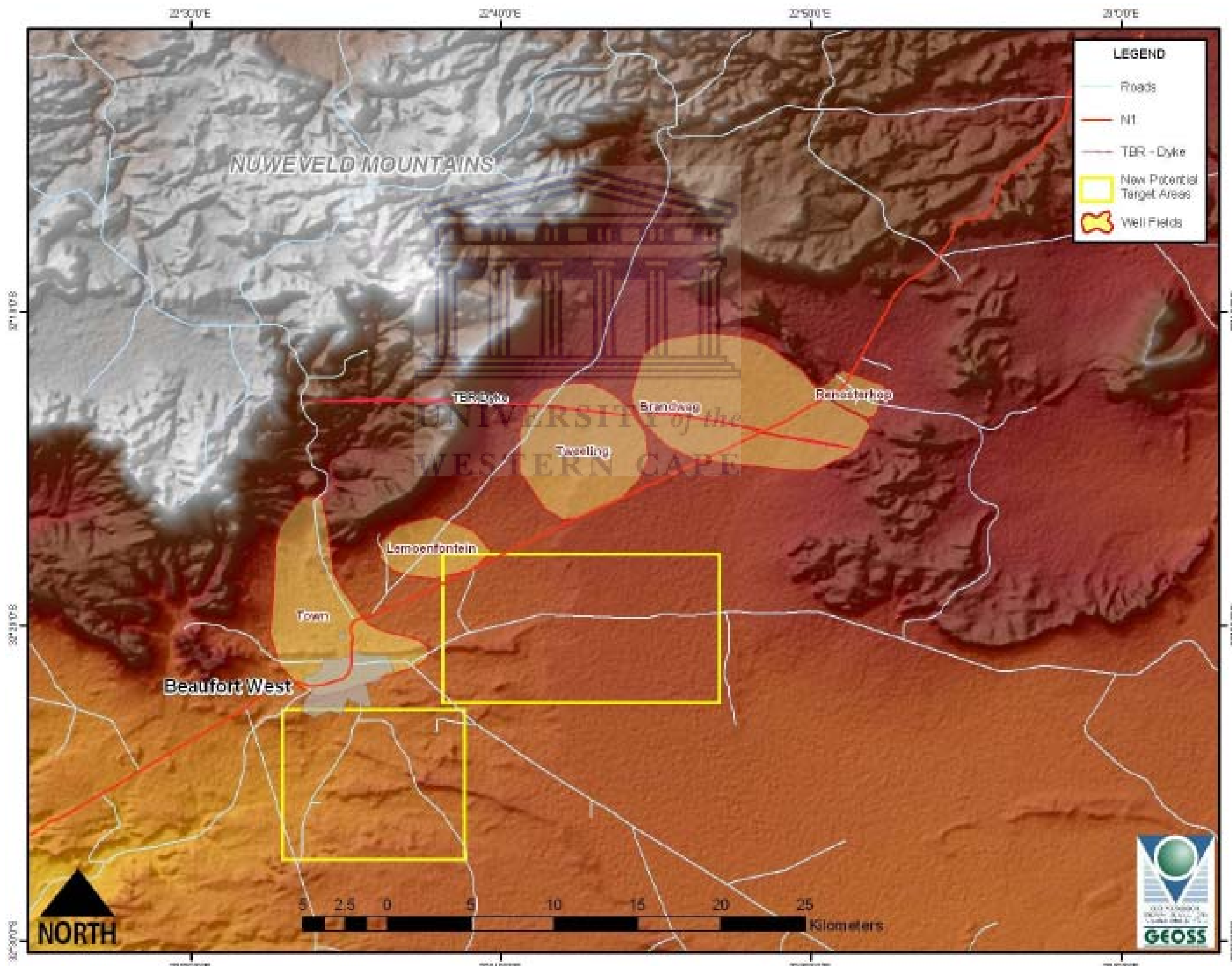



**Figure 13** : Location of wellfields and target areas for future exploration in the vicinity of Beaufort West (Rose and Conrad, 2007)

Rose and Conrad (2007) have delved deeper into the hydrogeology surrounding the town of Beaufort and explained the transport, flow and chemistry. According to Rose and Conrad (2007) the major flow direction is from the Nuweveld mountains in the north towards the town dyke in the south (Figure 14). The aforementioned authors highlight the fact that major dykes in the vicinity of the town play a role in determining groundwater flow. These dykes are:

- East – West trending stretching from the Nuweveld Mountains north of the Gamka Dam in an easterly direction cutting across the farms Tweeling, Brandwag and Renosterkop, otherwise called the TBR – dyke by Kotze et al (1997)

- The town dyke, which is also east west trending (Figure 14)

- Lastly the northwest southeast trending Hansrivier dyke, located on the cadastral farm after which it has been named by Rose and Conrad(2007).



Vogel et al (1980) also proved that localized recharge occurs in the immediate vicinity of the town. Rose and Conrad(2006) concur with this and prove conclusively , by means of isotopic analysis, that surface water and groundwater supplies are not linked. Furthermore groundwater to the south of the town is more saline than the groundwater in the wellfields to the north (Vogel et al, 1980). This also suggests that the two groundwater systems are separated by the town dyke (Rose and Conrad, 2007)

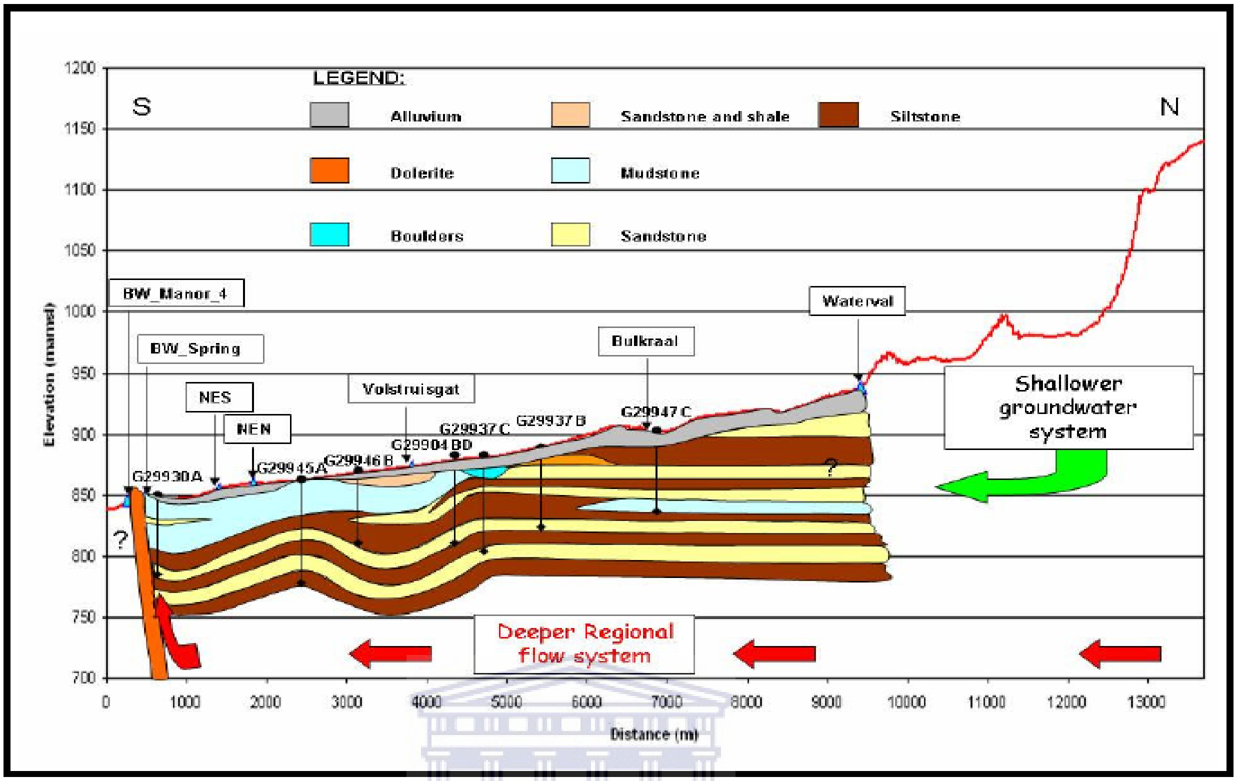



**Figure 14**: Conceptual Model of Beaufort West Town well field (Rose and Conrad, 2006)



More recently Nhleko and Dondo (2008) looked at regional flow of groundwater in the vicinity of the town of Beaufort West. Correlations of geological logs, digital elevation models and three dimensional cross sections were all utilized in order to understand the hydrogeological setting of these three aquifers. The study highlighted the fact that groundwater resources in the area is slowly depleting and more research is required in order to fully understand the aquifers and thus maximize their use (Nhleko and Dondo, 2008). It was also shown that flow is generally in a southerly direction and the both town dyke and Hansriver dyke in the area appear to act as flow barriers to groundwater, which compartmentalize the groundwater dynamics into north, middle and south regions. Moreover, the three compartments are linked by Gamka river and its tributaries which overflow the dykes. Nhleko and Ndondo(2008) also suggested that all the data for boreholes should be captured, specifically water strikes, as this plays a major role in determining which aquifers are being intersected as well as their yields.

# Chapter 5 Discussion of results:

The hydrogeochemistry data shows a trend from Ca-$HCO_3$ towards Ca-Mg-SO4-Cl type water (Figure 15). The groundwater in the vicinity of the recharge area, which according to Rose and Conrad (2007) is the Nuweveld mountains to the north of the town, displays a distinct Ca-$HCO_3$ signature. This is typical of freshly recharged rainwater (Fetter, 2001). Furthermore the error balance for these samples was less than 5%, thus indicating acceptability for use and confirming good sampling practices and protocols.

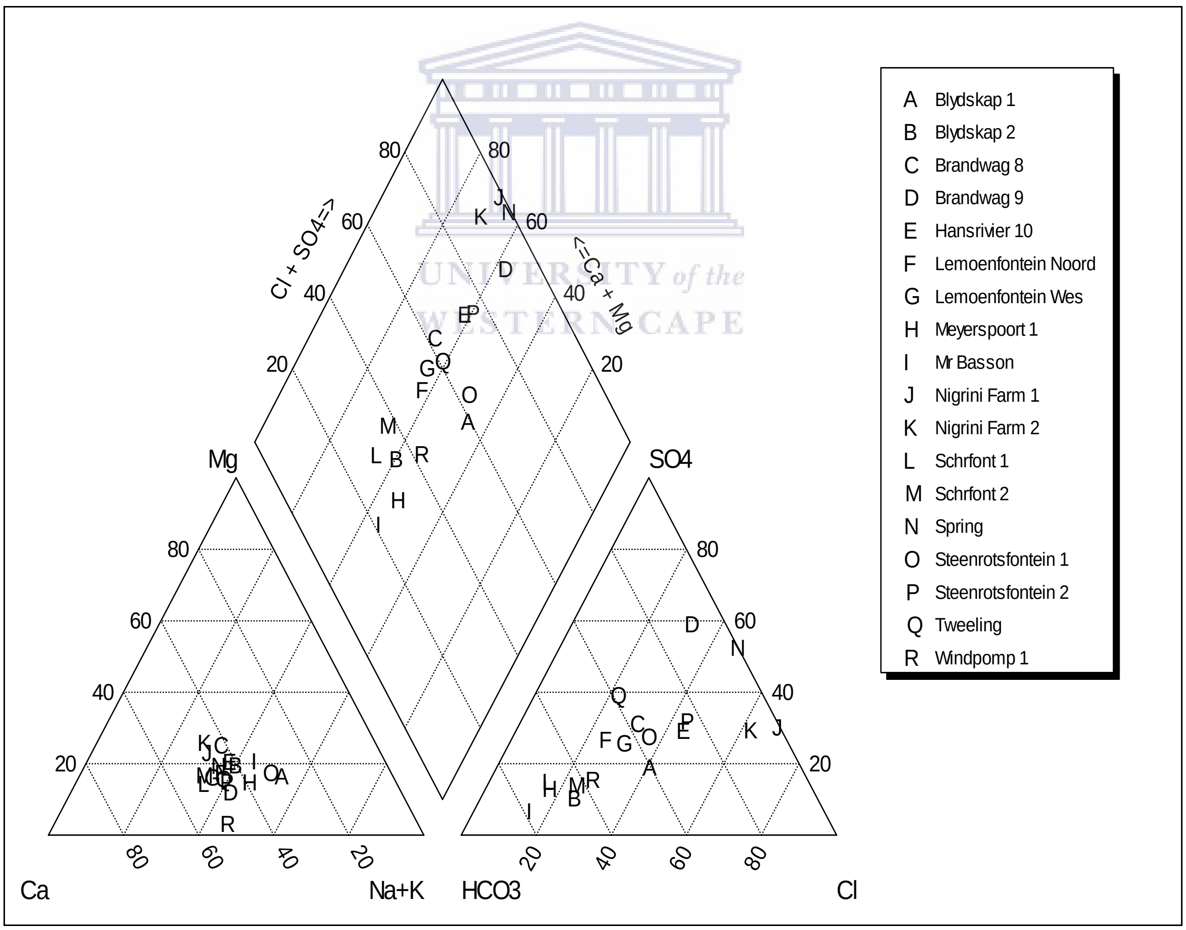



**Figure 15**: Piper plot showing the hydrogeochemistry of samples taken in the Beaufort West area.

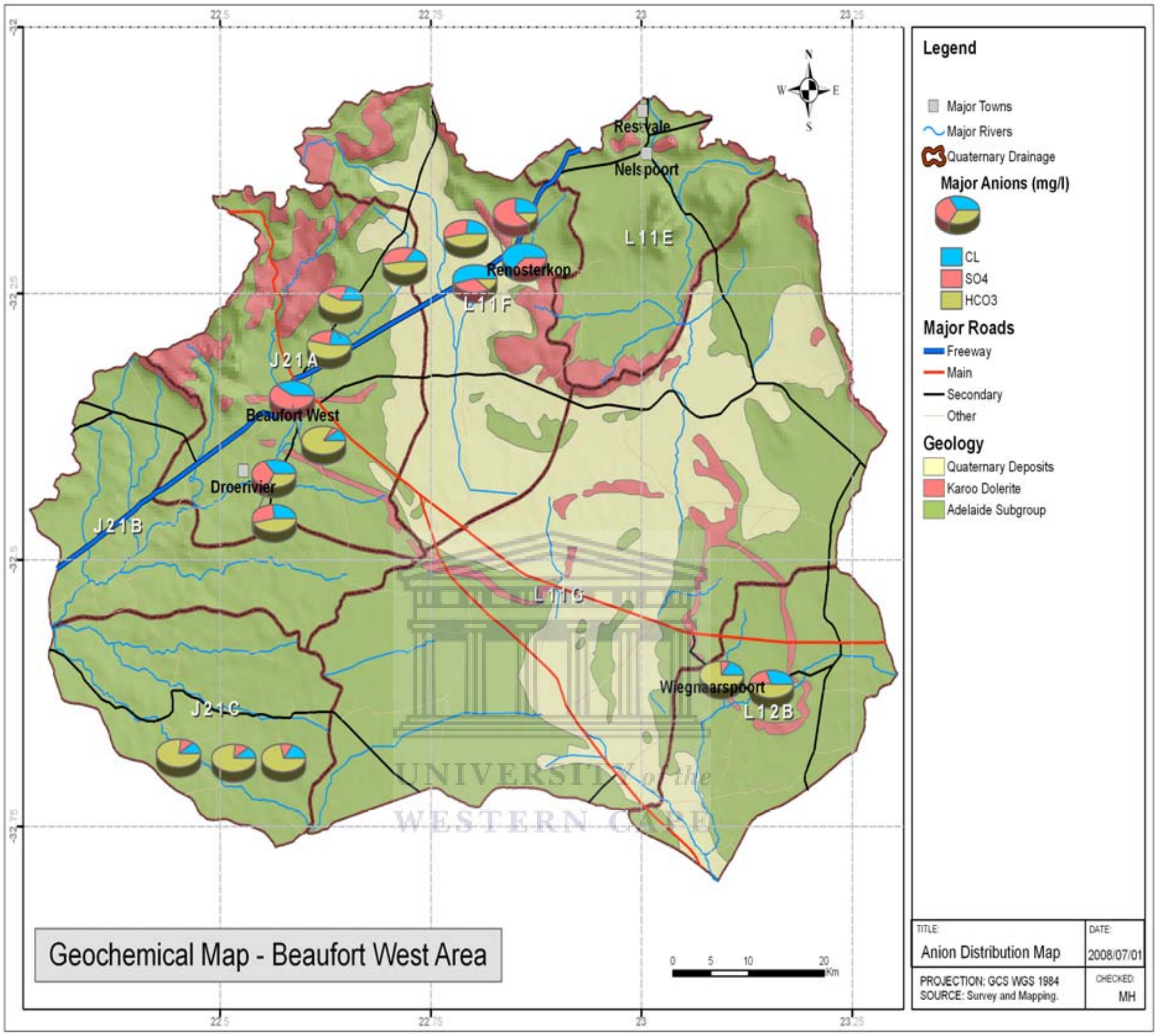



**Figure 16**: Location of groundwater samples and occurrence of major anions

It can also be seen from Figure 16 and Figure 17 that the groundwater in the south displays different characteristics to that in the north. Regan and Conrad (2006) have shown, by means of water chemistry, that the town dyke separates the system to the north and south of the structure. Vogel et al (1980) has also shown, by means of isotopes, that localized recharge does occur in the flatter areas around Beaufort. Thus one could conclude, as previously shown, that the two systems are geologically separated.

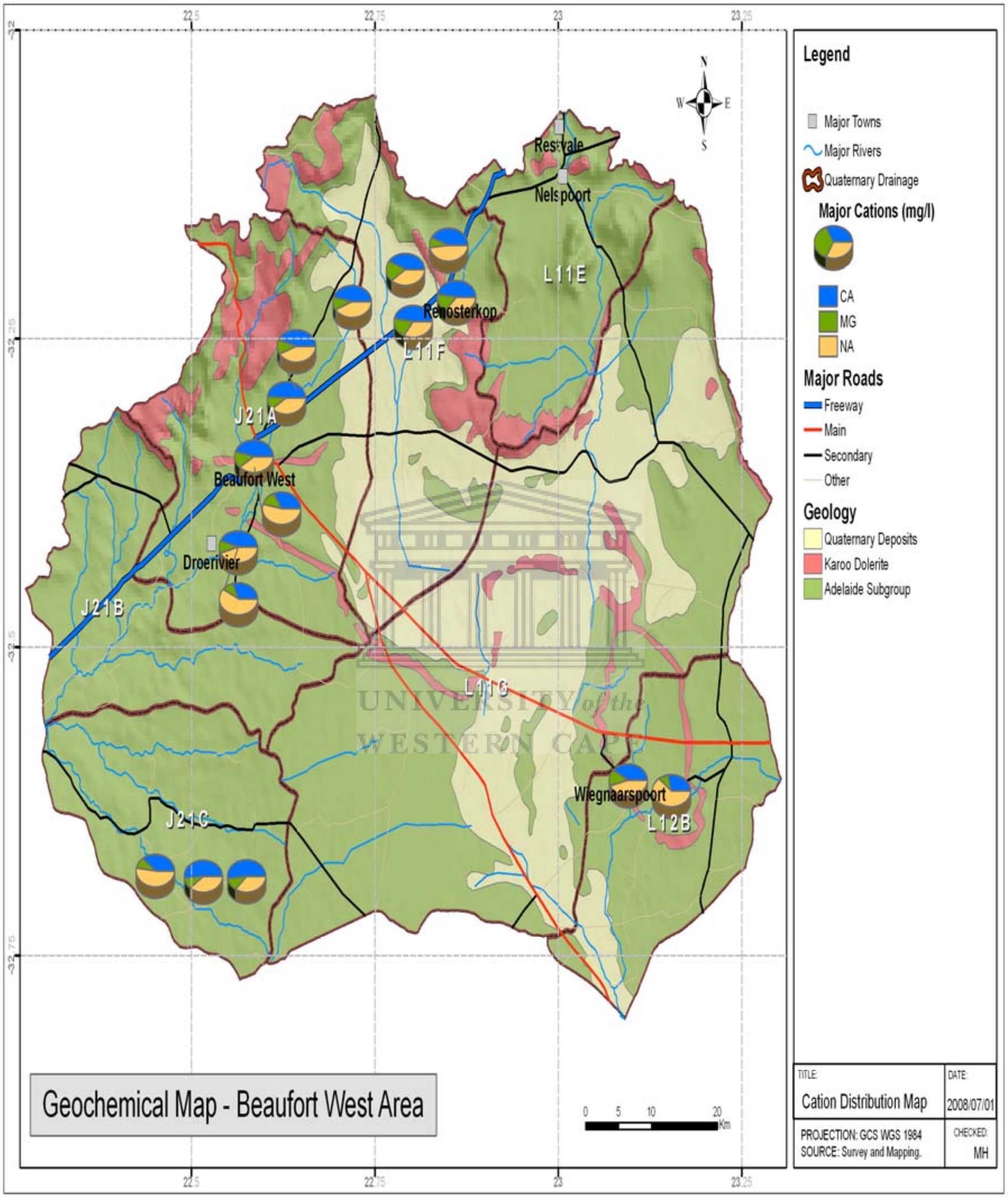



**Figure 17**: Location of groundwater samples and occurrence of major cations

The results from the radioactivity analysis do not highlight any anomalous points of interest (Table 7). Steenrotsfontein's higher radioactivity values could be attributed to the fact that the sample is located within a region of anomalously higher Uranium (CGS,2005). These values should have been expected considering the fact that the majority of the previously mentioned hydrogeochemical data sets allude to this (Scholtz, 2003 and Uramin, 2008). Furthermore Johnson et al (2006) has also stated that the uranium deposits are of a "marginal" grade and this must be the reason for the minimal amounts of Uranium being liberated into the groundwater.

| | Radioactive elements tested for in sample | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Sample Name** | **$U^{238}$** | **$U^{234}$** | **$Th^{230}$** | **$Ra^{226}$** | **$Po^{210}$** | **$U^{235}$** | **$Th^{227}$** | **$Ra^{223}$** | **$Th^{232}$** | **$Th^{228}$** | **$Ra^{224}$** |
| Steenrotsfontein | 641 | 1380 | 15.1 | 12.9 | 4.86 | 29.5 | 6.79 | 10.9 | 2.3 | 13.9 | 6.94 |
| Spring | 184 | 465 | 7.9 | 1.6 | 5.68 | 8.49 | 7.3 | 4.85 | 2.83 | 3.9 | 1.6 |
| Blydskap 1 | 123 | 554 | 7.9 | 9.49 | 6.56 | 5.68 | 2 | -1 | 1.3 | 1.8 | 3.18 |
| Blydskap 2 | 158 | 584 | 6.3 | 16.4 | 6.91 | 7.3 | 2.4 | -1.5 | 0.81 | 2.2 | 1.5 |
| Scheurfontein | 135 | 380 | 6.8 | 6.07 | 0.98 | 6.51 | 2.5 | 0.47 | 1.27 | 0.42 | 0.68 |

**Table 7**: Radioactivity results from NECSA analysis (values in mBq/l)

The concurrence with previous data sets proves that the methods of sampling and analysis used in the field are acceptable for radioactivity sampling and could be used for further studies. Other international best practices are further outlined in Appendix E

# Chapter 6 Conclusions and recommendations:

A groundwater sampling and monitoring protocol for radioactive elements in fractured rocks, which was developed using international best practices as well as local methodologies, proves that previously utilized methods are extremely effective. This protocol covers a wide range of methods for pre-sampling, sampling and post-sampling processes. Historical data in conjunction with the newly generated data set, stemming from this study, conclusively prove that the methods outlined by Weaver at al (2007) for sampling radioactive elements is applicable to fractured rocks.

Unfortunately due to limited infrastructure as well as field conditions not all the methods outlined in the protocol could be tested. Therefore it is suggested that the other methods outlined in the document should be applied in the field and the efficacy thereof should be scrutinized in future studies. A methodology for this could be utlilising multiple methods, like low flow sampling (Puls and Barcelona, 1996) as well depth specific sampling (Vogel,1980), on a single well and then comparing the results in order to check whether the radioactivity results are similar.



A relatively new method for sampling is DGT. These are based on the use of a chelator, which is an iron binding complex, in order to sample metals over a time period of a few days. Numerous case studies have been outlined and these show the applicability as well as the functioning of this specific method (INAP, 2002)

The exercise was also hindered by the fact that many mines have bought prospecting rights from farmers in the area. Thus farms which are currently being explored for uranium could not be accessed for research purposes. This problem could be alleviated with the aid of local government, in the form of a DWAF or DME official accompanying researchers.

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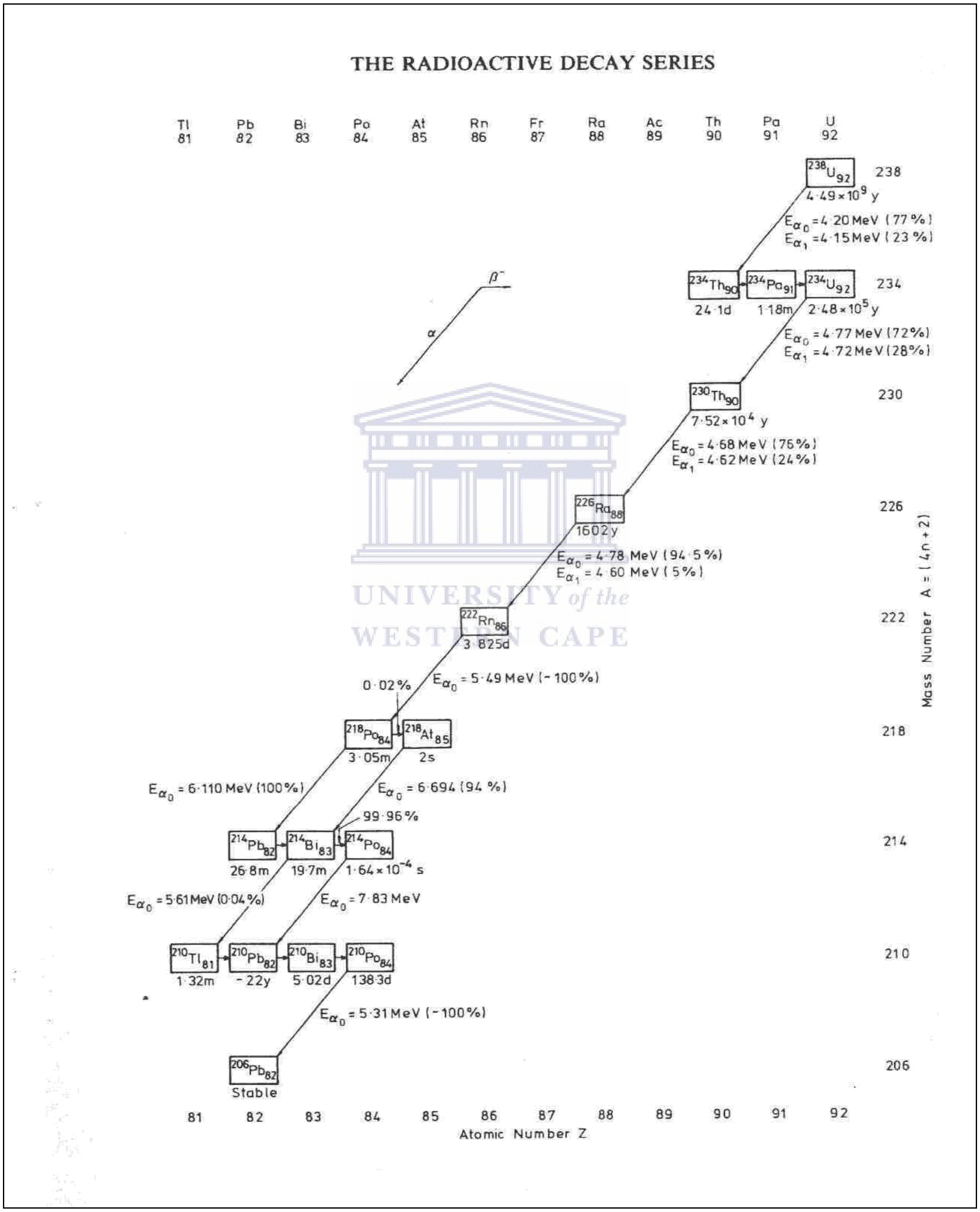
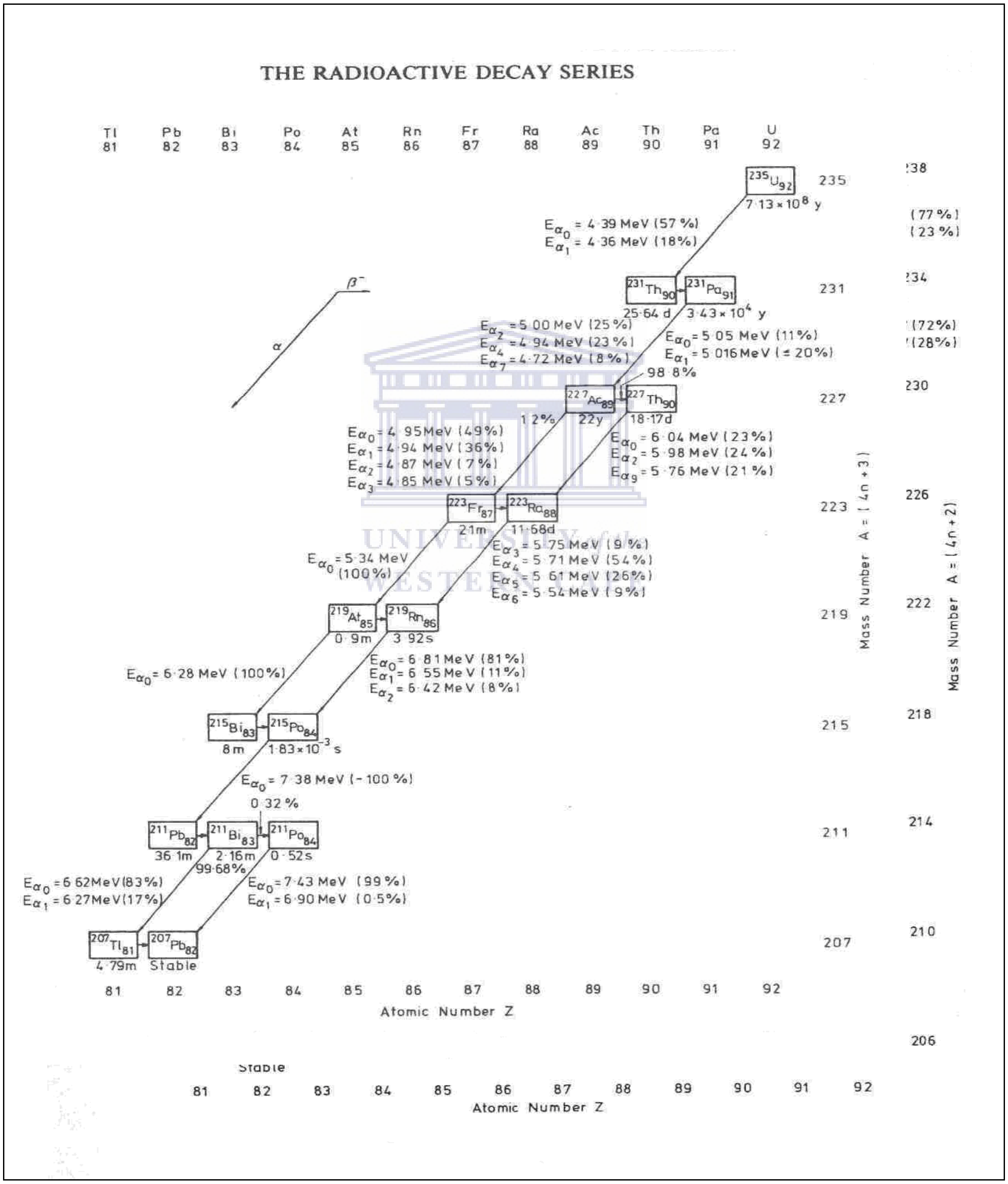
# 1. Appendix A Radioactive decay series 1



# 2. Appendix B Radioactive decay series 2



# 3. Appendix C Documented and predicted Uranium

# 4. Appendix D Groundwater quality analytical result

Report No.: **WT1904/2008**

## ANALYSES REPORT

Gaathier Mahed
Universiteit van Weskaapland

Date received: 19/05/2008
Date tested: 21/05/2008

| Origin | Lab. | pH | EC | Na | K | Ca | Mg | Fe | Cl | $CO_3$ | $HCO_3$ | $SO_4$ | B | Mn | Cu | Zn | P | $NH_4$-N | $NO_3$-N |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | No. | | mS/m | mg/l | | | | | | | | | | | | | | | |
| Blydskap 1 | 1904 | 7.7 | 127 | 152.9 | 6.7 | 73.4 | 24.9 | **0.08** | 150.7 | 108.4 | 251.1 | 94 | 0.55 | **0.00** | **0.01** | **0.03** | 0.04 | 1.75 | 8.16 |
| Blydskap 2 | 1905 | 7.6 | 99 | 87.9 | 8.7 | 80.0 | 23.6 | **0.09** | 88.1 | | 382.8 | 48 | 0.34 | **0.00** | **0.00** | **0.02** | 0.00 | 1.72 | 10.95 |
| Brandwag 8 | 1906 | 7.7 | 133 | 105.6 | 1.8 | 114.3 | 42.1 | **0.07** | 130.4 | 120.5 | 265.1 | 174 | 0.13 | **0.00** | **0.00** | 0.08 | 0.00 | 1.74 | 3.16 |
| Brandwag 9 | 1907 | 7.9 | 241 | 249.8 | 2.0 | 232.7 | 37.0 | **0.13** | 263.5 | 114.5 | 125.6 | 654 | 0.42 | 0.22 | **0.00** | **0.06** | 0.00 | 1.75 | 0.64 |
| Hansrivier 10 | 1908 | 7.7 | 189 | 166.2 | 6.6 | 158.0 | 47.7 | **0.14** | 264.4 | 93.4 | 260.3 | 232 | 0.23 | **0.00** | **0.00** | 0.24 | 0.00 | 1.73 | 12.60 |
| Lemoenfontein Noord | 1909 | 7.7 | 138 | 126.9 | 2.5 | 132.0 | 31.0 | **0.09** | 115.4 | 135.5 | 367.5 | 162 | 0.22 | **0.00** | **0.00** | 0.11 | 0.08 | 1.54 | 3.88 |
| Lemoenfontein Wes | 1910 | 7.7 | 155 | 131.8 | 2.8 | 157.8 | 31.8 | **0.09** | 173.6 | | 427.2 | 197 | 0.21 | **0.00** | **0.00** | **0.02** | 0.00 | 1.43 | 2.54 |
| Meyerspoort 1 | 1911 | 7.4 | 56 | 60.6 | 3.7 | 45.9 | 10.5 | **0.09** | 35.2 | | 246.5 | 36 | 0.10 | **0.00** | **0.01** | **0.01** | 0.00 | 1.46 | 1.81 |
| Mr Basson | 1912 | 7.7 | 124 | 135.2 | 4.3 | 87.0 | 32.7 | **0.10** | 77.5 | | 627.8 | 42 | 0.30 | 2.59 | **0.00** | **0.01** | 0.05 | 1.58 | 0.41 |
| Nigrini Farm 1 | 1913 | 2.5 | 669 | 132.1 | 3.6 | 169.4 | 51.9 | **0.08** | 243.2 | | 0.0 | 142 | 0.28 | **0.02** | **0.00** | **0.01** | 0.00 | 1.56 | 280.40 |
| Nigrini Farm 2 | 1914 | 7.7 | 415 | 286.0 | 3.1 | 388.6 | 135.1 | **0.16** | 868.0 | 90.4 | 185.3 | 548 | 0.30 | **0.00** | **0.00** | **0.03** | 0.00 | 1.40 | 50.60 |
| Schrfont 1 | 1915 | 7.6 | 83 | 74.5 | 2.7 | 96.4 | 16.5 | **0.08** | 52.9 | | 381.2 | 65 | 0.12 | **0.00** | **0.01** | **0.01** | 0.00 | 1.40 | 3.66 |
| Schrfont 2 | 1916 | 7.6 | 87 | 68.5 | 3.0 | 94.4 | 18.9 | **0.15** | 65.2 | 96.4 | 300.1 | 52 | 0.11 | **0.00** | **0.01** | 0.11 | 0.00 | 1.27 | 3.83 |
| Spring | 1917 | 2.3 | 977 | 61.3 | 4.4 | 70.0 | 18.4 | **0.13** | 33.5 | | 0.0 | 50 | 0.18 | **0.02** | **0.00** | **0.01** | 0.08 | 1.34 | 328.40 |
| Steenrotsfontein 1 | 1918 | 7.8 | 262 | 330.4 | 3.6 | 183.7 | 60.7 | **0.12** | 349.8 | | 600.2 | 357 | 0.60 | **0.00** | **0.00** | **0.02** | 0.07 | 1.47 | 69.60 |
| Steenrotsfontein 2 | 1919 | 7.7 | 405 | 390.8 | 9.8 | 392.5 | 78.3 | **0.13** | 621.2 | | 583.3 | 607 | 0.67 | 0.05 | **0.00** | 0.14 | 0.03 | 1.28 | 3.85 |
| Tweeling | 1920 | 7.8 | 137 | 131.4 | 2.7 | 141.1 | 29.1 | **0.15** | 107.5 | | 336.8 | 263 | 0.23 | **0.01** | **0.00** | **0.03** | 0.00 | 1.34 | 1.11 |
| Windpomp 1 | 1921 | 7.8 | 119 | 131.4 | 2.2 | 126.1 | 4.8 | **0.08** | 111.0 | | 396.6 | 84 | 0.26 | 0.04 | **0.00** | **0.05** | 0.00 | 1.19 | 10.44 |
| Methods[#] | | W05 | W04 | W01 | W01 | W01 | W01 | W01 | W07 | W06 | W06 | W01 | W01 | W01 | W01 | W01 | | W02 | W03 |

Values in **bold** is smaller than the lowest quantifiable concentration.
[#]Refer to BemLab work instructions - Accredited methods identified by reference number

**Sample conditions**
Samples in good condition.

**Statement**
The reported results may be applied only to samples recieved. Any recommendations included with this report are based on the assumption that the samples were representative of the bulk from which they were taken. Opinions and recommendations are not accredited.

| | |
|---|---|
| Dr. W.A.G. Kotzé (Director) | 23-05-2008 |
| ................................ | ................ |
| for BemLab | Date |

Enquiries: Dr. W.A.G. Kotzé
Arrie van Deventer

# Appendix E

# Sampling and Monitoring protocol

# For

# Radioactive elements

# In

# Fractured Rock aquifers

## Table of Contents

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# 1 Introduction:

In recent times various studies have characterized the extent to which natural radioactive contamination is occurring within groundwater ( Hainberger et al, 1974, Godoy and Godoy, 2004, Ilani et al , 2005). Unfortunately there seems to be no standard  sampling and monitoring protocol for radionuclides within secondary aquifers (Jousma and Roelofsen, 2003).A document of this nature is important due to the fact that a major part of South Africa is underlain by hard rock aquifers and they supply numerous towns with potable water for various uses (Woodford and Chevallier, 2002)

Weaver at al (2007) suggest that groundwater sampling is done for the following reasons:

- Assess groundwater quality for fitness of use
- Understanding hydrogeology of an aquifer
- Investigating groundwater pollution
- Water quality monitoring



These reasons are all important and thus the development of a protocol in order to provide a methodology for sampling is just as critical.

Jousma and Roelofsen (2003) have compared protocol and guidelines (Table 1). In excess of 400 international documents were reviewed and unfortunately no protocol relating to sampling and monitoring of radioactive elements within fractured rock aquifers has been found.(Jousma and Roelofsen,2003) The authors conclude by recommending that more research is required in hard rock aquifers as well as monitoring. Thus the need for a sampling and monitoring protocol of this nature is once again emphasized. Furthermore according to the classification system used by Jousma and Roelofsen(2003) this document should be considered to be a standard guide(Table 1)

| Category | Type of document | Definitions and Explanation |
|---|---|---|
| Guidelines | Handbook | A book that primarily focuses on giving information about a subject |
| | Guide | A compendium of information or series of options that focuses on providing methodological guidance |
| | Manual | A book that provides instructions for use of a  toll or program or for performing a specefic operation |
| Protocol | Standard guide | A standard compendium of information or series of options that focuses on providing methodological guidance, rather than specifying a course of action |
| | Standard test method | A standard procedure for determining or testing the properties of a system or the relation between them, aimed a t producing a test result |
| | Standard practice | A standard definite set of instructions for performing one or more specefic operations, not aimed at producing a test result |

**Table 1: A comparison between guidelines and protocols (adapted from Jousma and Roelofsen, 2003)**



## 2. Screening methods used for determining radioactivity in fractured rock aquifers

These methods make use of the detection of Radon gas in order to ascertain whether the groundwater is radioactive. This aids in determining whether a sample should be sent for further laboratory analysis for radionuclides. Thus costs could me minimized and no unnecessary work is done. The screening methods also give the individual an opportunity do in-situ analysis and thus reduce the probability of incorrect sample analysis, due to prolonged storage periods, degassing or transportation. The following methods have been identified as the most commonly used for determining Radon concentrations within fractured rock aquifers.

Amrani et al(2000) have compared the use of a liquid scintillation cell(LSC) to that of  an electret ion chamber (EIC). Newman and Talha (2006) have shown that the LSC seems to be a better method for determining radon concentrations in water, due to the many advantages. (Table 2). The LSC method makes use of a “cocktail”, which has a lighter density than water. The Radon gas then escapes into the overlying cocktail and is allowed three hours in order for secular equilibrium to occur between the inert gas and its daughter products

| **Liquid scintillation counting(LSC):** | **Electret ion chamber(EIC):** |
|---|---|
| ***Advantages***: | |
| easy, quick sample preparation | Simple measurement set up |
| small sample size required | easy, quick sample preparation |
| high alpha particle detection efficiency | |
| low detection levels for relatively short measurements | |
| ***Disadvantages***: | |
| Expensive equipment | Long measurement time required |
| Skilled analyst required | Expensive equipment |



**Table 2: A comparison between liquid scintillation counting and the electret ion chamber methods (adapted from Newman and Talha, 2006)**

Unfortunately a major disparity was found when comparing the readings, from the two methods (Amrani et al, 2000). The sampled boreholes showed great variation, when comparing the LSC reading to that of the EIC for the same water sample. It also seems as if the LSC method consistently produced lower readings than the EIC. The former method measures the radon concentration in units per time. Thus a conversion is required in order to acquire the reading in Bq/l. The latter measures voltage and then the original radon concentration in the water is inferred. This indirect method seems to be problematic. The process is further complicated by the use of a co-efficient, when using the EIS. Therefore the LSC seems to be a better method than the EIC(Amrani et al, 2000).

Zhou et al (2001) made use of alpha scintillation counting in conjunction with a Radon bubbler. Thus the gas was stripped from the groundwater sample by the bubbler and an alpha counter was used for determining the Radon concentration. This seems to be an effective combination of two methods. Thus no harsh chemicals are utilized and a minimal amount of gas could be lost to the atmosphere.  A downfall could be the fact that not all the Radon could have been displaced in the bubbling process.

With regards to local conditions, Lin(2007) has utilized the alpha card method in the Table Mountain Group . Wu et al (2003) extensively explain the field operation procedure of the aforementioned machinery. It works on the principle of stripping the Radon gas from the vadose zone gas, the equipment is also able to bubble the Radon gas out of water. The eminating gas is then measured in a gas proportional counter. Lin(2007) states that the count is termed pulse number in the alpha card instrument, from which the concentration of the radon gas can be estimated by means of the following equation:



$$C_{Rn} = JN_{RaA}$$

where $C_{Rn}$ is the concentration of Radon,  $N_{RaA}$ is the pulse number measures and J is the coefficient of the Radon concentration which is a constant and is fixed by the measuring equipment.

# 3 Sampling Protocol for radioactive elements in fractured rock aquifers:

## 3.1 Pre-sampling procedures:

Weaver et al (2007) outlines a comprehensive planning programme which delves into pre sampling procedures. This includes a list of field equipment and general groundwater sampling procedures. These practical tips are of the utmost importance when preparing to venture into the field.

Another important aspect is acquiring permission from land owners. In many instances boreholes are located on private property and it is crucial that farmers or landowners are consulted prior to sampling. This process is also helpful in the hydrocensus phase due to the fact that the land owner could provide valuable information with regards to numerous environmental factors in the area as well as history, as shown by Rose and Conrad (2007)

Lastly it is necessary to liase with the laboratory in order to ascertain which containers, preservatives and reagents are to be used when sampling for radionuclides(Weaver et al, 2007). Wilde et al (1998) suggest that a 1 litre polyethelyne bottle be acid rinsed and then the sample should be preserved to pH<2 using $HNO_3$. Levin (1983) on the other hand states that sample bottles should be thoroughly rinsed with 10% HCl and then emptied and rinsed thrice with de-ionised water. Levin (1983) also states that the samples should be taken as follows:

- 2l for the determination of the trace elements such as Al, As, Be, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Ti, Si, Zn

- 500ml for the determination of U, V and $NO_3^-$

- 250 ml for the determination of the major components $SO_4^{2-}$, $Cl^-$, $F^-$, $Na^+$, $K^+$, $Ca^{2+}$ and $Mg^{2+}$

The authors definitely took cognizance of the fact that the trace metal content of water could be altered in storage. Therefore the use of acid has been recommended in order to reduce the possibility of precipitation of heavy metals, which includes radioactive elements. Also the different acids and methods used are due to the varying procedures of the laboratories . Thus this proposed methodology would indicate that the sample is heading for a specific laboratory. Therefore one would have to liase with the laboratory of choice in order to determine the specific volumes of water required for analysis, types of bottles, treatment and storage of samples, among other things.

Previously used bottles should be rinsed with acid and soaked in de-ionised water for a few days before sampling (Weaver et al, 2007). New sample bottles on the other hand should be field rinsed with water directly from the sampling device (Wilde et al, 1998) Finally the sample bottle should preferably be plastic (Levin, 1983), this is due to the fact that glass could break and thus leakage would occur and therefore sample integrity would be questionable .

### *3.1.1 Downhole logging*

Prior to purging it is suggested that downhole logging is done. This will help to identify fractures within the subsurface(Cook, 2003). Anomolous increases in certain parameters infer the location of a fracture within the borehole (Figure 1). This would only occur if the well is screened at various intervals, or is entirely uncased. Furthermore various in-situ parameters such as temperature, pH, Electrical conductivity, dissolved oxygen as well as some dissolved ion concentration could be determined in the borehole, depending on the type of logging tool used(Weaver et al , 2007). Van Wyk et al (2009) warn that these anomolies could also infer a lithology change or even stagnant water at the bottom of a well, thus care should be taken when interpreting the logs

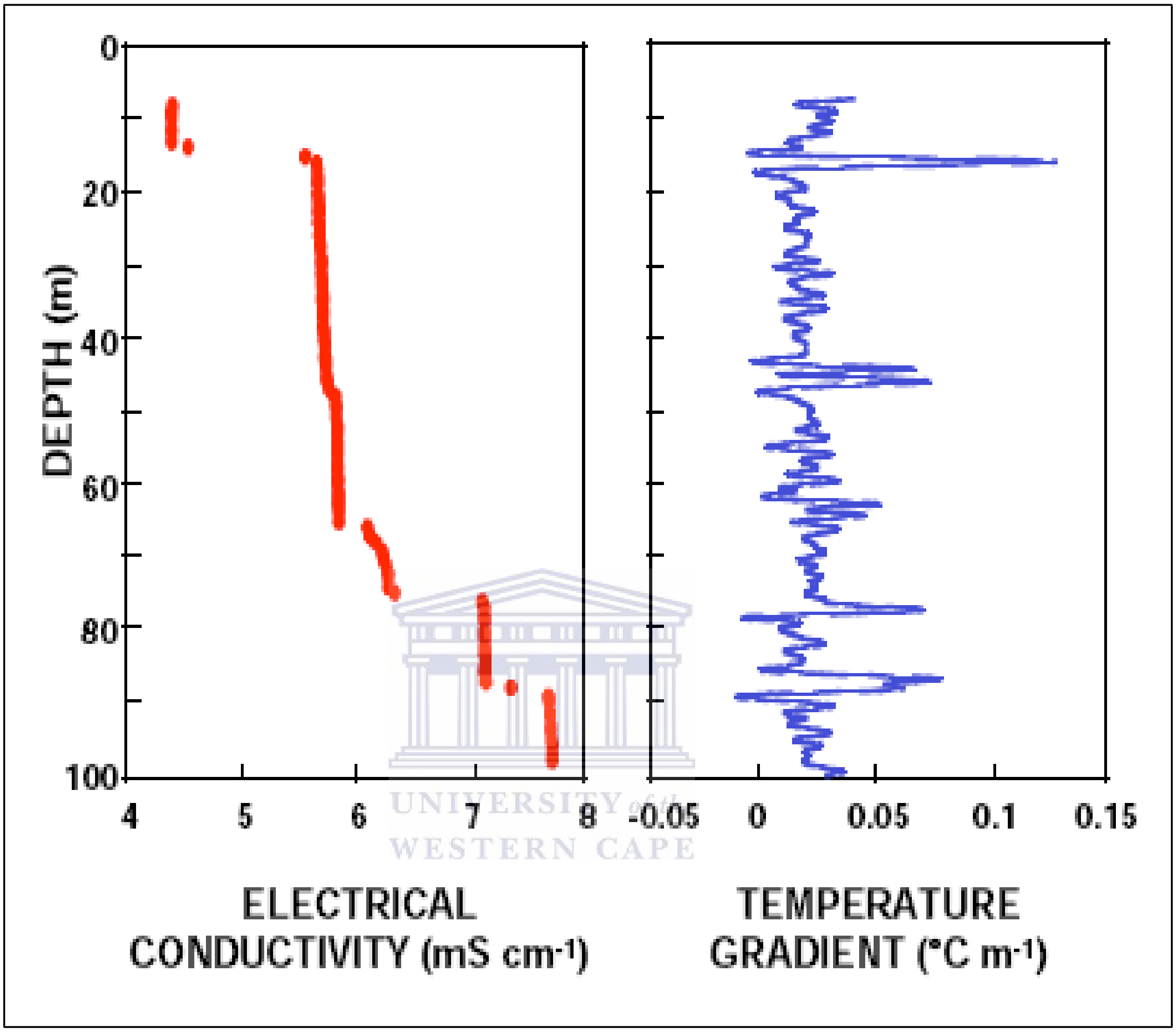



**Figure 1: The use of temperature and Electrical conductivity logging to determine fracture location in the subsurface.(Cook, 2003)**

Gamma ray logs, which are a form of radiation logging, would have to be the most applicable to radioactivity studies due to their ability to detect radioactive material within fractures (NRC, 1996). It has been previously shown that radioactive material concentrates in and around the immediate vicinity of the fracture due to leaching from the parent rock(Wood et al, 2004) . NRC (1996) outline the positive and negative aspects of the different methods and state the applicability of the methods to various scenarios(Table 3)

| Logging parameter | Applicability | Advantages | Disadvantages |
|---|---|---|---|
| Temperature | Detects temperature changes owing to flow in fracture systems | | |
| Resistivity | Detects clay in fractures | | |
| Gamma radiation | Detects radioactive material in fractures | | |
| Borehole imaging | Able to view fractures via a television | In situ representation of fractures | Shadows form due to imaging from oblique angles, thus interfering with interpretation |
| Flow metre | Directly detects flow in fracture | Determines hydraulic connection between fractures | |



**Table 3: Parameters used in borehole logging in fractured systems (NRC, 1996)**

Despite all of this there are some inherent problems when logging wells in fractured systems. The initial alteration of the rock material in the immediate vicinity of the well could be attributed to drilling ( Figure 2 ). This is further discussed in section 4.4 Also the area which could possibly be scrutinized is in the immediate vicinity of the well is quite limited. The combination of these factors could lead to misinterpretation of the underlying geology (NRC, 1996). Thus it has been shown that the combined use of a various methods yields better results and minimizes the misinterpretation of data (Cook, 2003).Furthermore certain field parameters which could be used in downhole logging are discussed in more detail in section 3.4

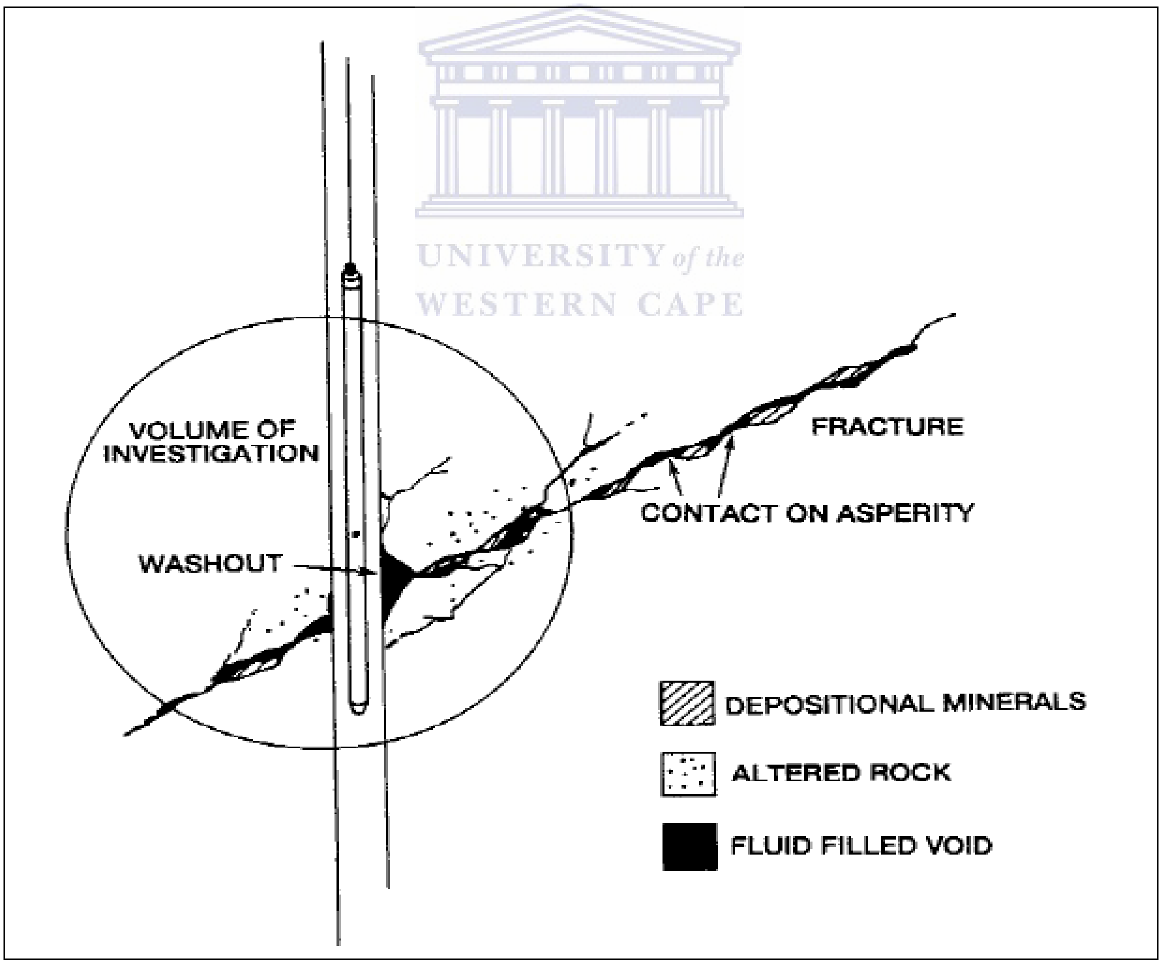



**Figure 2: Schematic of a natural fracture intersecting a borehole (NRC, 1996)**

### *3.1.2 Purging*

Before taking a sample the well should be purged. This is done in order to remove the stagnant water. Cook(2003) has compared sampling prior to purging as well as post purging. The author has concluded that the radon concentration within the well varies greatly due to the ability of the gas to diffuse (Figure 3). Thus a sample taken from an unpurged well would not be representative of in-situ conditions of the aquifer. This is especially true in fractured rock aquifers due to preferential pathways.

Also the well should be purged using a low flow approach (Puls and Barcelona, 1996). This minimises the oxidation of the sample and thus the alteration of in-situ chemical conditions. After the borehole has been purged the fractures would then be de-watered, followed by the matrix (Cook, 2003). This has important implications for chemical analysis as the conditions within a fracture differ to those of the matrix. It is especially important with regards to radionuclides due to the fact that we find an increase in Radon within these fractures (Wood et al , 2004). Cook (2003) has shown that the volume of water which should be purged must equate to two well volumes. It is critical to note that low flow sampling does not equate purging (Weaver et al, 2007)



After purging the well the use of a flow through cell would be advised. This is done in order not to expose the sample to the atmosphere and thus alter its chemical or physical state(Weaver et al, 2007). The flow through cell seems to be the best tool for direct field measurements, due to the ability of the device to measure multiple parameters(Wilde et al, 1998). When taking the sample the utmost care should be taken in order not to contaminate the sample.

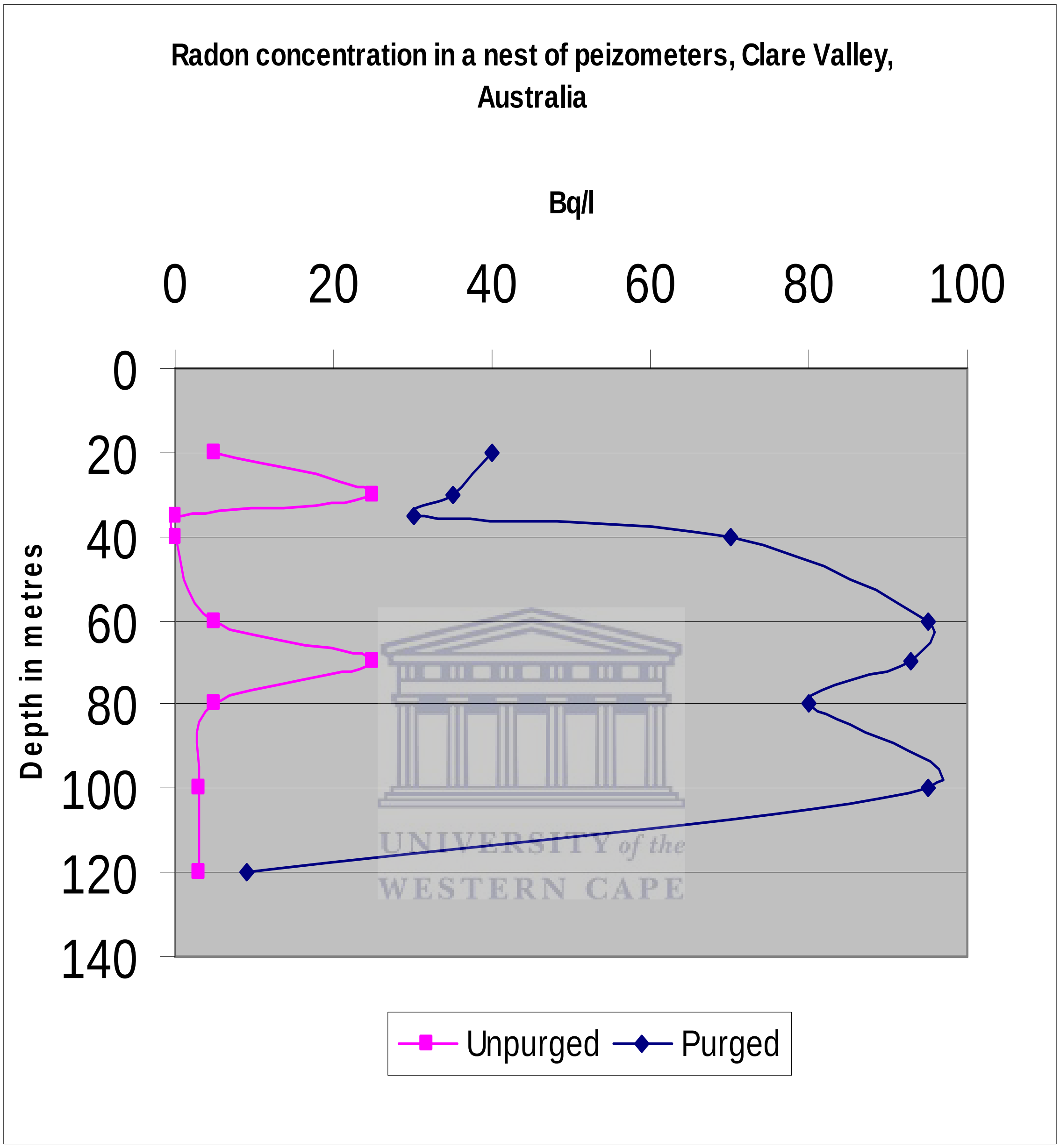


**Figure 3: A comparison between the Radon concentrations before purging (pink) as well as after purging two well volumes (blue) (Cook, 2003)**

## *3.2 Sampling devices:*

It is also of the utmost importance that the acquired sample is representative of the in situ conditions (Wilde et al, 1998). Thus the devices used in order to sample the groundwater are of the utmost importance. Barcelona et al (1985) stress the previous point by mentioning the important characteristics of a sampling device:

- The device should be simple to operate to minimize the possibility of operator error.

- The device should be rugged, portable, cleanable and repairable in the field.

- The device should have good flow controllability to permit low flow rates (= 100 mL/min) for sampling volatile chemical constituents, as well as high flow rates (> 1 L/min) for large-volume samples and for purging stored water from monitoring wells

- The mechanism should minimize the physical and chemical disturbance of ground-water solution composition in order to avoid bias or imprecision in analytical results.

Freyer et al (1997), concur with the aforementioned facts. The authors have also shown that the low flow sampling devices, which are used for Radon sampling, do not greatly affect the radon concentration (Figure 4). Thus these devices, like the bladder and submersible pump, are all aptly suited for sampling and fit the criteria previously mentioned by Barcelona et al (1985).

Unfortunately the bailer would not be an advisable option in boreholes intersecting multiple fractures due to the fact that it would sample water from the entire column and not at a specific depth or fracture.

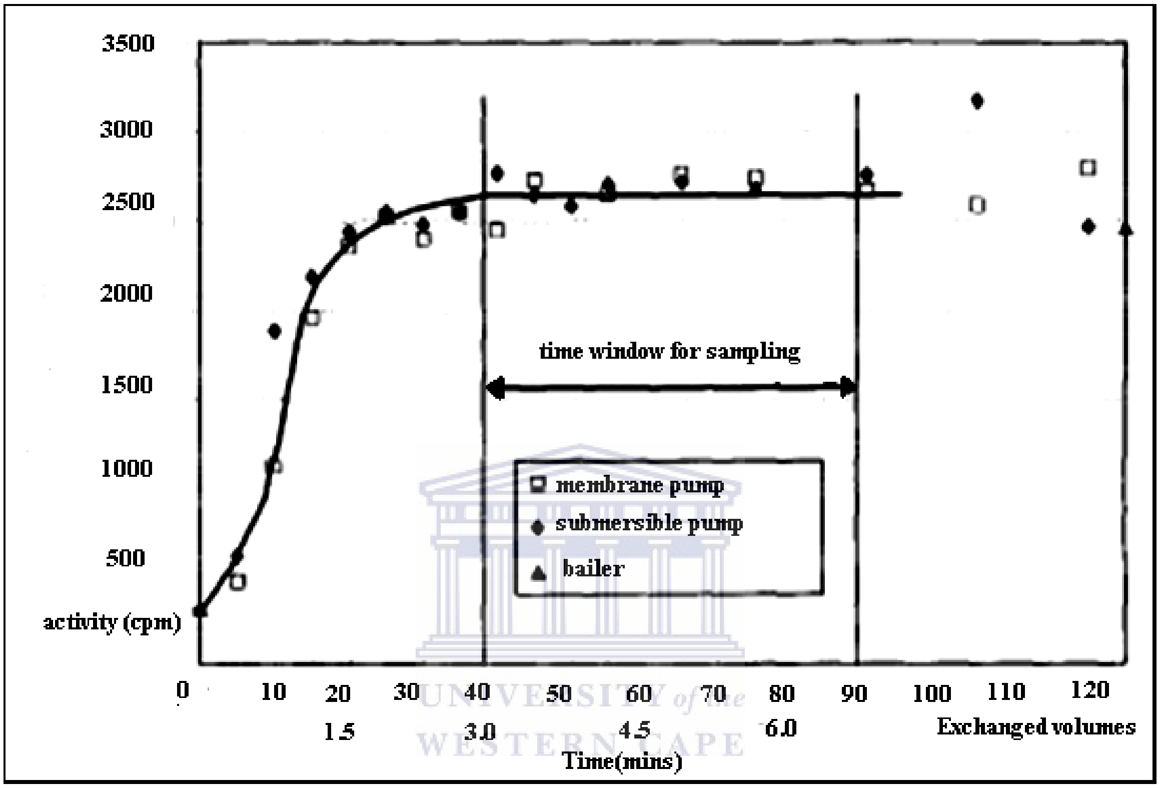


**Figure 4: A comparison of various sampling techniques and the radon concentrations acquired from each one ( Freyer et al, 1997)**

### 3.2.1 Packers:

The isolation of specific fractures in order to understand their hydrogeochemistry is critical. This can be done by using packers. These inflatable devices are placed above and below the fracture of interest, in order to isolate the area (Figure 5). Prior to this a pump is isolated within the structure. USGS (2001) have designed the BAT[3] (Bedrock Aquifer Transportable Testing Tool) specifically for sampling in fractured rock aquifers. Besides having packers and a pump it is also installed with three pressure transducers. One is located above the packers, between the packers and the last one is below the packers. These are utilized in order to monitor fluid pressure and correctly ensure that the packers are properly isolating the fracture of interest (USGS, 2001)

Puls and Barcelona (1996) strongly recommend that low flow sampling, in conjunction with packers, should be done in fractured rock aquifers. This approach should only be attempted after identifying the water bearing fractures and thus the sampling zone can be isolated.

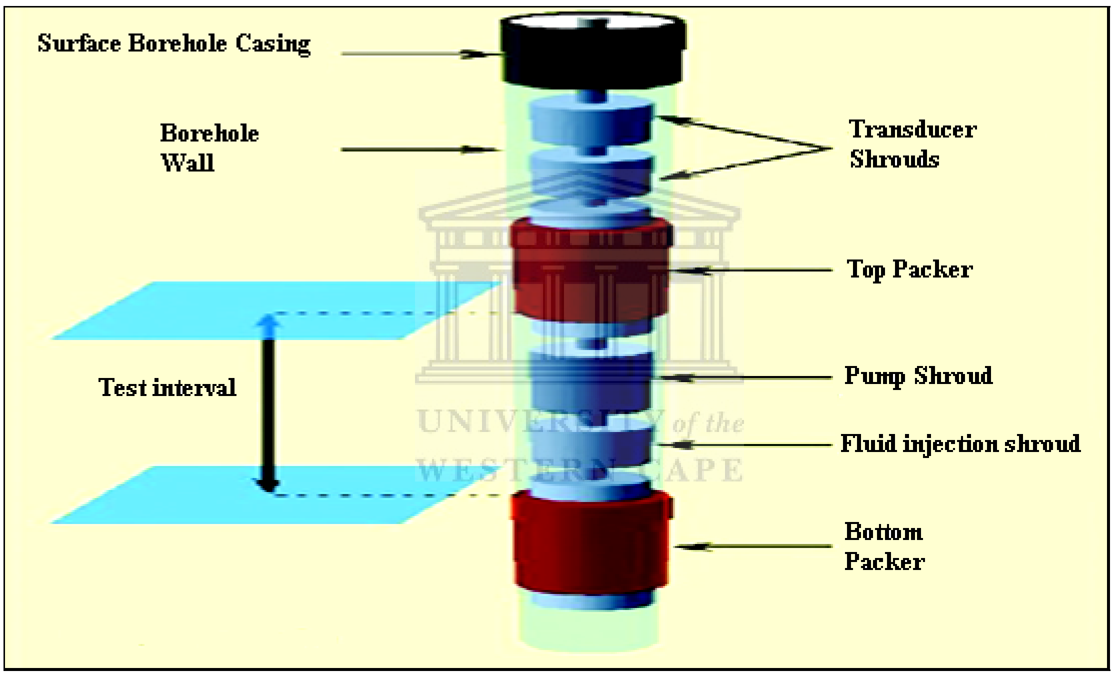


**Figure 5: Multifunction BAT3 in a bedrock borehole with borehole packers inflated to seal against the borehole wall.(adapted from USGS, 2001)**

This approach has been applied locally by Vogel et al (1980), without transducers, specifically for radioactivity. The success of the aforementioned method has unfortunately not been reproduced. Applicability and methodology to local conditions should be noted and this will definitely improve the quality of data stemming from fractured rock aquifers.

### 3.2.2 Depth specific samplers

Depth specific samplers have also been proposed as a viable option (Weaver et al, 2007). These are lowered into the borehole in order to gain a sample at the fracture or other area of interest. Unfortunately this method could artificially elevate turbidity in the well due to it disturbing the water while it is submerged (Parker and Mulherin, 2007). For this reason the Snap sampler™ has been developed. It is a passive sampling method allowing depth specific sampling of groundwater over a period of time. The sampler is left in the well in order to allow for equilibration after the initial disturbance caused by the insertion of the device into the well (Parker and Mulherin, 2007).This is especially useful in fractured rocks due to the fact that these conduits are the preferred paths of flow (Cook, 2003). Thus the sample would be representative of the aquifer and the actual flow chemistry over a time period and not a grab sample at one moment in time like other depth specific samplers.

Another useful sampling device is the DGT (Diffusive Gradient Thin Film). INAP (2002) outline the use and applicability of this chelator type sampler. It works in a similar manner to the Snap sampler™ due to the fact that the sample taken is over a period of time and not at one specific moment. Furthermore sample contamination is minimized and the sampler is easily deployed. Other advantages and disadvantages of the method are further mentioned by INAP(2002).



All of the aforementioned devices are viable sampling options for radioactivity in fractured rock aquifers. Care should be taken with regards to use and applicability and contamination. The choice of tool is dependant upon budget as well as availability of the equipment.

### *3.3 Field determinands:*

Some parameters are measured in the field for the following reasons(Weaver et al, 2007):

- to check the efficiency of purging
- to obtain reliable values of those determinands that will change in the bottles during transport to the laboratory
- to obtain some values that may be needed to decide on the procedure or sampling sequence immediately during the sampling run

It has also been suggested that radioactively contaminated groundwater should be sampled using similar methodology as for heavy metals (Wilde et al, 1998; Smedley et al, 2006; Weaver et al, 2007). This would entail the filtering of the sample, once it has been extracted from the aquifer (Levin, 1983). Typically a 0.45µm filter paper is utilized, in order to differentiate between dissolved and non-dissolved species (Yeskis and Zavala, 2002). Levin (1983), also suggests that the filter paper should be kept, if the suspended particles are to be analysed. This is important, taking into consideration that Radium precipitates under oxidizing conditions. Despite all of this, liasing with the laboratory is critical to understand their needs for analysis.

#### 3.3.1 Temperature

Ilani et al (2005) have shown how the temperature in groundwater, in conjunction with reducing conditions, could increase the radium content. On the other hand most of the economically viable uranium deposits have formed under similar conditions (Ivanovich and Harmon, 1983). Thus one can see that temperature of the water is a major determining factor for the type of radio nuclide. The radioactive decay of these radio nuclides also releases heat, thus increasing the surrounding temperature. It is also important to note that the temperature logging of a borehole, in conjunction with other parameters, could act as an indicator for fractures within the subsurface (Van Wyk et al, 2009)

The digital thermometer, which is quite accurate, has been proposed as the equipment of choice (Weaver et al, 2007).The use of mercury thermometers has been discouraged (Wilde et al, 1998). This is due to the health hazards which are associated with the heavy metal. Also the digital thermometers are usually incorporated into a pH metre, thus simplifying matters and one tool is transported instead of many. The metre should also be checked for batteries as well as calibrated, according to manufacturers instructions, on a regular basis (Levin , 1983)

### 3.3.2 Electrical Conductivity(EC)

The conductivity of water depends upon the presence of ions, their total concentration, mobility, valence, and relative concentrations, and on the temperature of measurement (Weaver et al, 2007). In order to reduce the possibility of error Radtke et al (2006) suggest that conductivity should be measured as close to the source as possible, using either a downhole or flowthrough-chamber sampling system. This principle of proximity should apply to all field parameters, irrespective of the method.

EC in conjunction with temperature has been used in order to characterize fractures in boreholes(Cook, 2003). The marked increase in EC is indicative of the inflow of water from another source through a fracture. There is also a definite relationship between the Temperature and EC. Ivanovich and Harmon(1983) have also shown that the mobility of uranium is directly related to the presence and concentration of certain ions. Ilani et al (2005) have shown that the radium content of groundwater is proportional to the chloride content. Thus there is a greater possibility for highly saline water to contain radium, rather than uranium. This would also be dependant upon whether there is any uranium bearing mineral in the flowpath of the groundwater.

Almeida et al(2004) concur with the aforementioned facts and have also shown that there is a significant correlation between uranium concentration and electrical conductivity

### 3.3.3 pH

pH could be defined as a measurement of the concentration of Hydrogen ions within a given solution. It is usually measured on a logarithmic scale and by definition can be viewed as:

$$pH = -\log_{10} [H^+]$$

Thus pH is a major factor controlling the valence state, solubility and the mobility of trace metals(Weaver et al, 2007). Furthermore in conjunction with TDS, and specific ions, it could determine dominant species of these trace metals, such as uranium. Mudd (2002) has shown that the mobility of uranium, in groundwater greatly increases with a decrease in pH. This would explain the general increase in radioactivity observed in the vicinity of gold mines (Winde, 2004). This parameter should not be considered on its own, but rather in relation to other chemical measurements in order to gain a complete understanding of the hydrogeochemistry.

The pH metre should also be calibrated on a regular basis. Weaver at al(2007) provide a step by step guide. The authors also advise that the user should consult the manual which accompanies their equipment.

### 3.3.4 Oxidation reduction potential (Redox):

Oxidation potential can be defined as the energy change, measured in volts, required in, order to add or remove electrons, to or from an element or compound (Allaby and Allaby, 2003). This is heavily dependant upon pH. Thus the redox potential, in conjunction with pH, dictates which ionic species would dominate within groundwater, or any water body for that matter. Radionuclides are no exception to the rules

Eh is a measure of the equilibrium potential relative to the standard hydrogen electrode, developed at the interface between a noble metal electrode, usually platinum, and an aqueous solution containing electroactive redox species (Nordstrom and Wilde, 2005). The units for measurement is usually millivolts(mV). The Eh meter would usually be incorporated into a pH meter, thus lightening the load for field trips. Nordstrom and Wilde (2005) extensively examine the methods and procedures relating to measurements as well as maintenance of the Eh meter. The authors stress the fact that the manufacturer's instructions should be consulted.



In mining activities the sulfides present are oxidized, thus leading to the acidification of the surrounding water and the release of metals. Acid Mine drainage (A.M.D), as it is commonly known, contains low levels of radioactivity when compared to nuclear waste. Therefore the mobility of uranium is largely controlled by Eh, pH and complexing ions

# 4 Monitoring protocol for radioactive elements in fractured rock aquifers:

Groundwater monitoring can be defined as the scientifically-designed, continuing measurement and observation of the groundwater situation (Jousma and Roelofsen, 2003). Ideally the design of network density and sampling frequency would be based on an optimization of the cost of monitoring and of the accuracy of collected and derived data related to the objectives of the network(Kovalevsky et al, 2004). In line with this, Netili et al (2007) further propose that groundwater monitoring and sampling sites should be selected to be representative of geographic distribution, geology, groundwater use, land-use and groundwater flow regimes amongst other factors..

With regards to radioactivity monitoring in the Karoo, Titus and Hohne (2007) have said that the current monitoring network will be utilized for radioactivity monitoring. It could also be logically assumed that the wells would have to fall within the Uranium province as well as intersect the uraniferous bearing sandstone.



Titus and Hohne(2007) have also examined the development of a radioactivity monitoring programme for groundwater. The goals of the programme would be :

- *National scale monitoring: Long-term, standardized measurements and observations of groundwater and in order to define status and trends of groundwater resources to determine its "fitness of use".*

- *Local scale monitoring: Subsequent monitoring could also be (based on availability of funds and for a subsequent phase) of finite duration, intensive and site-specific in order to measure and observe the quality of groundwater resources in selected impacted groundwater sites at South Africa*.

## *4.1 Monitoring well location*

Decisions about the placement and construction of monitoring wells are among the most difficult in developing an effective monitoring program(Barcelona et al , 1985). Therefore it is important to understand the current flow regime and this is done by developing a conceptual model which utilizes the available data (Jousma, 2006).

Hunt (2007) argues that geostatistics , in conjunction with GIS, could be used as an effective tool for optimizing monitoring well location. In order to do this one would require data in the area. This is due to that fact that this statistical modeling is based on the assumption that there is a relationship between samples according to their position and its relationship with its neighbours (Clark, 1987)

The semi variogram is utilized for this purpose and works on the aforementioned premise of correlation among samples due to distance. The semi-variogram is determined as follows (Zhou, 1992):



- Several groups (*m*) of distances between measurement locations with an average distance *d* are defined. For example, $d_1$ is the group where the distances between the locations are small, whereas $d_m$ is the group with the largest distances;
- For each distance group $d_k$ the possible pairs of measurements locations *i* and *j* are identified ($n_k$: all possible pairs);

For each distance group $d_k$ the variogram value $\gamma$ *(dk)* is calculated using the following equation:

$$\gamma(d_k) = \frac{1}{2n_k} \sum_{1}^{k} \ (Z_i - Z_j)$$

where $Z_i$ and $Z_j$ are the measured variables at locations I and j. This could be the amount of Radon in groundwater or some other concentration of a radioactive element. The process is repeated at varying distances (Hunt, 2007). Finally these values are plotted onto an experimental semi-variogram (Figure 7)

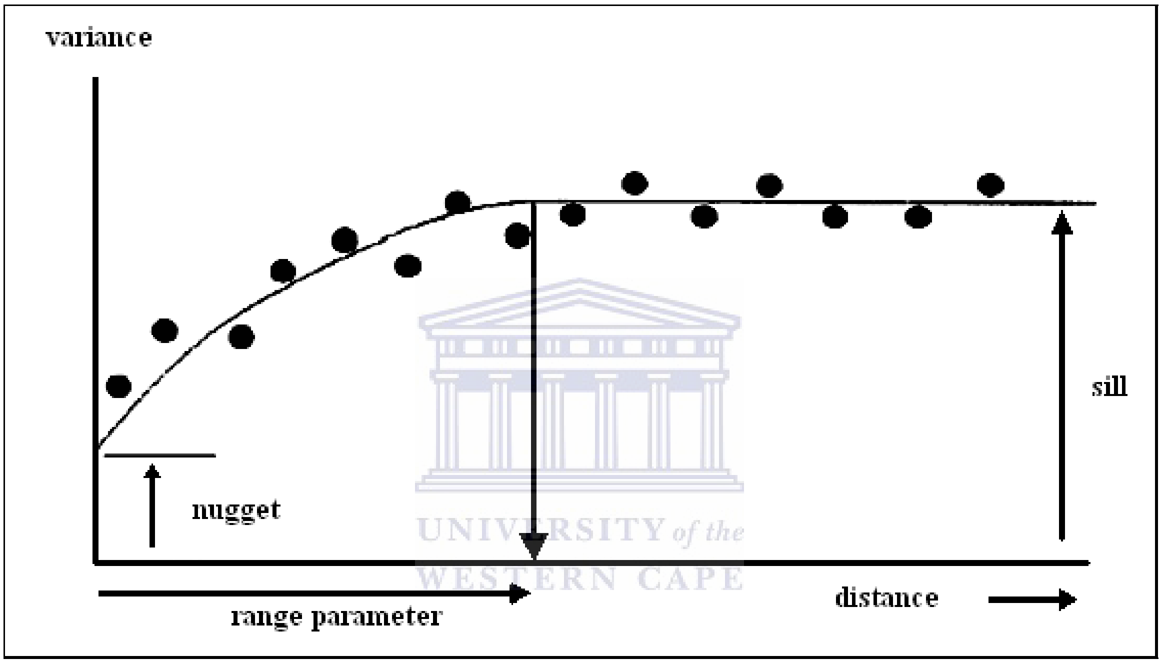


**Figure 7: Experimental (dots) and theoretical (line) semi-variogram (Kovalevsky et al, 2004)**

This semi variogram forms the basis for a spatial interpolaton technique known as kriging. The area of interest is then covered by a grid and each block within the grid is filled by an estimated value determined by the kriging process. This is usually done with a software suite and a 'smoothed out' picture is given for the location of the elements at hand. After all the calculations three layers are projected, namely:

- Number of samples
- Kriging efficiency map
- Geoscientific knowledge

Finally a combination of all the above layers leads to the highlighting of areas which require additional sampling (Hunt, 2007). This fourth and final layer is the one which is used in order to maximize the location of future monitoring wells. This method takes into consideration the possible heterogeneities of the subsurface by including the layer with geoscientific knowledge. In the aforementioned layer one could possibly include features affecting groundwater flow, such as lineaments and dykes(Cook, 2003). Another possibility could be the inclusion of the ore body. This method in conjunction with geostatistics seems to be the best option for maximizing monitoring well location.

Unfortunately this type of modelling also has its downfalls. Problems with Kriging arise in the initial stages of the assumptions. Firstly true variance of the *single* distance-weighted average is replaced with the false variance of a *set* of distance-weighted averages (Mercks, unpub ). Also flow in fractured rock aquifers is quite heterogenous and modelling this process is quite complex(Cook, 2003). As we all know all models are wrong but some are useful. Therefore despite the fact that it is based on many assumptions, it is still a quantitative method.

### *4.2 Sampling frequency:*

EPA (1992) promotes the hourly sampling of fractured aquifers for field determinands. This protocol was developed specifically for nuclear waste facilities and the parameters which would be measured on an hourly basis would include those which a data logger could determine. These include temperature, TDS and water level. This would aid in determining whether leakage has occurred from the storage facility and also aid in determining anomalous inflows of contaminants in groundwater, in a natural setting. The aforementioned could be inferred from an increase in TDS, pH and temperature. It is an effective monitoring strategy and the aforementioned parameters would act as indicators for the contamination of groundwater (Table 4).

Kua (2006) has sampled for radon on an hourly basis. This continual sampling was done at a spring, located along a fault. The anomalous decrease in Radon proved to be an indicator for a major earthquake in the region (Kua et al, 2006). Monitoring of such a nature should only be implemented when a similar purpose and outcome is intended. Budgetary constraints would play a major role and the geologically active areas require monitoring of such a nature in order to alleviate the possible impacts on human lives. A monitoring programme like this would only be applicable where one finds a similar situation.

| Analyte Group | Description of Parameters |
|---|---|
| Contamination Indicator Parameters | pH, specific conductance (field measurement) |
| Radiological Indicator Parameters | Gross alpha, gross beta, tritium |
| Volatile Organic Compounds | Volatile Organic Compounds |
| Semivolatile Organic Compounds | Semivolatile Organic Compounds) and tributyl phosphate |
| Metals | Antimony, arsenic, barium, beryllium, cadmium, chromium,<br>cobalt, copper, lead, mercury, nickel, selenium, silver, thallium, tin, vanadium, zinc |
| Special Monitoring Parameters for Early Warning Wells | Aluminum, iron, manganese |
| Radioisotopic Analyses: alpha- , beta- , and gamma-emitters | C-14, Cs-137, I-129, Ra-226, Ra-228, Sr-90, Tc-99, U-232,<br>U-233/234, U-235/236, U-238, total uranium |
| Strontium-90 | Sr-90 |

**Table 4: Groundwater sampling analysis agenda (WVDP Site Environmental Report, 2000)**



Durrani and Ilic (1997) have shown that a seasonal variation of Radon occurs in the subsurface. This could be attributed to the increased moisture during the wet season, thus trapping the Radon in the groundwater. In the dry season the soil moisture content is not as high and thus the soil is more aerated. Therefore the Radon gas is able to rise through the available pore spaces and escape into the atmosphere (Figure 7)

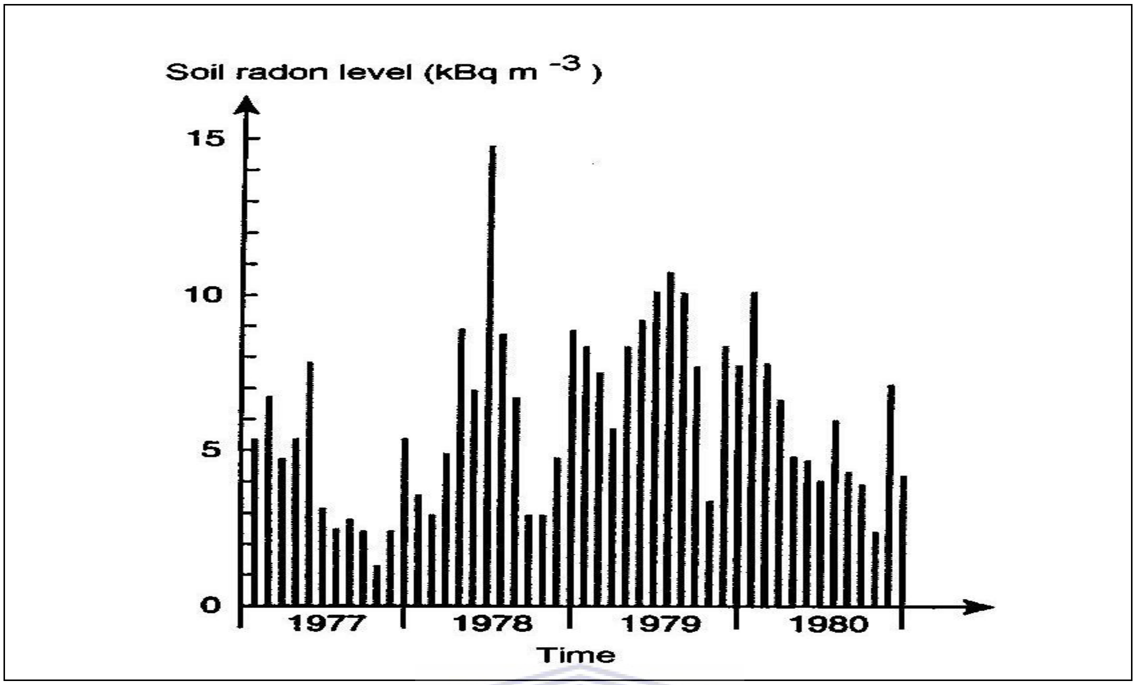


**Figure 8: Seasonal variation of Radon occurrence in soil (Durrani and Ilic, 1997)**



Thus according to Durrani and Ilic (1997) it would be advisable to sample twice annually, once after the wet season and again after the dry season. This seems economically viable and efficient enough in order to determine variation in terms of the Radon concentration in groundwater. This seasonal sampling in conjunction with monitoring of field parameters would be the ideal strategy in order to monitor the presence of radionuclides in groundwater.

A statistical analysis could also be done in order to effectively ascertain sampling frequency. This would mean that a substantial amount of data would be required and it would have to stem from the area of interest. As a crude guideline you need about five samples from groundwater source with seasonal variation to indicate variability (Weight and Sonderegger, 2000). The step trend which emerges in Figure 7 is one of the types of patterns which could possibly occur. The purpose of trend analysis, in statistical terms, is a determination of whether the probability distribution from a series of observations has changed over time (Helsel and Hirsch, 2002). The simplest statistical method which could be used to ascertain this variability would have to be based on historical data (Kovalevsky et al, 2004). Furthermore it could also be said that the monitoring programme would have to take cognizance of background levels, that is prior to human impact, as well as adjust the monitoring programme in order to account for the increased variability introduced by human impact (Kovalevsky et al, 2004)

### *4.3 Monitoring well design:*

The controlling factors in well installations are usually sanitation, stability, and an estimated minimum useable well life of 25 years (Kovalevsky et al, 2004). EPA (1992) concur with the aforementioned and categorically state that the monitoring well casings and screenings should:

- be resistant to chemical and microbiological corrosion and degradation in contaminated and uncontaminated waters

- be able to withstand the physical forces acting upon them during and following their installation, and during their use

- not chemically alter ground-water samples, especially with respect to the analytes of concern



Kovalevsky et al (2004) are of the opinion that the entire length of the well should be uncased. Despite this the aforementioned authors immediately contradict themselves and categorically state that in order to prevent collapse, especially in consolidated rocks, wells should be cased. Barcelona et al (1985) state that is when wells are slotted along their entire length, water stemming from these wells are indicative of water quality stemming from the entire well and not specific fractures. Therefore it is advisable to screen wells only at the depths of the fractures (Cook, 2003).

It could also be said that when constructing a monitoring well, in consolidated formations, it would be advisable to install screens at the depths which fractures occur. Another option would be cordoning off of the individual fractures with the same well. This could be done by means of permanent packers or individual seals. However the effectiveness of the well seals between intervening monitoring points is often suspect and the care and time necessary to properly seal these types of wells are not justified when compared to the straightforward procedures for sealing separate holes for vertically nested wells (Barcelona et al, 1985)

The EPA (1992) suggest the use of PTFE (polytetrafluoroethylene) when constructing a monitoring well screen due to its resistance to radiation, oxidation , chemical and biological attack as well as weathering. Other advantages, according to EPA (1992), include.

- Can be used under a wide range of temperatures;
- Inert to attack by the environment, acids, and solvents;
- Fairly easily machined, molded, or extruded;
- Most inert casing for monitoring metals

.

Unfortunately there are also many disadvantages when using the aforementioned material for screening and well casing (EPA, 1992). These are:

- Only slotted casing is available for screens;
- Non-stick nature of PTFE may cause annular seal failure;
- Moderate weight and low strength per unit length;
- Ductile behavior of PTFE ("creep" or "cold flow") may result in the partial closing of well intake openings (i.e., screen slots);
- PTFE casing and screen is unsuitable for driven wells; and
- Higher cost relative to PVC (Polyvinyl chloride).

Due to these disadvantages PVC has also been recommended as a suitable material for the construction of screenings and well cases. This is due to the fact that it is much cheaper and resistant to Acid Mine Drainage. (Weight and Sonderegger, 2000). According to the EPA (1992) other advantages of PVC include:

- Readily available
- Low maintenance
- Lightweight for ease of installation
- Flexible and workable
- Low cost relative to PTFE

Unfortunately PVC also has its disadvantages. These are minimal when compared with other materials and thus the reason for it being so widely used in the construction of wells (Weight and Sonderegger, 2000). EPA (1992) state the following as disadvantages for the use of PVC in well construction:



- Unsuitable for driven wells
- May fail if subject to high temperatures
- May fail if subject to high pressures
- Long-term exposures of some formulations of PVC to the ultraviolet rays of direct sunlight (above-ground portions of casings) and/or to low temperatures may cause brittleness and gradual loss of impact strength that may be significant;

These materials have been highlighted due to their suitability for sampling radioactive elements (EPA, 1992). Therefore the use of any other material, specifically in well and screen construction, would not be advocated. This is in order to maintain the integrity of the groundwater sample as well as the results stemming from the analysis.

### *4.4 Drilling methods:*

EPA (1992) has listed the following factors as important when considering drilling procedures:

- Drilling should be performed in a manner that preserves the natural properties of the subsurface materials

- Contamination and/or cross-contamination of ground water and aquifer materials during drilling should be avoided

- The drilling method should allow for the collection of representative samples of rock, unconsolidated materials, and soil

- The drilling method should allow the owner/operator to determine when the appropriate location for the screened interval has been encountered

- The drilling method should allow for proper placement of the filter pack and annular sealants.

- The borehole should be at least 4 inches larger in diameter than the nominal diameter of the well casing and screen to allow adequate space for placement of the filter pack and annular sealants

- The drilling method should allow for the collection of representative groundwater samples.

- Drilling fluids (including air) should be used only when minimal impact to the surrounding formation and ground water can be ensured.

### 4.4.1 Percussion

This method is also known as cable tool drilling and is probably the most primitive. A heavy drill bit is repeatedly lifted and allowed to crush the underlying geology. The tool then mixes the loosened particles with water to form a slurry at the base of the borehole. If little or no water is present, water is added in order to form this slurry (Driscoll, 1989). When the penetration rate is significantly retarded, then a bailer is sunk into the hole in order to remove the drill chips. At times a sand pump could also be utilized (Driscoll, 1989).The drill is usually powered by a motor located on the rig

The mobility as well as ability to drill with minimal amounts of water, specifically in arid regions, are some of the advantages of this method (Kovalevsky et al, 2004). Unfortunately the limitations of this type of drilling include depth and the fact that it is a slow and tedious process (Driscoll, 1989)

| Advantages | Disadvantages |
|---|---|
| Rigs are relatively cheap, require little maintenance and are easy to move in rugged terrain or where space is limited | Relatively slow rate of progress when compared to other rigs of similar capacity |
| Machines have low energy requirements | Economic and physical limitations to depth and diameter |
| Reliable for a variety of geological conditions | Each drill can only complete a certain number of holes per year |
| Require less skilled operators and smaller crew than other rigs of similar capacity | Well casing must be driven, during drilling, in order to prevent collapse of borehole. |

**Table 5: Advantages and disadvantages of percussion drilling (Kovalevsky et al ,2004)**

### 4.4.2 Rotary

This method was developed in order to increase drilling speeds and to reach greater depths in most formations (Driscoll, 1989). Another factor contributing to this methods great versatility is the fact that it has a variety of additives which enhance the drilling environment (Weight and Sonderegger, 2000). The direct rotary system works by means of a rotating drill bit at the lower end of a drill pipe. This pipe transmits the rotating action from the rig to the bit. While this occurs a drilling fluid is pumped down the pipe and up along the cavity between the uncased hole and the drill stem. Kovalevsky et al (2004) states that the purpose of the drilling fluid is to lubricate and cool the bit, to pick up material from the bottom of the hole and to clean the hole by transporting the cuttings to the surface. The major types of drilling fluid include:

- air
- water
- Foam
- Stiff foam
- Mud



These are ranked in order of hole stability (Weight and Sonderegger, 2000). Also the type of fluid used would depend upon the rock formation expected, the available equipment, experience of the drilling crew and occasionally the environmental regulations (Kovalevsky et al, 2004)

Forward rotary drilling is ideal for harder geologic materials and faster drilling scenarios (Weight and Sonderegger, 2000). Unfortunately this method is not able to drill wells with large diameters, but reverse rotary drilling is well suited for this function (Driscoll, 1989)

| Advantages | Disadvantages |
|---|---|
| Penetration rates are high and drilling depth capacities are great | The cost of a rotary rig is much higher than a cable tool rig of equal capacity and maintenance and repairs are more complex |
| Minimal casing is required during the drilling operation and permits use of most geophysical logging equipment | Requires a much more skilled and larger crew with drilling fluid knowledge and experience |
| Rig mobilization and de-mobilisation is rapid | Mobility may be limited by land surface, mostly slope or wetness |
| Well screen can be set easily as part of the casing installation | Collection of accurate sample requires special procedures and the use of drilling fluids may cause plugging of certain formations |

**Table 6: Advantages and disadvantages of direct rotary drilling (Kovalevsky et al, 2004)**



### 4.4.3 Air rotary

The air rotary drilling method was developed primarily in response to the need for a rapid drilling technique in hard rock hydrogeology (Kovalevsky et al, 2004). The penetration rates are faster and the bit life is longer, when compared to water based drilling (Driscoll, 1989). (Table 7)

The percussion effect delivered by the down the hole air hammer method is similar to the cable tool method. Bit types vary in size, but are usually made from carbide, which is quite resistant to abrasion. The rapid striking of the rock with use of a pneumatic drill delivers the crushing blows to the underlying geology. Thus air is continuously supplied to cool the bit and remove cuttings.

Driscoll (1989) has shown that the copious volumes of air utilized are extremely effective in rapid removal of cuttings. Thus we find that the hammer always strikes a clean rock surface, therefore maximizing its efficiency.

| Advantages | Disadvantages |
|---|---|
| Penetration rates are high | Maintenance costs are high |
| Cuttings removal is rapid | Initial cost of large compressor is high |
| Estimates of the yield from a particular aquifer feature, which has been penetrated, can be made during drilling | Drilling depth is limited by available air pressure |

**Table 7: Advantages and disadvantages of air rotary drilling (Kovalevsky et al, 2004)**

# 5 Conclusion

Jousma and Roelofsen (2003) have categorically stated that there is a lack of research in fractured rock aquifers as well as the monitoring thereof. Thus there is a dire need for documents of this nature. Therefore it is suggested that the other methods outlined in the document should be applied in the field and the efficacy thereof should be scrutinized in future studies. A methodology for this could be utlilising multiple methods, like low flow sampling (Puls and Barcelona, 1996) as well depth specific sampling (Vogel,1980), on a single well and then comparing the results in order to check whether the radioactivity values are similar.

A relatively new method for sampling is DGT, as previously mentioned. These are based on the use of a chelator, which is an iron binding complex, in order to sample metals over a time period of a few days. Numerous case studies have been outlined and these show the applicability as well as the functioning of this specific method (INAP, 2002). It would be advised to use this method in future to determine its applicability



Further research is required as well as the large scale implimentation of the protocol in order to ascertain the applicability thereof. Thus the continued understanding of hard rock aquifers could be fostered. This is of the utmost importance if the scientific community is to continue to advance and solve problems like water supply from these saturated geological units.

The data stemming from the studies should be put to good use and aid in the development of an effective monitoring programme as highlighted in the protocol. It is useless if the data is not utilized to its maximum capacity (Kovalevsky et al, 2004).This can only be done if statistical analysis is brought into play. Also an effective database management system would be needed in order to maximize the use of data.

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