Predicted Spatial Distribution of Naturally Occurring Arsenic, Selenium and Uranium in Groundwater in South Africa -Reconnaissance Survey-

Final Report to the
Water Research Commission

by

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"Mapping of Naturally Occurring Hazardous Trace Constituents in Groundwater"

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EXECUTIVE SUMMARY

INTRODUCTION

In South Africa groundwater is being heavily utilised for rural water supply. Approximately 2/3 of rural communities are dependent on groundwater. Some of these water supply systems are located in geological units known or suspected to contain natural sources of trace constituents in economic or sub-economic concentrations. Although some of these constituents may be economically valuable commodities, they may be toxic to humans and livestock if present in even low concentrations in drinking water.

In most cases the concentration of trace constituents in groundwater is unknown and little or no attention is paid to their possible presence in water during the planning of water supply systems. In other cases, water samples are analysed from new boreholes only, however, the mobility of trace constituents is associated with long term alteration of the hydrochemical environment, which can be induced by pumping, hence the mobility of these constituents can be altered in time. Consequently, their presence in solution may only occur after a prolonged period. Therefore, the potential exists to have water supply systems producing water of an unacceptable quality and where the problem remains unknown for many years until detrimental effects are recognised by health practitioners.

The recent findings that groundwater in large areas of West Bengal, Vietnam Ghana, Bangladesh, Argentina, Chile, China, Hungary, Mexico, USA, Ghana and elsewhere is heavily enriched with naturally occurring arsenic, point to the fact that this shortcoming is global in extent (Smedley & Kinniburgh, 2002). In most cases, the documentation of toxic trace constituent concentrations has occurred *subsequent* to the identification of non-reversible toxic effects. These conditions could have been detected if adequate geological and geochemical information and expertise had been obtained prior to the development of water supplies.

Arsenic, together with fluorine, are now currently recognised as the most widespread naturally occurring and serious inorganic contaminants in drinking water associated with groundwater sources (Smedley & Kinniburgh, 2002). Localised groundwater arsenic problems are being reported from an increasing number of countries and many new cases are likely to be discovered worldwide (Smedley & Kinniburgh, 2002).

The fact that trace constituents are relatively common in South African rocks suggests their distribution and mobilisation should be of concern. The affinity of arsenic, selenium and other non-metals with gold, copper, nickel, zinc, lead, cobalt, silver and other ores suggests that trace constituents can be widespread in South Africa. Arsenic and selenium, unlike most other toxic metals and metalloids, are fairly easily dissolved through a range of pH and Eh conditions, which may lead to significant dissolution where high concentrations are present in rock. This has prompted an assessment of the distribution of these constituents in the environment and the factors that control their mobility.

Uranium is another trace constituent commonly encountered in the South African geological environment. Its potential mobility under a wide range of natural hydrochemical environments requires that its distribution be documented. Its economic importance has resulted in its distribution being well documented in South Africa, however, little is known about its occurrence in groundwater.

Naturally occurring selenium is another trace element of concern in the South African geological environment, however, little is known about its occurrence.

Until recently, As, U and Se were not on the list of constituents in drinking water routinely analysed for, so little is known about their distribution, both in South Africa and internationally. Consequently, situations where local and international water quality guidelines are exceeded were identified unexpectedly only after serious impacts on human or animal health were recognised. Several such incidents have been identified in South Africa: in the Northern Cape Province and Limpopo Province arsenic concentrations of over 1000 ug/l have been recorded; a statistically significant correlation between groundwater chemistry and the high prevalence of haematological abnormalities (related to leukaemia) was reported for an area in the Northern Cape Province; epidemiological studies done on animals consuming poor quality water (e.g. with high arsenic concentrations) in rural areas have shown adverse impacts e.g. skin lesions (Meyer, pers. com.). Despite this, little information on the regional occurrence of these constituents is available.

Knowledge of the presence and distribution of groundwater potentially contaminated with natural sources of these constituents would be of great value, as it would permit water planners and water service providers to identify regions where water supplies should be screened for these constituents regularly. The major factors that need to be considered to provide guidance to water service authorities undertaking a rapid assessment of water supplies for trace constituents are:

- An assessment of the occurrence of trace constituents in terms of potential geological sources and anthropogenic sources
- The mobilisation and transport of these constituents under existing and predicted geochemical environments

The current South African groundwater database does not support identification of areas with high concentrations of trace constituents that may form a potential hazard due to incomplete data and difficulties in detecting these trace constituents. A broad based sampling programme will be time consuming and expensive. In addition, knowledge of the presence of these constituents is required in order to optimise the distribution of such a monitoring network. Without an understanding of trace constituent distribution and mobility, a large-scale monitoring programme is necessary.

Anthropogenic sources of trace constituents resulting from industrial and mining activities are readily identified and monitoring of water quality near such sources is accepted practice. Natural sources have not been identified and their distribution is currently unknown. Consequently, this study focuses on identifying natural sources of occurrence.

A qualitative knowledge of the natural sources of As, U and Se in South African geology, and their potential mobility in groundwater would be of great value to national authorities as it permits water planners and health workers to identify regions where water should be screened for trace constituents. Significant cost savings would result as a national monitoring programme could be focused on high-risk areas rather than nation wide monitoring.

To meet this goal the following research objectives were formulated for the project:

- To identify hydrochemical processes by which these constituents could become mobile in groundwater.
- To produce a map delineating regions of South Africa where naturally occurring As, U and Se could pose a risk to groundwater potability

These objectives were met by:

- compiling geological target maps based on an understanding of the South African geological environment to predict where As, U and Se bearing minerals could be present.
- reviewing the SAMINDABA minerals database to plot known occurrences of As and U and other constituents known to be associated with As, U and Se bearing minerals
- reviewing national scale regional soil geochemistry sampling to identify regions of known trace constituent anomalies
- reviewing the process by which these constituents are mobilised into the groundwater environment, the expected compounds they form, and the mobility of such compounds under natural hydrochemical conditions found in groundwater.

Although documentation of the extent of occurrence of these trace constituents in South Africa may be perceived as alarmist, it is important to note that occurrence in the host rock does not necessarily equate to mobilisation in groundwater. In many cases host minerals are not exposed to hydrochemical conditions required for mobilisation and transport to occur. Alternatively, the lack or presence of other ions may result in interference, causing trace constituents to be sorbed or precipitated, or the lack of specific ions may prevent soluble complexes from forming. Therefore local conditions of trace constituents in groundwater should be viewed as the exception rather than the rule. Consequently, an understanding of geochemical processes and conditions is important to understand whether the presence of trace constituents in the host rock may lead to a risk of their presence in groundwater.

In addition, the identification of a geological Formation or Complex lithology as potentially containing arsenic, uranium or selenium does not necessarily imply the entire Formation contains these minerals. In many cases mineralisation is patchy or erratic hence occurrence is localised. However, at the scale of the national maps, the entire Formation needs to be identified as being potentially As, U or Se bearing since not all localities can be identified.

GEOLOGICAL OCCURRENCE OF ARSENIC, URANIUM AND SELENIUM IN SOUTH AFRICA

Since large deposits of organic rich sediments do not occur in South Africa, arsenic and selenium bearing minerals are primarily associated with geological settings where sulphide mineralisation has taken place. It is expected that the dissolution of sulphide minerals bearing arsenic and selenium would be the dominant source of these constituents in South African aquifers. Uranium on the other hand is not necessarily associated with sulphides and can occur in sedimentary environments as well as igneous rocks with a felsic character. In order to identify South African lithologies where these constituents might be present, conceptual geological models where sulphide mineralisation or uranium deposits occur were identified.

Arsenic, uranium and selenium bearing minerals are commonly found in geological environments that can be classified as carbonaceous shales, Cu-U sandstones, porphyry uranium/copper/molybdenum deposits, Volcanogenic Massive Sulphide deposits (VMS), Pegmatite–Uranium veins, Tin Granophile systems, Hydrothermal Terranes, Mafic Igneous Sulphides, Platinum Group Element seams, Lead–Zinc deposits, Nickel-Copper sulphides, Phosphates and geothermal springs. These target geological models all occur in South Africa, and are well known for the economic minerals they contain, however, the extent to which these geological environments contribute hazardous trace constituents to groundwater is unknown. These geological models were classified according to the mode of mineralisation and reviewed in terms of potential source areas for arsenic, selenium and uranium mineralisation.

Potential target areas of arsenic and selenium mineralisation were identified based on the occurrence of sulphide mineralisation. Sulphide mineralistion is associated with deposits of antimony, chromium, coal, copper, gold, molybdenum, phosphates, platinum, tin, iron, uranium, zinc, sulphur and manganese ores, and with sedimentary exhalative deposits (SEDEX). The occurrence of these ore deposits in South Africa were identified (Wilson & Cole, 1998), and the lithologies in which they were located flagged on the 1:1 000 000 geological map of South Africa. These lithologies were considered to be potentially arsenic and selenium rich due to documented sulphide mineralisation. Where these deposits only occur within specific domains of a lithological unit, the sulphide rich provenance of the lithological unit was limit by the domain boundary.

The uranium target geology was chosen on the basis of existing geological data based on widespread uranium exploration. Domains were selected according to the documented occurrence of uranium.

MAPS OF THE OCCURRENCE OF ARSENIC, URANIUM AND SELENIUM

The following maps were produced by the study:

- Maps of predicted Arsenic, Selenium and Uranium occurrence
- Maps of Arsenic and Uranium occurrence based on the metallogenic map of South Africa
- Map of Potential Hazard of Arsenic Occurrence in Groundwater

REPORTED OCCURRENCES

In total 1514 boreholes in South Africa have been sampled for arsenic. Of these 252 contained measurable arsenic. 200 of these boreholes had concentrations exceeding the WHO limits (0.01 mg/l).

The results may also not be comprehensive, since many geological units contain no monitoring boreholes, have never been sampled for arsenic, or contain samples taken from localities not subjected to localised sulphide mineralisaton.

High concentrations of arsenic (>0.1 mg/l) are recorded in the following geological units:

- Tygerberg Formation of the Malmesbury Group: One borehole north of Cape Town records a concentration of 10 mg/l of arsenic. It has been intruded by Cape Granites, and as a result has been hydrothermally altered and may contain veins including copper tin and molybdenum sulphides.
- Timeball Hill and Rooihoogte Formation: One borehole west of Potchefstroom contains 7 mg/l of arsenic. Arsenic is associated with stratiform gold-quartz-carbonate-sulphide veins.
- Kirkwood Formation: Eight boreholes in the Algoa basin contain arsenic concentrations between 0.25-1.6 mg/l. No sulphide minerals exist in this Formation, however, the Formation is a marine shale with abundant organic material. Arsenic is believed to occur due to the oxidation of pyrite.
- Kalahari Group: One borehole located north of Sishen contains 0.5 mg/l of arsenic. The arsenic is believed to be related to the underlying Dwyka Group, which contains black shales.
- Adelaide Subgroup: Nine boreholes in the southwestern Karoo basin in the vicinity of Beaufort West contain arsenic concentrations between 0.13-0.3 mg/l. Arsenic is associated with roll front uranium deposits.
- Quaternary deposits: Four boreholes in the sands of the Cape Flats contain 0.11-0.14 mg/l of arsenic. The source of arsenic is unknown, but it may be related to the release of sorbed arsenic from the dissolution of arsenic-bearing hydrous oxides due to changes in Eh-pH.
- Volksrust Formation: 3 boreholes north of Calvinia contain between 0.14-0.2 mg/l of arsenic. The arsenic is believed to be associated with carbonaceous black shale.

CONCLUSIONS AND RECOMMENDATIONS

The study found that little documentation on the geological occurrence of arsenic and selenium exists for South Africa, however, the wealth of literature on economic mineralisation permits a regional prediction of the possibility of occurrence of arsenic and selenium bearing minerals. This information has been used to derive maps of predicted arsenic and selenium geological occurrence. By comparison, uranium occurrence in South African geology is well documented, although its occurrence in groundwater has only been documented in limited case studies.

Arsenic and selenium, where present in water, may pose a major risk since they are soluble in water under a range of naturally occurring Eh and pH conditions. Water is a major pathway of their mobilisation. They accumulate in biological tissue and when ingested by livestock are converted to forms passed on through other pathways.

An understanding of the extent of mobilisation of arsenic, uranium and selenium into groundwater occurrence is problematical for the following reasons:

- The occurrence of arsenic in groundwater is unknown in many geological units suspected to contain arsenic, since many geological units contain no monitoring boreholes, have never been sampled for arsenic, or contain samples taken from localities not subjected to localised sulphide mineralisaton.

- Little or no data exists to verify the extent of selenium and uranium in groundwater on a national scale since the National Monitoring Network (ZQM) does not monitor these parameters

- Boreholes of the ZQM are not necessarily sited to monitor trace constituents

- The lack of Eh data and the poor quality of most pH data prevents an identification of regions where redox and pH conditions are suitable for mobilisation of trace constituents.

- Their mobilisation is dependent on Eh and pH conditions, which may vary over time, especially in surroundings experiencing water level fluctuations due to pumping, consequently trace constituent concentrations may vary in time.

- The potential difference in trace constituent concentration over time in boreholes after drilling and its dependence on pumping regimens, suggests long term monitoring is required

Field studies in 12 localities in 4 Districts identified as being potential arsenic and selenium bearing due to sulphide mineralisation found that arsenic and selenium incidence is high when sampled at point of use. However, 5 samples taken from purged boreholes in these localities found that arsenic is not necessarily present in the dissolved phase in groundwater above WHO guideline concentrations. Nationwide, 200 boreholes of 1514 boreholes sampled nationally for arsenic have been found to contain arsenic concentrations above WHO standards.

Due to the lack of national scale long term monitoring of trace constituents in groundwater, it has not been possible to verify whether trace constituents are widespread in the dissolved phase in all the identified target zones. As an alternative, it is recommended that livestock, blood chemistry, and other health related data be used to provide clinical biochemistry information for the purpose of validating predicted high-risk areas and communities.

A generic level risk assessment (using fixed tabulated guideline values) is recommended as the first step in determining baseline hazardous exposures for various trace constituents in the geochemical environment that may contribute to adverse effects on health, productivity, and product quality. Any potential hazards

identified would then require further site-specific investigation regarding the water chemistry, soil composition, animal and human health.

In high risk areas, a water quality monitoring programme is essential in order to assess dose and intake levels from water borne pathways. Monitoring of pumping boreholes in geological units suspected of containing arsenic, uranium and/or selenium should therefore be initiated.

The use of geochemical speciation models may also play a role in providing further information on the dissolution and mobilisation of trace constituents. The use of a predictive model in areas where naturally-occurring and industry-related hazardous constituents are known or suspected to occur a vital component to understanding expected concentration trends and to:

- Prevent adverse effects on human and animal users of groundwater,
- Improve the sustainability of animal production in communal systems,
- Provide meaningful and scientifically founded risk-management strategies.

The study has identified regions where naturally occurring As, Se and U are present, hence has identified regions where monitoring can be focused in future.

It is recommended that:

- Monitoring of pumping boreholes in geological units suspected of containing arsenic, uranium and/or selenium as well as other trace constituents should be initiated
- A comprehensive analysis of the full spectrum of trace constituents be initiated
- Clinical data from health and agricultural sources, such as blood chemistry of livestock and other toxicity tests, be used to supplement geological data on the occurrence and mobility of trace constituents and identify problem areas
- Sampling be undertaken both at source (borehole) and point of use of water (tap) to identify mobilisation and transport pathways, as well as risk of exposure.
- A follow up study be undertaken to verify the occurrence of trace constituents in areas identified as being at risk, and to clarify policy issues as a basis to safeguard people and livestock against harmful constituents ingested through drinking water.

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Mapping of Naturally Occurring Hazardous Trace Constituents in Groundwater

The Steering Committee responsible for this project, consisted of the following persons:

Mr. K. Pietersen	Water Research Commission (Chairperson)
Dr IM Msibi	Water Research Commission
Mr. E. van Wyk	Department of Water Affairs and Forestry
Prof. Okujeni	University of the Western Cape
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1. INTRODUCTION

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Historically, as new occurrences of high arsenic levels have been documented, treatment facilities have been provided and the problem has receded from the public eye. This approach has been reactive rather than proactive, with treatment being implemented only after documented evidence of impacts on human health. Only in the USA has a proactive approach been implemented where the mapping of arsenic occurrence is being mapped on a county scale (Welsh et al., 2000). This mapping programme has been based on an extensive sampling programme to map arsenic occurrence at a county level. It has been reported that about 10% of the 30 000 arsenic analyses exceed 10 μg/l. Most of these occurrences lie in the more arid western regions of the country. There have been few other systematic hydrogeological investigations of arsenic occurrence in other parts of the world.

The fact that trace constituents are relatively common in South African rocks suggests their distribution and mobilisation should be of concern. The affinity of arsenic, selenium and other non-metals with gold, copper, nickel, zinc, lead, cobalt, silver and

other ores suggests that trace constituents can be widespread in South Africa. Arsenic and selenium, unlike most other toxic metals and metalloids, are fairly easily dissolved through a range of pH and Eh conditions, which may lead to significant dissolution where high concentrations are present in rock. This has prompted an assessment of the distribution of these constituents in the environment and the factors that control their mobility.

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Naturally occurring selenium is another trace element of concern in the South African geological environment, however, little is known about its occurrence.

Arsenic (As), uranium (U) and selenium (Se) can all be classified as heavy metalloid oxyanion forming elements, together with silver, tin, molybdenum, vanadium and chromium. Although not necessarily the most toxic, As, U and Se are more mobile under a wider range of naturally occurring groundwater conditions; hence they pose a potentially more widespread problem than other trace constituents.

Until recently, As, U and Se were not on the list of constituents in drinking water routinely analysed for, so little is known about their distribution, both in South Africa and internationally. Consequently, situations where local and international water quality guidelines are exceeded were identified unexpectedly only after serious impacts on human or animal health were recognised. This situation has occurred in West Bengal and Bangladesh, where tens of millions of people where exposed to high levels of arsenic, and thousands have already been diagnosed with severe poisoning symptoms.

Several such incidents have also been identified in South Africa: in the Northern Cape Province and Limpopo Province arsenic concentrations of over 1000 ug/l have been recorded; a statistically significant correlation between groundwater chemistry and the high prevalence of haematological abnormalities (related to leukaemia) was reported for an area in the Northern Cape Province; epidemiological studies done on animals consuming poor quality water (e.g. with high arsenic concentrations) in rural areas have shown adverse impacts e.g. skin lesions (Meyer, pers. com.). Despite this, little information on the regional occurrence of these constituents is available. Consequently, the link between environmental geochemistry and epidemiological problems needs to be established on a regional basis.

Knowledge of the presence and distribution of groundwater potentially contaminated with natural sources of these constituents would be of great value, as it would permit water planners and water service providers to identify regions where water supplies should be screened for these constituents regularly. The major factors that need to be considered to provide guidance to water service authorities undertaking a rapid assessment of water supplies for trace constituents are:

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To meet this goal the following research objectives were formulated for the project:

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These objectives were met by:

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Although documentation of the extent of occurrence of these trace constituents in South Africa may be perceived as alarmist, it is important to note that occurrence in the host rock does not necessarily equate to mobilisation in groundwater. In many cases host minerals are not exposed to hydrochemical conditions required for mobilisation and transport to occur. Alternatively, the lack or presence of other ions may result in interference, causing trace constituents to be sorbed or precipitated, or the lack of specific ions may prevent soluble complexes from forming. Therefore local conditions of trace constituent occurrence in groundwater in concentrations high enough to be considered hazardous to health following long term exposure should be viewed as the exception rather than the rule. Consequently, an understanding of geochemical processes and conditions is important to understanding whether the presence of trace constituents in the host rock may lead to a risk of their presence at undesirable levels in groundwater.

In addition, the identification of a geological Formation or Complex lithology as potentially containing arsenic, uranium or selenium does not necessarily imply the entire Formation contains these minerals. In many cases mineralisation is patchy or erratic hence occurrence is localised. However, at the scale of the national maps, the entire Formation needs to be identified as being potentially As, U or Se bearing since not all localities can be identified.

The report has been structured so that minerals containing arsenic, uranium and selenium are described in Chapter 2, as well the hydrochemical conditions required for their mobilisation. The occurrence and probable occurrence of these constituents in South Africa is discussed in Chapter 3. Chapter 4 presents the methodology by which the documented occurrences were translated into national scale maps.

2. LITERATURE SURVEY

2.1 Health Hazards

Health hazards from trace constituents are both dose and exposure related. In addition, risk is also affected by ingestion through pathways other than water, and by interaction between constituents.

Although types of effects are usually defined for a single constituent cause and effect relationship, the outcome of exposure to multiple constituents is usually poorly described. This is relevant for interactions between As and Se, and F and Se. For example, does Se enhancing bile excretion of As (Hirumnuma, 1999) protect against As accumulation, and will this result in an induced a Se-deficiency over long-term exposure?" Does concurrent exposure to F and Se potentiate the adverse effects of dental fluorosis? These difficulties in predicting the outcome of events are further complicated in situations where long-term exposure to excessive concentrations of one constituent induces a secondary deficiency of another constituent, for example, excessive selenium exposure may induce a copper deficiency in cattle.

In many case studies a major obstacle to conducting a differential diagnosis of a disorder or disease is the lack of appropriate clinical biochemistry information and reference values, specifically for sub-chronic and chronic conditions with multiple hazard exposure. The ability to identify areas where excessive exposure may result in either primary excess, or an induced secondary deficiency, will aid management actions to address the causative nature, as opposed to treating symptomatically. Knowledge of geochemical anomalies thus forms a valuable tool in observational epidemiology.

Variations in observed concentrations are of particular importance in terms of animal and human health when occurring simultaneously with times of increased water demand, such as lactation and high environmental temperatures, and the value of a water quality monitoring programme linked to water quality management strategies for reducing risk, cannot be over emphasised.

2.1.1 Health Hazards from Arsenic

Arsenic is a common element generally present at low concentrations in water, soil and rock. Although an essential nutrient at low concentrations, ingestion of water containing physiologically significant levels of arsenic has affected the health of millions worldwide. Drinking water containing high arsenic levels generally originates from groundwater, where there is a link between its occurrence and the aquifer geology.

Arsenic has been associated with skin damage and problems (Bowen's disease, hyperpigmentation, depigmentation, keratosis, skin cancer), circulatory system problems (peripheral vascular disorders) and an increased risk of internal cancer. There is a link between cardiovascular (Blackfoot disease, Raynaud's syndrome), respiratory and neurological disease and the ingestion of and exposure to arsenic (Gorby, 1994). Arsenic is a documented (Class A) human carcinogen that is toxic when ingested or inhaled and is classified as one of the most prominent environmental

sources of cancer mortality in the world (Welch et al., 2000). Health hazards from inorganic arsenic (typically the form of arsenic in water) *exceed* those from organic arsenic. Cancerous lesions are associated with drinking water having concentrations of arsenic > 0.1 mg/l. Arsenic concentrations of < 0.1mg/l in drinking water is associated with increased rates of skin cancer, heart disease, infant mortality and birth defects. Concentrations of 9 - 10 mg/l in drinking water have resulted in severe gastrointestinal disorders, impairment of bone marrow function, and neurological abnormalities (Korte & Fernando, 1991).

Single, once-off exposure to a high concentration can have serious effects (DWA&F, 1996). Both chronic and acute poisoning occurs, with chronic poisoning characterised by skin lesions, of which some are carcinogenic, and acute poisoning characterised by peripheral nervous system damage, upper and lower respiratory, gastrointestinal and cardiovascular failure, and may result in death.

Arsenic poisoning in human beings is dose and exposure related and the health effects are delayed. In extreme cases of chronic poisoning, progressive signs include loss of appetite, fainting, nausea and vomiting, dry throat, shooting pains, diarrhoea, nervous weakness, tingling of hands and feet, jaundice and erythema of the skin. Long-term steady exposure results in dry falling hair, brittle loose nails, skin rashes, darkening of the skin, exfoliation and hyperkeratosis on the palms and soles (Chihota, 1996). Skin lesions usually appear as symptoms after a 5-year minimum exposure period. Various sources of drinking water often contain differing concentrations and forms of arsenic and as a result the prediction of health effects cannot easily be achieved. It is thought that malnutrition and Hepatitis B can accentuate the effects of arsenic poisoning. Studies suggest that arsenic disrupts the activity of glucocorticoids, which help to regulate blood sugar and suppress tumours, it is also suggested that arsenic promotes the growth of tumours triggered by other carcinogens (Alpert, 2001).

Wang and Huang, (1994) claimed that no morbidity cases were found where potable water arsenic concentrations were less than 0.1 mg/l but morbidity increased exponentially as aqueous arsenic increased. Mild arsenic poisoning was observed between 0.1 mg/l and 0.2 mg/l (Smedley *et al*., 1995).

Urine is a good indicator of environmental arsenic exposure, as arsenic tends not to accumulate in the body. Care must be taken when sampling urine as recent seafood consumption may raise organic arsenic levels (arsenobetaine – low toxicity), and for this reason both organic and inorganic arsenic should be analysed for in urine. If the aim of sampling urine is to check exposure to arsenic groundwater, care must be taken not to choose individuals who may have been exposed to airborne arsenic from smelters or from some other arsenic source.

In parts of Central Africa arsenic rich groundwater associated with volcanic activity has lead to the development of Black Foot disease, which is associated with lethargy and blackening of the skin on hands, face and feet. In Bangladesh arsenic groundwater consumption has led to an epidemic affecting hundreds of thousands of people showing symptoms in the form of skin lesions. Many cases of chronic and acute endemic arsenic poisoning related to potable water have been documented around the world. Most notable cases have occurred in Taiwan, (Chen *et al*., 1994), in

Argentina (Astolfi, 1971), Chile (Zaldivar, 1974), China (Wang and Huang, 1994) and Mexico (Cebrian *et al*., 1994).

The toxicity of naturally occurring arsenic increases from the least toxic organic forms to arsenate forms (As +5) to the more toxic arsenite forms (+3) and methylated organic arsenic forms (As 3+) and to the most toxic arsine form (As 3+, As 3-). The arsines are compounds of hydrogen and arsenic (Planer-Friedrich, 2001) that form only in reducing environments. Their boiling point is also low hence they are extremely volatile. The arsenite species is the most toxic form of soluble inorganic arsenic and is known to be up to 60 times more toxic then arsenate due to its reactivity with and inhibition of sulphhydryl bearing enzymes in human metabolism and several 100 times as toxic as methylated arsenic. (Squibb & Fowler, 1983). However, As +5 appears to be dominant in natural waters. However, Korte (1991) suggests that this may be due to poor preservation resulting in the oxidation of As+3 to As+5 prior to analyses; hence historical speciation data must be viewed with caution.

The most toxic form is arsine gas, followed by inorganic trivalent compounds, organic trivalent compounds, inorganic pentavalent compounds, organic pentavalent compounds and elemental arsenic (Planer-Friedrich, 2001).

Arsines > MMAA > DMAA > As^{3+} > As^{5+} > Organic As

Toxicity

The organic forms of monomethylarsonous acid (MMAA) and dimethylarsinous acid (DMAA) are key intermediates in the biotransformation pathway by which As +5 is reduced to As+3 then to organic arsenic.

Each individual arsenic form has an individual toxicity and environmental pathway, and each form has several Eh and pH dependant compounds. The most toxic forms of arsenic that humans would typically be exposed to are found in groundwater. Arsenic 5+ is most mobile under oxidising conditions, whereas As +3 is mobile is also mobile under the mildly reducing conditions frequently found in groundwater.

2.1.2 Health Hazards from Uranium

Uranium has no known metabolic function in animals and is currently regarded as non-essential (Berlin & Rudell, 1986). Uranium ingested from drinking water is accumulated primarily in the bones and kidneys; this can cause kidney disease (nephritis) and generally increases the lifetime risk of cancer. Uranium is readily oxidised to the highly soluble uranyl ion, which is easily mobilised in surface and groundwaters. Uranyl ions replace calcium in the hydroxyapatite complex of bone crystals (Moss, 1985). Once equilibrium is attained in the skeleton, uranium is excreted in the urine and faeces. Very little uranium is found in the liver (WHO, 1998).

2.1.3 Health Hazards from Selenium

Although an essential element, the range between requirement and toxicity is narrow, and according to Underwood & Suttle (1999) Se is the most hazardous trace element

supplemented in livestock rations. Chronic exposure in humans via the water and feed to levels in excess of requirements can cause discoloration of skin, pathological deformation of nails, alopecia, excessive tooth decay, loss of cognitive abilities, and listlessness. Adverse chronic effects that may be noted in livestock include: induced copper deficiency; disruption of thyroid function; teratogenic effects (reported in pigs, sheep and cattle); cardiac atrophy; erosions of joints of long bones; hepatic cirrhosis, anemia; alopecia (specifically tail region); epidermal hoof lesions.

This is of relevance in communities in the Limpopo and North-Western Provinces as both have a high incidence of fluorosis, making it difficult to distinguish between Se and F as to the causative or relative contribution by each constituent in the manifestation of the dental lesions observed. The occurrence of teratogenic effects due to Se excess has been reported in pigs, sheep and cattle, but not yet quantified in humans (ATSDR, 1989; USEPA, 1986). Drinking water Se contributions to the total Se intake of people is especially true in the rural context given the known positive correlation between water Se levels and Se levels in livestock milk, and maternal breast milk.

If selenium intake occurs only from water, then the concentration at which chronic selenosis may occur in beef cattle is 0.7 mg/L (Underwood & Suttle, 1999). In humans, levels in drinking water above 0.05 mg/l, have been associated with hair or fingernail loss or damage, numbness in fingers or toes and with circulatory problems. Other symptoms include gastrointestinal disturbances, discoloration of the skin, decay of the teeth, dermatitis, neurological disturbances and skin lesions. It is know to potentially cause damage to the peripheral nervous system and to cause fatigue and irritability. Acute oral doses of selenite and other selenium compounds cause symptoms such as nausea, diarrhoea, abdominal pains, chills, tremor, numbness in limbs, irregular menstrual bleeding and marked hair loss.

Although in itself a valuable source of selenium, drinking water may contribute to excessive selenium exposure when dietary levels are high (selenium & vitamin E supplements). Selenium in the natural aquatic environment is usually of the selenite (4+) or selenate (6+) forms, depending on oxidation and reducing conditions. Usually, under oxidising or alkaline conditions the more soluble selenate form predominates, as opposed to the more toxic selenite. Inorganic selenium is regarded as being a **pro-oxidant**, whereas organic forms are noted for their anti-oxidant properties.

Recommended daily intakes of selenium have been set at 0.0017 mg/kg of body weight in infants and 0.0009 mg/kg of body weight in adults (WHO, 1996). The recommended daily allowance (RDA) in the United States for dietary considerations is set at 0.055 mg/day for women and 0.070 mg/day for men. A concentration of 0.001 mg/l in drinking water corresponds to an intake of 0.002 mg of selenium per day (National Research Council, 1989). There is no evidence to suggest that selenium (apart from selenium sulphide) has the potential to cause cancer from lifetime exposures in drinking water.

2.2 Concentration Guidelines

Guidelines have been set based on risk to health based on long term exposure to a fixed concentration. However, dose is affected not only by concentration but also by ingestion (volume) and exposure to other pathways or intakes. Where intake is higher than the assumed rate, and where exposure to the source is regular and long term, adverse effects occur at lower concentrations. For example, livestock are commonly exposed to a regular water source and often graze on vegetation containing additional concentrations accumulated from the soil, hence adverse effects may appear sooner than in humans whose dosage is restricted to water sources.

Another shortcoming of all guidelines is that they do not account for the form of a constituent, which is Eh-pH dependent. For example, the trivalent inorganic form of arsenic is more toxic than the more common pentavalent form. In addition, they do not account for exposure. Rural communities relying on a single source for long periods of time are therefore more at risk than others ingesting higher concentrations during limited periods due to bioaccumulation in tissue.

2.2.1 Arsenic

Following the accumulation of global evidence of the chronic health effects of arsenic in drinking water, in 1993 the World Health Organisation (WHO) reduced the standard from 50 μg/l to 10 μg/l. This can be attributed to increasing evidence of carcinogenesis resulting from long term exposure. The Japanese, European Community and US-EPA have followed suite. The South African target water quality guideline is 10 μg/l and up to 200 μg/l is considered a tolerable concentration.

2.2.2 Uranium

The chemical guideline value for the toxicity of uranium was derived using a total daily intake approach and yields a guideline value of 0.03 mg/l, which assumes a 60 kg adult consumes 2 litres of drinking water per day (WHO, 1998). The US-EPA limit is 0.02 mg/l. The South African Water Quality Guidelines do not have a specific guideline for Uranium and a tentative guideline based on gross alpha and beta emmitance is proposed.

2.2.3 Selenium

The European Union proposal for selenium concentration is 0.01 mg/l in drinking waters. The World Health Organization health guideline is also 0.01 mg/l (WHO, 1998). The US EPA limit is set at 0.05 mg/l. The South African Target Water Quality Guideline is 20 μg/l, with the maximum limit at 50 μg/l for long-term use.

2.3 Geological Sources of Arsenic, Uranium and Selenium

2.3.1 Arsenic Bearing Minerals

Arsenic is a semi-metal (metalloid) that occurs as a major constituent in more than 200 minerals, including elemental arsenic (4 modifications), 27 arsenides (associated with Ni, Fe, Pt, Co), 13 sulphides and 65 sulfosalts (associated with Ag, Co, Cu, Fe, Ni, Pb, Tl), 2 oxides (associated with Cu, Pb), 116 arsenates (associated with Al, Ba, Ca, Co, Cu, Fe, Mg, Na, Ni, Pb, Zn), 7 silicates, and 11 arsenites (associated with Ca, Mn, Pb, Zn) (Baur and Onishi, 1978). According to Thornton (1996), 60% of arsenic-bearing minerals consist of arsenates, 20% are sulphides and sulfosalts, and 20% are arsenides, arsenites, oxides, silicates and native arsenic.

Most arsenic minerals are ore minerals and their greatest concentration occurs in sulphide rich mineralised areas in close association with the transition metals: Cd, Pb, Ag, Au, Sb, P, W, and Mo. The most abundant form is the sulphide arsenopyrite FeAsS and its related species arsenian Fe $(S,As)_2$, which is common in mineral veins. Other common sulphur minerals of arsenic include realgar, orpiment, marrite, liveingite, tennantite, dufresnoysite, lorandite, vrabite, and wallisite. Native arsenic, which is also abundant in hydrothermal veins Many other arsenic sulphides are associated with mineral veins containing hydrothermal nickel and copper ores.

As the chemistry of arsenic follows closely that of sulphur, arsenic is also present in varying concentrations in common rock forming sulphide minerals, of which pyrite is the most abundant. Arsenic concentrations in sulphides may range as follows: Galena (5-10000ppm); Sphalerite (5-17 000ppm); Chalcopyrite (80-5000ppm); Pyrite (100-77 000 ppm); and Marcasite (20-26 000 ppm) (Baur and Onishi, 1978).

Arsenic is often present in low temperature sedimentary environments formed under reducing conditions, where such minerals are common. Such conditions are found in organic rich sedimentary environments, such as black shales, and coal bearing beds. Minerals containing arsenic in this form are not stable in aerobic systems and oxidise, with the subsequent release of sulphate, acidity and associated trace constituents. This mechanism is one of the causes of the release of arsenic into groundwater during oxidation caused by pumping, and the presence of arsenic related problems around coalmines.

Quartz, feldspar, plagioclase, biotite, amphibole, pyroxene, olivine, magnetite, ilmenite, pyrrhotite, calcite and apatite may also contain arsenic, however, these minerals are not important contributors of arsenic to whole rock geochemistry and its concentration in these minerals vary collectively from 0.089ppm to 6ppm (Baur & Onishi, 1978), except for apatite which can have concentrations of up to 1000 ppm.

High arsenic concentrations are also present in many oxide minerals and hydrous metal oxides, such as iron oxides, magnetite, and aluminium and manganese oxides, either as part of the mineral structure or as sorbed species.

2.3.2 Arsenic in Rocks

Arsenic occurs in most igneous rocks, such as peridotites, dunite, serpentinite, basalt, gabbro, andesite, syenites, rhyolites and granophyric rocks. The arsenic content of these rocks is negligible, cumulatively ranging from 0.1 - 15.6ppm (Baur & Onishi, 1978).

In most sedimentary rocks, arsenic concentrations are also negligible, ranging from 0.9-42 ppm. There are a few however, in which arsenic does show elevated concentrations (Thornton, 1996). These include argillaceous deposits containing a large proportion of sulphide minerals formed under reducing environments. Examples would include copper shales (100 - 900 ppm), reduced marine sediments such as marine black carbonaceous shales (3 - 490 ppm), some phosphorites (0.4 - 188 ppm), and organic carbon- rich deposits. Arsenic is known to be adsorbed to clay mineral surfaces (Hinkle & Polette, 1999; Lin and Puls, 1999).

Metamorphic rocks generally reflect the igneous or sedimentary precursor composition (Thornton, 1996; Baur & Onishi, 1978). Most contain between 5 - 10 ppm of arsenic. Elevated arsenic occurrences can therefore largely be narrowed down to igneous rocks associated with ore-forming processes and sulphide mineralisation, reduced marine sediments, and sedimentary rocks where arsenic co-precipitated with iron hydroxides and sulphides. Arsenic is thus most enriched in rocks associated with various mineral deposits (Baur & Onishi, 1978).

2.3.3 Arsenic in Soils

Arsenic concentration in soil is usually elevated relative to its occurrence in rocks, with the lowest concentration in soils derived from granites, and the highest in soils developed on sulphide ore deposits (Thornton, 1996). Higher levels of arsenic are also associated with alluvial soil, soil with a high organic content, and groundwater affected by geothermal activity. Arsenic is liberated from rocks via the weathering process, during which it may be mobilised as salts of arsenic- and arsenous acid (Thornton, 1996). Concentration and liberation in soils may be influenced by the adsorption of arsenic onto secondary Fe-, Al-, and Mn oxides, as well as clay minerals and organic matter (Hinkle & Polette, 1999; Lin & Puls, 1999). The roasting of coal and sulphide ore releases arsenic trioxide into the atmosphere, which reacts with alkaline earth oxides to form arsenates, which are subsequently deposited in the soil. Arsenates of Fe, and Al are the dominant phases in acidic soils, and are less soluble than the Ca variety present in calcareous soil. Hinkle and Polette (1999) note that the fact that iron oxides dissolve under reducing conditions, whilst sulphide minerals precipitate under such conditions, which may facilitate arsenic transfer between the two solid phases.

2.3.4 Uranium Bearing Minerals

The mode of occurrence of uranium in rock forming minerals is uncertain, although possibilities include isomorphous substitution, concentration in lattice defects, adsorption along grain boundaries, and inclusion as microcrystals (Pertlik et al, 1978). Concentrations range from 0.05ppm to 8.1ppm for olivine, pyroxene, hornblende,

muscovite, biotite, feldspar and quartz, collectively. Accessory minerals such as allanite, apatite, epidote and garnet range from 30ppm - 1000ppm, collectively, with most averaging above 50ppm. Monazite has a concentration range of 500 - 3000 ppm, whilst zircon has a range of 100 - 6000 ppm (Pertlik et al, 1978). Titanite has a range of 10-700ppm, and Xenotime a range of 300 - 40,000 ppm.

Uranium occurs in a variety of minerals but is concentrated in a few species of minor abundance. Uranium occurs in a number of oxides, carbonates, sulphates, phosphate-arsenates, vanadates, silicates, niobates-tantalates-titanates, and molybdates (Dahlkamp, 1991; Pertlik et al, 1978). These minerals are usually supergene minerals, and consist of uranium plus another cation. The most common and important uranium-bearing mineral is the oxide uraninite, whose compositional formula varies between UO_2 and U_3O_8. Other important ore minerals are coffinite, brannerite and carnotite.

The variation in compositional formula is the result of oxidation of the former to the latter. It commonly occurs in hydrothermal veins and disseminated deposits in sedimentary rocks. It is oxidised to the highly soluble uranyl ion UO_2^{2+}, which is easily mobilised in water.

2.3.5 Uranium in Rocks

Uranium is wide spread in nature, occurring in granites and mineral deposits. The uranium content in igneous rocks vary greatly according to petrological subgroups, and therefore generalisation in discussing uranium concentration in igneous rocks is difficult. A generalisation can be made however, that uranium increase is proportional to increase in silica content. Hence uranium content is higher in felsic rocks such as rhyolites and granites, and is less abundant in ultramafic rocks.

Uranium concentration in ultramafic rocks is extremely low, ranging between 0.009 ppm-0.84 ppm for dunite and gabbro respectively (Pertlik et al, 1978). Basaltic rocks range between 0.10 ppm - 0.56 ppm, alkaline rocks between 0.04 ppm - 19.7 ppm, silicic extrusives 5 ppm, and granitoids between 2.2 ppm - 6.2 ppm.

In sedimentary rocks, uranium concentration ranges from 0.45 ppm - 3.21 ppm in sandstones, 2 ppm – 8 ppm in shales, 6ppm-1244ppm in black shales, 11.4 ppm in bauxites, 5 ppm in bentonites, 0.35ppm-2.34ppm in limestones, 0.03ppm – 2 ppm in dolomites, 50 ppm – 300 ppm in phosphate rocks, and 4.5 ppm - < 6000 ppm in coals and other organic deposits.

Metamorphic rocks display a broad range of uranium concentration, averaging between 2ppm-5ppm (Pertlik et al, 1978). Some of the highest concentrations have been observed in paragneiss (7 ppm), diatectite (11.2 ppm), and orthoclase metacrysts (45 ppm).

2.2.6 Uranium in Soils

The oxidation of uranium to the fairly soluble uranyl ion makes for easy mobilisation during surficial processes. In contrast, thorium is relatively insoluble, and is adsorbed

onto clay minerals and residual minerals, whilst uranium is distributed in ground waters (Pertlik et al, 1978). Not much information is available on the behaviour of uranium in the soil environment.

2.3.7 Selenium Bearing Minerals

Selenium is not related to rock-forming silicates (Fischer et al, 1978), and is most abundant in sulphide minerals, such as galena (commonly 0 – 15 ppm, but can be 50 – 1000 ppm); arsenopyrite (42 – 57 ppm); pyrrhotite (5 – 63 ppm); marcasite (0 – 11 ppm); chalcopyrite (commonly between 10 – 50 ppm, but can be as high as 2100 ppm); pyrite (commonly between 0 – 50 ppm, but can be as high as 300 ppm); sphalerite (commonly between 10 – 50 ppm, can be as high as 900 ppm). According to Edmunds and Smedley (1996), the affinity to sulphides is related to the strong affinity of selenium to organic material.

Selenium occurs in close relationship with sulphur as selinides (-2) with Cu, Pd, Ir, Rh, Li, Sr, Ba, Ag, Pb, Zn, Cd, Hg, Co, Ni, Fe and Bi, in sulphide minerals, hence it is associated with metal deposits. Selenites (Se +4) and selenates (+6) can also occur with oxygen and metals, however, such minerals are scarce.

Almost all known selenium minerals are selenides, occurring in small quantities. Most are found in low temperature hydrothermal deposits where sulphur is not present. Selenides therefore occur in very restricted areas. Where sulphides are present, selenium occurs in the lattice of common sulphides, such as pyrite, pyrrhotite, chalcopyrite, arsenopyrite, galena and sphalerite, hence the occurrence of selenium is strongly linked to that of sulphides. Selenium is most stable in elemental form in natural surface conditions.

2.3.8 Selenium in Rocks

Selenium concentration in igneous rocks is very low, ranging from 0.05-0.21ppm for the entire spectrum of igneous rocks. Selenium content in igneous rocks accompanies sulphide minerals. It is found in rocks of magmatic origin and hot hydrothermal conditions, where it enters pyrite, arsenopyrite and chalcopyrite minerals, or galena in lead-zinc deposits. Selenium is common in volcanic sulphides.

In sedimentary rocks, selenium is mainly found in clay-rich rocks (Fischer et al, 1978), with concentrations ranging from 0.2- 35ppm. Selenium is a common component of black shales, and may or may not be associated with molybdenum, where concentrations of up to 300 ppm can be encountered (Yudovich, 1984).

High concentrations are found in sedimentary rocks of Carboniferous to Tertiary age due to the extensive volcanic activity during this period. During massive volcanic exhaling, selenium was ejected as particles and as a gas, and was subsequently deposited in sediments and oceans where it was incorporated into sedimentary rocks.

Large concentrations of selenium are common in coal and uranium deposits, especially uranium roll front deposits.

There is no data available on the selenium content of metamorphic rocks, but all indications are that the concentration is probably determined by the precursor. Selenium is not mobilised under metamorphic conditions (Fischer et al, 1978).

2.3.9 Selenium in Soils

Selenium may be present as four species in soils, namely selenide, elemental selenium, selenite, and selenate (Sharmasarkar et al, 1998). Oxidation of materials in mine dumps is commonly the cause of formation of these species in soils. Sulphides and selenides are easily oxidized to selenites, which in turn are sorbed onto ferric hydroxide in the soil environment where it is precipitated (Edmunds and Smedley, 1996; Fischer et al, 1978). Selenium is generally far less mobile in the soil environment than uranium. Selenates are rare in soils due to the extremely high oxidation potential needed for their formation, and theoretically will only be found in extremely dry, alkaline conditions.

2.4 Occurrence in Groundwater

Most potentially hazardous trace constituents occur in solution as cations whose solubility increases as pH decreases. At the near neutral pH of most groundwater their mobility is severely limited by precipitation, co-precipitation as oxides, hydroxides, carbonates or phosphates, or by adsorption to hydrous metal oxides, clays or organic matter. However, oxyanion forming constituents such as As, U and Se become increasingly less sorbed as pH increases. As a result they can persist in solution at higher concentrations than other trace metal constituents as pH increases. Consequently, oxyanion forming As, U and Se can be common trace constituents in groundwater in comparison to other metals and metalloids. Relative to other oxyanion forming elements arsenic is the most problematic because of its mobility under a wide range of redox conditions. Selenium is mobile as selenate under oxidising conditions but is immobilised under reducing conditions due to sorption or reduction to its metal form.

2.4.1 Arsenic

Arsenic exists under oxidation states of 0, +3, -3, and +5 but in natural waters is most commonly found as inorganic oxyanions of trivalent arsenite (+3) or pentavalent arsenate (+5). Organic arsenic may form in surface waters due to biological activity but is rarely quantitatively important, except where significant industrial pollution occurs. Arsenic is unique amongst heavy metalloid oxyanions in its sensitivity to mobilisation at the range of pH found in groundwater (6.5-8.5), and its mobility under both oxidising and reducing conditions.

Arsenic forms no single cations but reacts with inorganic acids, depending on pH to form As+3 or +5 oxyanion compounds. Dissolved As+5 ($H_2AsO_4^-$ and $HAsO_4^{2-}$) compounds sorb readily onto Fe, Mn and Al oxides or hydroxides, as well as onto clay minerals and organic matter, hence As +5 occurs at low concentrations. This may not be the case in fractured rock environments, where access to these products of weathering is limited; hence As+5 can be mobile.

Dissolved As+3 occurs mainly as the neutral H_3AsO_3 compound and therefore undergoes no sorption or exchange processes (figure 2-1). Consequently, it is 4-10 times more mobile than As+5. The most common attenuation process for As+3 is precipitation as As_2S_3 under strong reducing conditions. Improvements in sample analysis in recent years have also demonstrated that As+3 is more prevalent than previously believed. The more toxic As +3 form only occurs over a narrow range of Eh, which is considered mildly reducing (0.25-0 V) under the normal range of pH (6-8.5) (Figure 2-2). Since these Eh conditions are widespread in groundwater, As+3 may be more mobile than As+5.

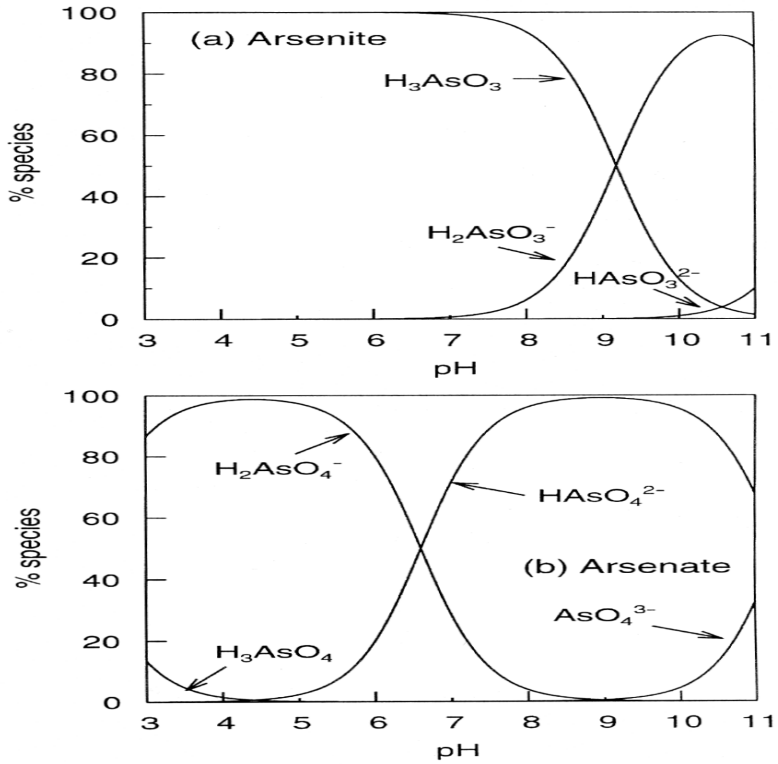

Figure 2-1 Occurrence of As+3 and As+5 with pH.

Organic As results from the transformation of inorganic arsenic by fungi or bacteria. It is much less abundant than inorganic arsenic.

Redox potential (Eh) is the most important factor controlling As speciation (Figure 2-2). Under oxidising conditions As+5 is found as $H_2AsO^-_4$ at low pH (<6.9) and as $HAsO_4^{2-}$ at higher pH (figure 2-3). Under mildly reducing conditions at a pH of less than 9.2 As+3 is found as H_3AsO_3. At near neutral pH the transition from As+3 to As+5 occurs at an Eh of approximately 0 mV. However, under acidic conditions of 5, H_3AsO_3 forms under oxic conditions of +200 mV. In groundwater the ratio of As+3 to As+5 can vary greatly as a result of variations in the abundance of redox-active solids that control the adsorption of As+5. Under stronger reducing conditions in the presence of sulphide, As+3 precipitates as realgar (AsS) or oripent (As_2S_3). At very low Eh values arsine AsH_3 (aqueous) can be formed.

Changes in redox conditions caused by pumping are an important in terms of changing the mobility and behaviour of many elements, including arsenic. The

initiation of a cycle of pumping causes water levels to drop, exposing arsenic bearing minerals to weathering by oxidation. Subsequent water level recovery mobilises weathered product ions and allows oxygen to enter the aquifer, further enhancing oxidation. This process results in the long term mobilisation of trace constituents.

The slow rate of many redox reactions such as the oxidation of pyrite implies that changes in arsenic concentrations resulting from water level fluctuation can take a long time to occur and are not immediately detectable. As a result, arsenic speciation does not necessarily occur as predicted under equilibrium conditions, hence mobile As+3 can persist under oxidising conditions. The slow rate of reaction also suggests that the presence of arsenic in solution may only be detected after a significant period of pumping and the problem is not readily apparent in new boreholes.

Background concentrations in groundwater in most countries are less than 10 µg/l (Smedley & Kinniburgh, 2002), however, ranges of up to 5000 µg/l have been reported under natural conditions. Most reported cases of high arsenic have been naturally occurring, however numerous industrially induced, albeit local occurrences, are reported.

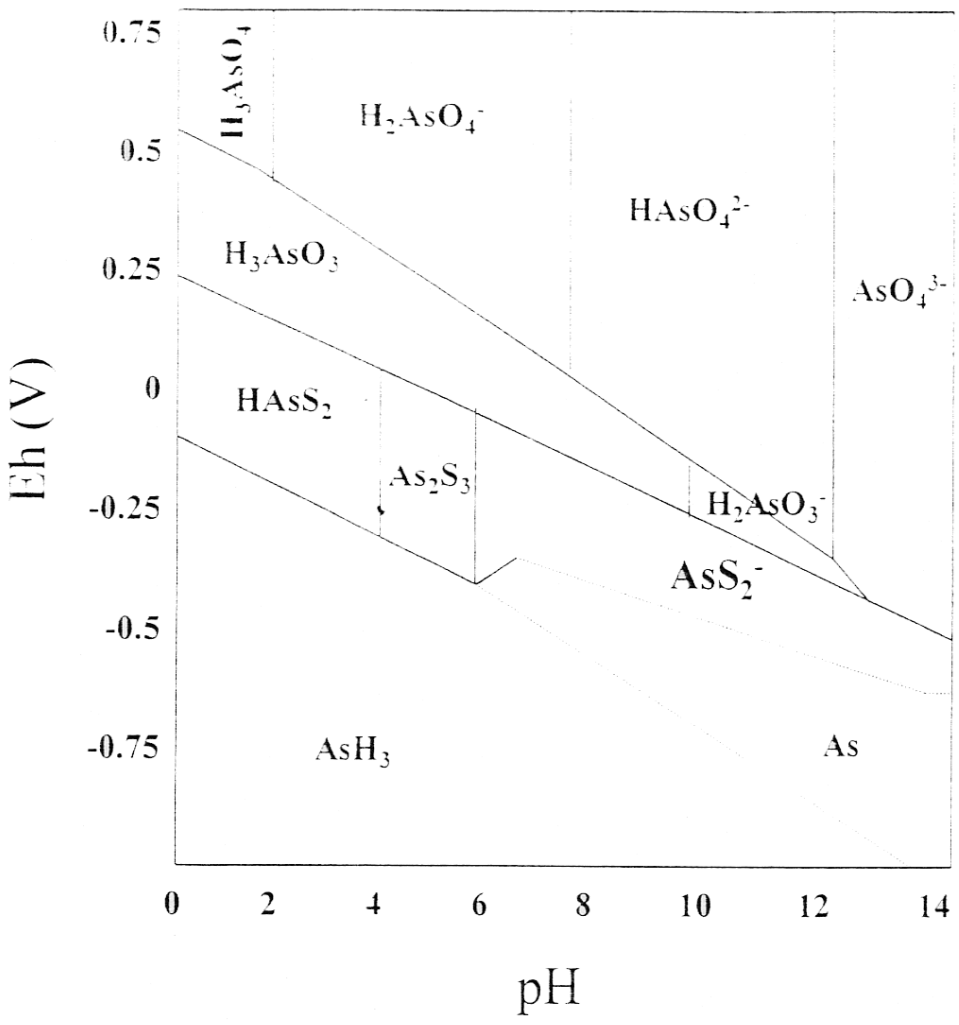

Figure 2-2 Phase Diagram of arsenic speciation

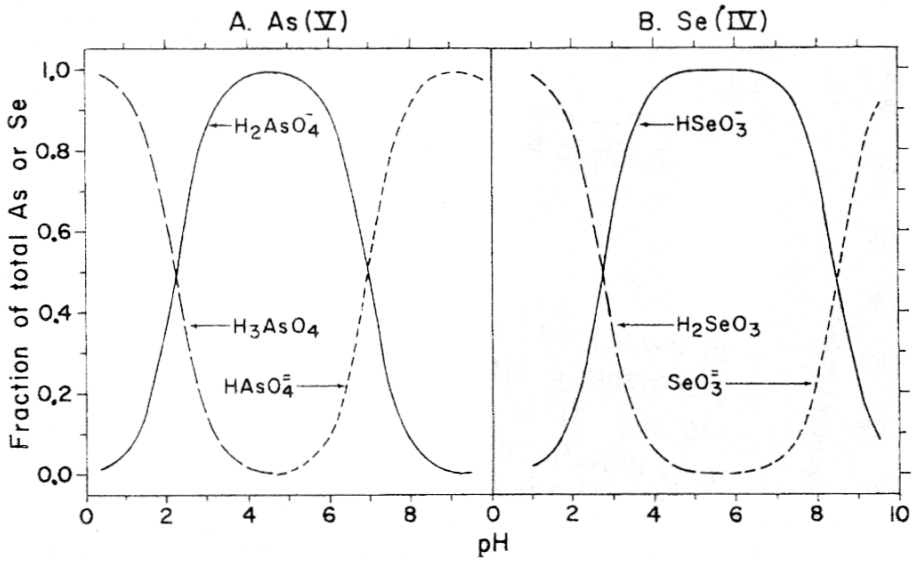

Figure 2-3 Occurrence of As+5 and Se+4 as a fraction of total As and Se.

In South Africa, the most common source of naturally occurring arsenic is in zones of sulphide ore mineralisation. However, arsenic can also be present in regions where no sulphide mineralisation occurs. Groundwater arsenic problems occur under both reducing and oxidising environments in aquifers containing As sorbed onto iron and manganese oxides, in clay rich aquitard lenses. Arsenic is also an important trace constituent of geothermal fluids, and can occur in aquifers where geothermal waters are present. These can occur under both under humid and semi-arid conditions. The following environments can be considered to be potentially arsenic bearing:

Reducing environments:	Recent alluvial and deltaic aquifers rich in organic matter and with a neutral pH
	Black shales
	Geothermal environments
Oxidising environments:	Volcanogenic sediments
	Alluvial basins
Sulphide mineralised environments:	Sulphide ore mineralisation

Alluvial and deltaic deposits with reducing environments created by the trapping and decay of large volumes of organic material are common sources of As +3. Other common natural sources include sedimentary rocks of marine origin containing carbonaceous material, weathered volcanic rocks, geothermal areas, and zones of hydrothermal ore mineralisation.

Most studies have focussed on arsenic contamination in reducing environments located in alluvial or deltaic systems (e.g. Bangladesh, Argentina). Very few studies have concentrated on As occurrence in groundwater in hard rock environments, which is most prevalent case in South Africa. These have focused primarily on As contamination related to mining activity. Examples include As contamination resulting from the oxidation of arsenopyrite due to tin mining in Thailand (Williams,

1997), the Ashanti region of Ghana where gold mining has exacerbated the oxidation of arsenopyrite, resulting in localised high As concentrations. In the United States, arsenic contamination has been associated with gold, lead, zinc and silver mining.

In Wisconsin, the oxidation of pyrite and marcasite present in a horizon of a sandstone aquifer has resulted from large-scale groundwater abstraction (Schreiber et al., 2000). An increasing number of elevated As concentrations have also been recorded in parts of the world with local sulphide mineralisation that has not been mined. These include British Columbia and Bavaria. This suggests that the extent of this problem could be wide spread in hard rock systems, although on a local scale.

2.4.2 Uranium

In uraniferous regions, groundwater can have uranium concentrations of 1-120 ppb (Langmuir, 1978). Lopatkina (1964) found that, where uranium is derived from weathered granites, dissolved uranium concentrations were related to the weight percent of uranium in rock by:

$$U\ (ppb) = 20 * U(wt\%) \times TDS\ (ppm)$$

However, local diversity exists due to:

- Uranium content in source rocks and its leachability
- The degree of hydraulic isolation of the water and dilution from fresher water
- The influence of evapotranspiration
- The pH and Eh of water
- The concentration of fluoride, sulphate, calcium, potassium and phosphate with which to form complexes
- The presence of sorptive material such as organic matter, Fe, Mn oxyhydroxides and clays

Uranium occurs naturally in +2, +3, +4, +5 and +6 valence states, but only the U +4 and U +6 forms are stable. In solution uranium forms a variety of compounds by hydrolysis, as well as range of carbonato species, depending on pH and Eh (figure 2-4). In pure water U +6 uranium may exist in the form uranyl (UO_2^{2+}) and U +4 uranium (U^{4+}) ions and their hydrates. In the presence of other salts (except in perchlorates solutions) the uranyl ions will form cation or anion complexes and so will the less known U^{4+} ion. U +4 is extremely insoluble, hence the U+6 forms are most commonly encountered in groundwater, where it occurs as UO_2^{2+}.

U +4 is soluble only at a pH of less than 1.5 in reduced environments. U +5 is stable in reduced groundwater below a pH of 8, where it can occur as UO_2^{+} and $U(OH)_5^{-}$.

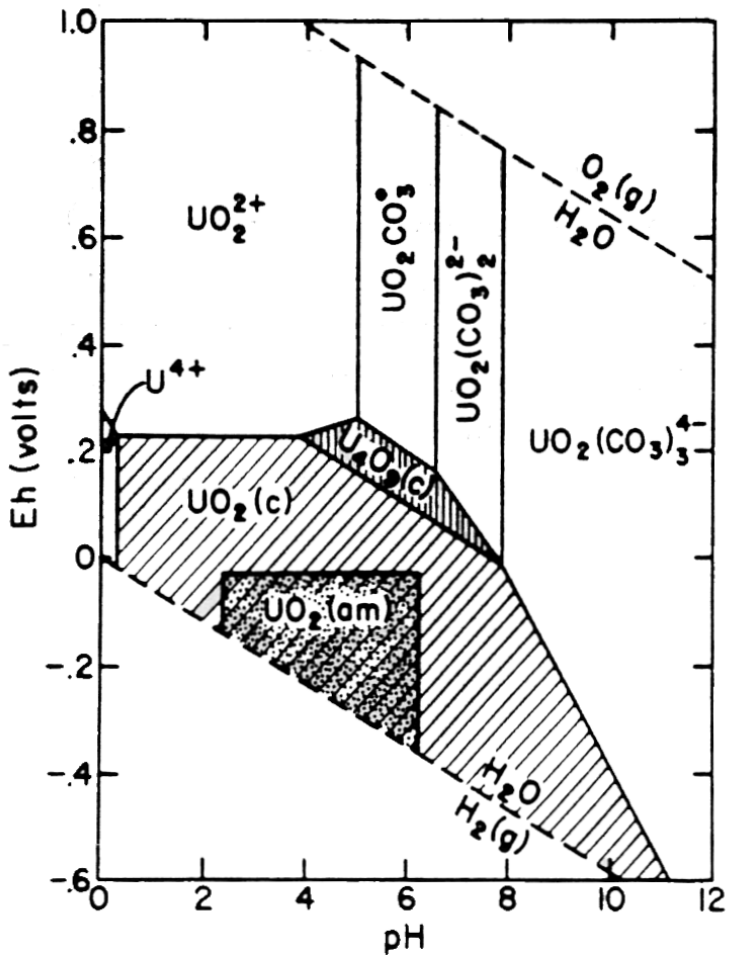

Figure 2-4 Phase diagram of uranium speciation in pure water.

The UO_2^{2+} species will occur only at low pH (<5). Under normal pH conditions >6, the U+6 hydroxyl form of $(UO_2)_3(OH)_5^-$ is the dominant form, or UO_2CO_3 and $UO2(CO3)_2$ in the presence of dissolved oxygen and CO_2. However, in typical groundwaters U +6 forms cation and anion complexes with fluoride (predominantly UF_2^+ at pH <3.5), phosphate ($UO_2(HPO_4)_2^{2-}$ at pH >4) and a variety of carbonate forms under acid, neutral and alkaline conditions respectively (figure 2-5). Fluoride complexes dominate to pH 4, phosphate complexes dominate to pH 7.5, and carbonates dominate from pH 7.5. Sulphate complexes (UO_2SO_4) may exist together with UO_2^{2+} up to a pH of 7.

Among the complex uranium ions the uranyl carbonate ions are most stable and will predominate not only in the bicarbonate but also in the neutral sulphate and chloride or weakly acidic or weakly alkaline groundwaters (from pH 5.8), which usually contain a certain amount of bicarbonate ion. In the common weakly acid, neutral and weakly alkaline groundwaters different uranium compositions occurs as predominantly uranyl di-carbonate ($UO_2(CO_3)_2(H_2O)_2^{2-}$) and tri-carbonate anions $UO_2(CO_3)_3^{4-}$.

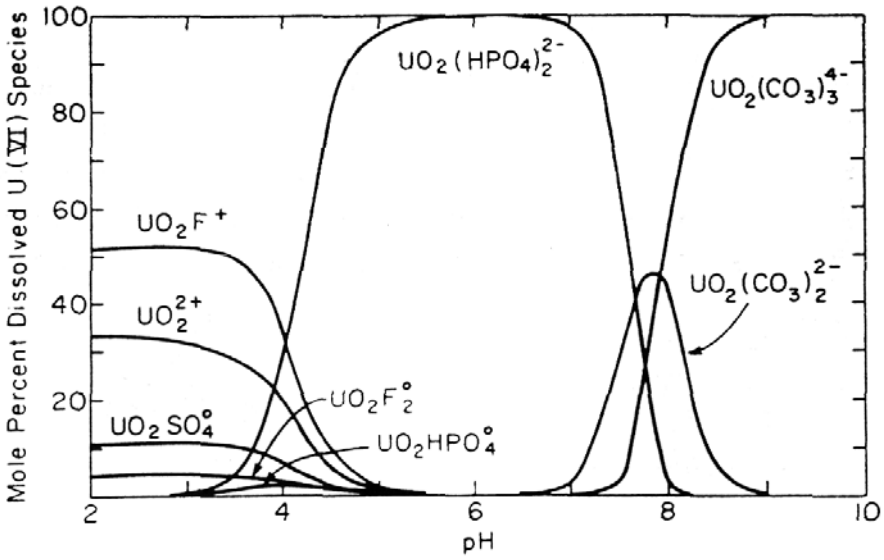

Figure 2-5 Uranium speciation with pH.

2.4.3 Selenium

Selenium is found in sulphide ores and in regions of volcanic activity. Selenium appears in oxidation states of –2, 0, +2, +4, and +6. The most important oxidation states in the environment are –2 (selenides, H_2Se and HSe^-), which are present under reducing conditions, 0, which is present under slightly oxic conditions, +4 (selenites, H_2SeO_3, $HseO_3^-$, SeO_3^{2-}) (figure 2-3), which are present under oxic conditions, and +6 (selenates, SeO_4^{2-}), present under strongly aerobic conditions (figure2-6). Selenides decompose in water. Selenium in its ground state is very insoluble, selenites are strongly sorbed onto iron hydroxides, and selenates are the most mobile.

Selenium can substitute sulphur in both organic and inorganic compounds. The large range of oxidation states allows it to participate extensively in donor and receptor reactions. However, during the weathering process Se and S follow very different pathways because sulphur is easily oxidised to soluble sulphates, whereas selenium needs strong oxidising conditions to form soluble selenates.

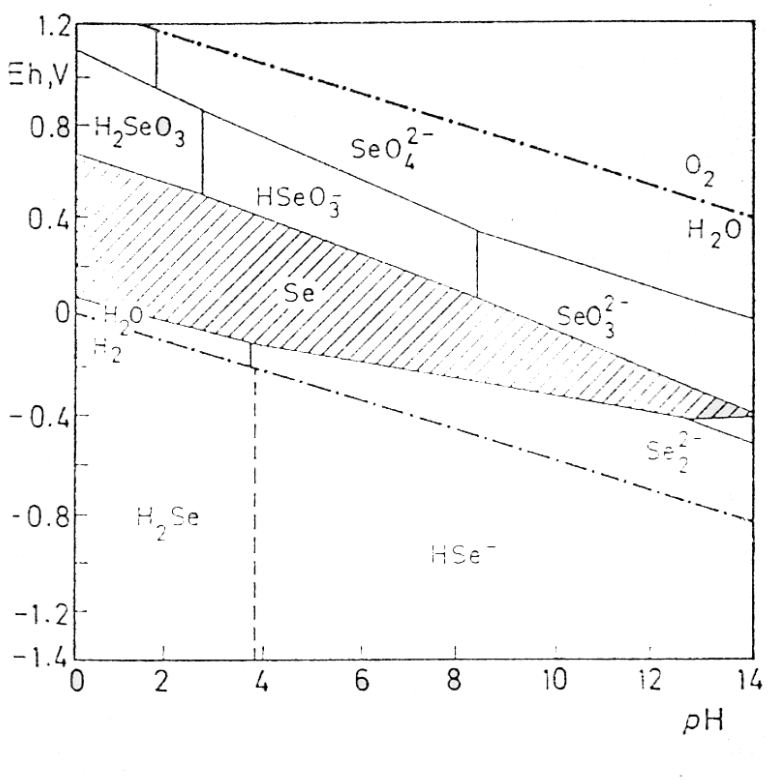

Figure 2-6 Phase diagram of selenium speciation

2.5 Mobilisation

Trace elements, once liberated to groundwater, are redistributed by complex geochemical processes such as water/solid interactions, precipitation, complexation and colloidal interaction. Many of these processes are reversible, hence concentrations can vary with changing geochemical environments. Hence it is important to understand not only where these elements are potentially introduced, but also the processes that control their mobility. Given this complexity, it is not possible to characterise groundwater by once off sampling, since geochemical conditions are not static. Deterministic models such as PHREEQC and MINTEQ can play a role in predicting the mobility and speciation of constituents under various geochemical scenarios.

This section outlines some of the basic processes and generalities controlling the mobility of arsenic, uranium and selenium.

2.5.1 Arsenic

Knowing the type of interactions involved between groundwater and the rock mass is important to determine how changes in water chemistry can affect arsenic concentrations. The major minerals binding arsenic are the minerals described in 2.3.1. Arsenic can also commonly be found sorbed onto metal oxides, particularly Fe,

Al and Mn oxides as surface complexes, depending on pH conditions. Clays also adsorb arsenic, which restricts its mobilisation. Under neutral conditions dissolved Fe+2 tends to precipitate as ferric hydroxide, with the resultant adsorption and co-precipitation of As+5. However, As+5 is soluble in fractured rock environments where Fe and Al colloidal particles are not present. Arsenic adsorption is also affected by the presence of competing ions, in particular phosphate and selenium.

Arsenic mobilisation requires an alteration in geochemical conditions that triggers the oxidation of pyrite bearing minerals, or the release of sorbed or mineralised As into solution, and a mechanism to retain As in solution and prevent it being flushed away. In areas where arsenic is present in sulphide minerals, oxidation by influxes of oxygen or other oxidising agents is the mechanism to mobilise As. In most of the well documented regions of arsenic mobilisation As has been present as a sorbed element associated with oxide minerals, and the most important trigger has been desorption/ dissolution from oxide minerals under high pH and oxidising conditions (Oxidation model) or by desorption due to a change to reducing conditions (Reduction model).

Arsenic mobilisation by the oxidation model

Under aerobic and acidic to near neutral conditions arsenic occurs primarily as arsenate and its mobility is restricted by sorption onto ferric hydroxide, a product of the oxidation of arsenopyrite or other iron rich minerals. As pH increases to above 8 along the flow path by mineral weathering, Arsenic desorbs, resulting in increasing arsenate concentrations in solution.

Arsenic mobilisation by the reduction model

This reductive dissolution process causes the release of sorbed arsenic from the dissolution of arsenic-bearing hydrous oxides due to change in Eh-pH.

Where large volumes of organic carbon are buried, strongly reducing conditions occur. This occurs in areas of rapid sediment accumulation, such as alluvium and deltas, and where the ingress of oxygen is limited by the low permeability of overlying fine-grained material. Under these conditions, As+5 is reduced to As+3, which is less strongly sorbed.

The reduction of organic material (either natural sedimentary-organic matter or anthropogenic organic carbon) under reducing conditions involves the reduction and dissolution of iron oxyhydroxide (FeOOH) and ferric hydroxide ($Fe(OH)_3$ by a biologically mediated dissimilatory process and releases to groundwater both Fe+2 and the sorbed load, including arsenic as As+3. The process generates HCO_3^- ions and so produces the relationship between $HCO3^-$ and arsenic. The stoichiometry of the reaction yields HCO_3^- and Fe+2 in a mole ratio of 2 according to the reaction:

$$4\ Fe(As)OOH + CH_20 + 7\ H_2CO_3 = 4\ Fe^{2+}(As^{3+}) + 8\ HCO_3^- + 6\ H_2O$$

However, other reactions, such as the dissolution of calcite, also release HCO_3^-, hence in practice the molar ratio of Fe+2 and HCO_3^- does not necessarily occur at a ratio of 2.

The more toxic form of As+3 is not readily sorbed and moves 5-6 times faster than As+5 under acidic (pH <5.7) oxidising conditions (Gulen et al, 1979.). Under neutral conditions As +5 moves faster but its rate of migration is still less than As +3.

Arsenic mobilisation by sulphide mineral dissolution

Sulphide minerals are the most important natural source of As and oxidation of these minerals may release large volumes of As into groundwater The raising and lowering of the water table in response to pumping provide optimal conditions for the weathering of arsenic minerals due to oxygenation and the release of arsenic into solution. In Bangladesh wells that had safe drinking water when first sampled were found to be contaminated with arsenic at a later date. The cause has been attributed to the dissolution of pyrite in shallow horizons of the aquifer due to oxidation induced by dewatering (Bridge and Husain, 2001).

The potential difference in arsenic concentration in boreholes between when they are first drilled and after a period of pumping causing a local change in the oxidation state of the aquifer suggests that long term monitoring is essential.

Oxygen penetration into the aquifer groundwater through abstraction or other means raises Eh, results in the exposure of arsenopyrites to oxygen and releases $H3AsO4$ (As +5), Fe+2 and sulphates:

$$FeAsS + 7/2\ O_2 + 4\ H_2O = Fe(OH)_3 + H_3AsO_4 + SO_4^{2-} + 2H^+$$

The model considers that oxidation of arsenopyrites will result in the production Fe+2 ions and sulphates (SO_4-2). The former is in turn oxidised to ferric (Fe+3) iron. The ferric iron will form insoluble $Fe(OH)_3$ (ferric hydroxide) or possibly jarrosite $KFe_3(SO3)_2(OH)_6$. Depending on pH, H_3AsO_4 will disassociate to $H_2AsO^-_4$ at low pH (<6.9) and to $HAsO_4^{2-}$ at higher pH. This process will be accompanied by a lowering of the pH in the groundwater, unless buffered by the dissolution of carbonate.

At depth in the aquifer bedrock is less weathered and oxidation of sulphides results in mildly reducing conditions and As +3 may become an important proportion of total arsenic.

In the absence of free oxygen, inorganic oxidation of the pyrite mineral is still possible. This occurs in anoxic systems via a two-step bacterially mediated process involving nitrates. The direct oxidation of pyrites by nitrates is not possible in anoxic environments.

Because pyrite can contain up to 6.5% arsenic the dissolution of pyrite by this equation can release large amounts of As into solution. Arsenic concentrations exceeding 1000 µg/l have been recorded in groundwater where these sulphide minerals are present near or above the water table (Schreiber, 2000).

Geogenic arsenic released by the oxidation of sulphides has been shown to be the cause significant As concentrations in boreholes in many instances (e.g. Welch et al, 2000). In South Africa, mineral dissolution is likely to be the most important source

of arsenic mobilisation due to the absence of significant sediment aquifers where oxidation and reduction can desorb arsenic.

It is clear that the proper combination of arsenic source material and microenvironment is needed for any one of these processes to be operational (Schreiber et al., 2000). A summary of arsenic occurrence, the mechanisms for its mobilisation and the controlling factors is shown in table 2.1

Table 2-1 Summary of arsenic mobilisation

Redox Condition	As phases	Reaction	Factors affecting mobility
Oxidising	Bound to Fe, Mn, Al hydroxides	Adsorption/desorption	pH, presence of competing anions, oxygen, Fe^{3+} concentrations
		Precipitation	
	Sulphide minerals	Oxidation	pH, presence of iron reducing bacteria, O_2 and NO_3 concentrations
Reducing	Bound to Fe Mn, Al oxyhydroxides	Adsorption/desorption	Oxidation state of As, pH, presence of competing anions, oxygen, Fe^{3+} concentrations
		Dissolution	Presence of organic carbon
	Sulphide minerals	Oxidation	pH, presence of iron reducing bacteria, and NO_3 concentrations
Sulphidic	Sulphide minerals	Precipitation	Sulphide, iron, arsenic concentrations

2.5.2 Uranium

Uranium as uraninite is extremely insoluble at the pH values of normal groundwater, however, its solubility in groundwater is enhanced by the formation of complexes by hydrolysis. U+4 forms insoluble uraninite at normal pHs and its solubility is below 0.05 ppb, well below detection limits. However, The presence of fluoride enhances U+4 solubility at a pH<4, however, fluoride does not impact on U +4 complexing at a pH above 4. Since naturally occurring pH of groundwater is generally above 4.5, fluoride speciation has not been considered in the following discussion.

In normal groundwaters at pH values of 4.5-8 and under anoxic conditions, uranium is mobilised as hydroxyl complexes ($U(OH)_5^-$). However, because of the low solubility of the hydroxy complexes uranium concentrations are generally below detection. $U(OH)_5^-$ reaches a solubility of only 0.1 ppb at a pH of 8. Consequently, uranium is not mobile under anoxic conditions, and it precipitates as uraninite.

In oxidised waters from a pH of 5 to 7.5 phosphate complexes of U +6 dominate ($UO_2(HPO_4)_2^{2-}$, even with phosphate concentrations as low as 0.1 ppm (figure 2-7). From a pH of 7.5-10 U +6 is mobilised as carbonate complexes form $(UO_2)(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$) (figure 2-8).

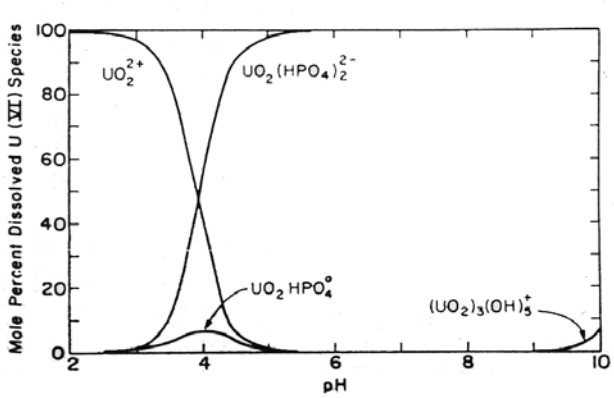

Figure 2-7 Uranium speciation as phosphate complexes.

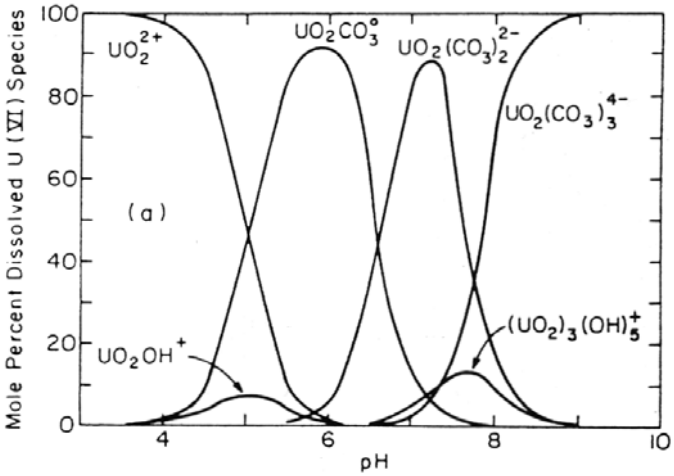

Figure 2-8 Uranium speciation as carbonate complexes.

Uranyl is strongly sorbed in the pH range 5-8.5, hence under normal groundwater conditions it is the least mobile. However, complexing agents can inhibit sorption. In oxic groundwater uranium +6 interacts strongly with solids, especially Fe containing oxides and hydroxides. However carbonates form strong complexes with uranyl ions and inhibit precipitation. Uranium is precipitated from such waters in the quadrivalent form when the uranyl carbonate complexes are destroyed by oxidation- reduction reactions. The Eh value at the beginning of precipitation of Uranium from groundwaters varies from 0 to about – 0.2v, depending on the concentration of Uranium in the solution, the magnitude and character of the salts in the water, its pH and the concentration of the HCO_3^- ion.

2.5.3 Selenium

Under oxidising conditions selenium bearing sulphides are rapidly oxidised. The resulting selenite ions are very stable and can migrate in groundwater until sorbed onto iron hydroxides.

Hydroxides of Fe, Al and Mn adsorb selenite and selenate. Adsorbtion is greater for selenite and selenate at lower pHs, since selenite and selenate have negative charges. Selenite adsorbs at a much greater range of pH than selenate. Increasing pH leads to desorption with selenate being completely desorbed at pH 7-9, while selenite is only fully desorbed at a pH of 10. At a pH of between 4.5-6.5 50% of selenate is desorbed (Macgregor, 1997). Since selenate is not readily adsorbed at a pH > 7, its mobility is strongly associated with redox state and it is mobile in primarily alkaline environments.

However, pH is not the only factor controlling selenite and selenate adsorption and mobility. Eh, the concentration of selenium and other competing ions also interact with hydroxides, and clays can also interact with how selenium sorbs onto particles. The redox condition in combination with pH determines selenium speciation, which affects the mobility and sorption characteristics. Phosphate, arsenate, molybdate, fluoride and sulphate and organic compounds all reduce sorption of selenium. Heavy metals such as Cd, Cu, Co and Zn all increase the adsorption of selenium. Therefore, in selenium rich regions, the application of phosphate fertilisers could cause desorption of selenium, which would oxidise to selenate and be leached into groundwater. Clays generally only sorb selenite at low pH (<5).

3. GEOLOGICAL OCCURRENCE OF ARSENIC, URANIUM AND SELENIUM IN SOUTH AFRICA

3.1 Conceptual Geological Models of Arsenic, Uranium and Selenium Occurrence in South Africa

Arsenic and selenium bearing minerals are primarily associated with geological settings where sulphide mineralisation has taken place. Since large deposits of organic rich sediments do not occur, it is expected that the dissolution of sulphide minerals bearing arsenic and selenium would be the dominant source of these constituents in South African aquifers. Uranium on the other hand is not necessarily associated with sulphates and can occur in sedimentary environments as well as igneous rocks with a silicic character. In order to identify South African lithologies where these constituents might be present, conceptual geological models where sulphide mineralisation or uranium deposits occur were identified.

Arsenic, uranium and selenium bearing minerals are commonly found in geological environments that can be classified as carbonaceous shales, Cu-U sandstones, porphyry uranium/copper/molybdenum deposits, Volcanogenic Massive Sulphide deposits (VMS), Pegmatite–Uranium veins, Tin Granophile systems, Hydrothermal Terranes, Mafic Igneous Sulphides, Platinum Group Element seams, Lead–Zinc deposits, Nickel-Copper sulphides, Phosphates and geothermal springs. These target geological models all occur in South Africa, and are well known for the economic minerals they contain, however, the extent to which these geological environments contribute hazardous trace constituents to groundwater is unknown. These geological models were classified according to the mode of mineralisation (Table 3.1 and 3.2) and reviewed in terms of potential source areas for arsenic, selenium and uranium mineralisation.

3.1.1 Arsenic and Selenium

The following geological settings and ore deposits are known to contain arsenic and selenium or arsenic/selenium-bearing minerals. Some of the deposits are bi-modal, and mineralisation can be attributed to two different geological settings. To avoid repetition, each deposit has only been listed under one setting.

Some of these deposits have a documented occurrence of arsenic in South Africa, while in others arsenic/selenium is undocumented in literature but suspected due to the presence of sulphide minerals (Table 3.1). No references to the occurrence of selenium in South African rocks could be found.

3.1.2 Uranium

The following geological environments are associated with uranium mineralisation (Table 3.2). There has been extensive exploration conducted in South Africa for uranium, and therefore it is assumed that most if not all of the important geological sources of uranium concentration have been noted.

Table 3-1 Geological models of sulphide mineralisation and their occurrence in South Africa

Geological Model	Documented As occurrence	Likely occurrence of undocumented As & Se
Archean Lode Gold Deposits (Roberts, 1987; Smedley, Edmunds and Pelig, 1996; Thornton, 1996).	• All the auriferous deposits in the Barberton Greenstone Belt, especially at Sheba, Fairview, and New Consort Gold Mines (Hammerbeck, 1998). • In the Gravelotte Group of the Murchison Greenstone Belt (Hammerbeck, 1998).	• All the Greenstone hosted gold deposits (Murchison-, Pietersburg- Barberton-, Giyani-, and Kraaipan Greenstone Belts (Ward and Wilson, 1998).
Disseminated Gold Deposits (Romberger, 1985; Smedley, Edmunds and Pelig-Ba, 1996; Thornton, 1996).		
Placer Gold Deposits (Smedley, Edmunds and Pelig-Ba, 1996; Thornton, 1996)	• The Sabie-Pilgrim's rest Gold Field, in sections of the Theta Reef, Glynn's Lydenburg Mine, Bevets Reef, and the Button Reef (Hammerbeck, 1998). These are situated in the Black Reef-, Oaktree-, Upper Monte Christo-, Eccles-, Rooihoogte-, and Timeball Hill Formations of the Transvaal SuperGroup in Mpumalanga. • The Witwatersrand SuperGroup gold fields and all its mines in the Central Rand Group, West Rand Group, Dominion Group, and Ventersdorp Contact Reef (Robb and Rob, 1998).	

Porphyry Copper Deposits (McMillan and Panteleyev, 1980).		• The Uitkomst Complex, which cuts the Transvaal SuperGroup in Mpumalanga. • Phalaborwa Igneous Complex • Riviera Pluton - Cape Granite • Lutzputs and Jacomynspan deposit deposits of the Namaqualand Complex.
Sedimentary and volcanogenic exhalative deposits or Sedimentary-type Stratiform Ore Deposits (Morganti, 1981).		• Copper deposits in South Africa: Okiep deposits, Aggeneys deposits, Putsberg deposit. These deposits are hosted in the Klein Namaqualand Suite, the Concordia Granite, and Brandewynsbank Granite-gneiss of the Gladkop Suite, all of which belong to the Namaqualand Complex.
Tin Granophile Deposits with Cassitterite and Sulphides	• In the Mutue Fides-Stavoren tinfields (Hammerbeck, 1998). These are hosted in the Lebowa Granite and surrounding felsitic contacts. • In the Potgietersrus tinfields (Hammerbeck, 1998). These deposits are hosted in the individual intrusions of the Lebowa Granite Suite, including the Lease Granite and Bobbejaanskop Granite. • In close proximity to contacts between the Bushveld Granite and Rooiberg Felsites, in the granite (Hammerbeck, 1998	• Cape Granites

Mississippi Valley-type Lead Zinc Deposits (Anderson and Macqueen, 1982).		• Hydrothermal deposits in Transvaal dolomites (Pb-Zn deposits)
Unconformity-type Uranium Deposits (Marmont, 1987).		
Rollfront Uranium Deposits (Dahlkamp, 1991)	• Sandstones of the Adelaide Subgroup, Beaufort Group, southwestern part of the Karoo Basin, (Cole, 1998). Dwyka Group, Whitehill Formation - Ecca Group, Elliot Formation, Molteno Formation	
Copper deposits related to skarn formation (Dobbe, 1991)		
Sandstone hosted copper deposits (Chen, 1988)		
Sedimentary Iron Deposits (Thornton, 1996; Baur and Onishi, 1978).		
Manganese Deposits (Thornton, 1996; Baur and Onishi, 1978).		
Platinum Deposits and Fe-Ni-Cu-PGE Deposits (Macdonald, 1987; Graig and Vaughan, 1994).		• PGE seams – Bushveld Complex
Volcanogenic Massive Sulphide Deposits (Lydon, 1988).		• Bien Venue – Barberton • Areachap Mine-sulphide orebody north of Upington, Kielder deposit, Prieska deposit, Boksputs deposit (Wilson,

		1998).
Silver-Bismuth-Cobalt-Nickel-Arsenic-Uranium Vein Ores (Graig and Vaughan, 1994).		• Namaqualand and Kwazulu-Natal Pegmatite veins in granites
Black Shales		• Ecca Group (Vryheid and Pietermaritzburg) shales • Dwyka Group (N. Cape) • Malmesbury shales • Silverton shales • Coronation Shale of the Hospital Hill Sub Group of the Witswatersrand SuperGroup • Ceres Subgroup of Bokkeveld Group
Peat and Coal Deposits (Edmunds and Smedley, 1996; Hinkle and Polette, 1999; USGS, 2000).		• All the Karoo SuperGroup coal fields in RSA (Snyman, 1998). These are situated in the Vryheid Formation of the Ecca Group; the Normandien Formation of the Beaufort Group; the Molteno Formation; the Warmbad-, and Turfpan Formations on the Springbok Flats; the Grootegeluk Formation in the Ellisras subbasin; the Volksrust Formation in the Tuli subbasin; the Mikambeni-, and Madzaringwe Formations in the Tshipise-Pafuri sub-basin
Geothermal springs		Significant geothermal circulation is encountered primarily in the Cape: Brandvlei, Olifantsvlei; KZN: Shushu; Northern Province: Tugela spring, Tshipise; Mpumalanga; Badplaas

Table 3-2 Geological models of uranium mineralisation and their occurrence in South Africa

Geological Model	Documented U occurrence
Proterozoic and Phanerozoic Unconformity deposits (Dahlkamp, 1991)	• Associated with gold in quartz-pebble conglomerates of the Witwatersrand SuperGroup. This includes the Upper- and Lower Reef of the Dominion Group; various reefs in the Central Rand Group which are the most significant source of uranium in the Wits; West Rand Group; Ventersdorp Contact Reef (AIEA and IAEA, 2000; Cole, 1998). Uranium is predominantly present as uraninite.
Subconformity-Epimetamorphic deposits with or without alibitized sediments (Dahlkamp, 1991)	
Granite and non-granite related vein deposits (Dahlkamp, 1991)	• Steenkampskraal, 70km north of Vanrhynsdorp as well as similar vein-type deposits on the farms Roodewal 74, Uilklip 65, Buffelsfontein 515 (Cole, 1998). The deposit is hosted in a vein in the granite-gneiss of the Namaqualand Complex. Uranium is present in monazite. • George Pluton in the Cape Granite Suite (Cole, 1998). Uranium is present in zircon, apatite, biotite, sphene and allanite. • The Pongola Granite south of the Swaziland border, (AIEA and IAEA, 2000; Cole, 1998). • In the sandstones of the Weltevrede Formation, Witteberg Group, on the farm Wit Poort 110/16 (Cole, 1998). Uranium is hosted in zircon. • Granites, gneiss, and pegmatites of the Namaqualand Complex (AIEA and IAEA, 2000; Cole, 1998). Uranium is present in biotite, zircon, magnetite, monazite, gadolinite, niobium-tantalum oxide phases and apatite. • Hydrothermal veins at the Albert Silver Mine in the Verena Porphyritic Granite 40km north-northeast of Bronkhorstspruit, on the farms Leeuwfontein, Welverdiend, and Roodepoortje (Cole, 1998).

	Uranium is present in pitchblende and metazeunerite. The veins intrude the Verena Porphyritic Granite.
Peneconcordant and rollfront sandstone deposits (Dahlkamp, 1991)	• The Adelaide Subgroup sandstones of the Beaufort Group, Karoo SuperGroup (AIEA and IAEA, 2000; Cole, 1998). Uranium is present as coffinite, uraninite, molybdenite, pyrite, arsenopyrite, and chalcopyrite. • Sandstones in the Late Triassic Molteno and Elliot Formations between Clocolan and Qwa-Qwa. The primary uranium-carrying phase is uranophane (Cole, 1998). • The Natal Group 16km southwest of Gingindlovu (Cole, 1998).
Breccia complex deposits (Dahlkamp, 1991)	
Surficial deposits such as duricrust sediments, peat bog, karst cavern and pedogenic occurrences (IAEA, 1984)	• Recent aged Quaternary heavy mineral sands at Richards Bay (AIEA and IAEA, 2000). • Surficial deposits consisting of lacustrine (carnotite in pans), fluvial (carnotite in ancient channels), and pedogenic (carnotite in calcrete and gypcrete) sediments in the North Western Cape Province (AIEA and IAEA, 2000).
Uranium- and gold dominated quartz-pebble conglomerates (Dahlkamp, 1991)	• Associated with gold in quartz-pebble conglomerates of the Witwatersrand SuperGroup. This includes the Upper- and Lower Reef of the Dominion Group; various reefs in the Central Rand Group which are the most significant source of uranium in the Wits; West Rand Group; Ventersdorp Contact Reef (AIEA and IAEA, 2000; Cole, 1998). Uranium is predominantly present as uraninite. • In quartz-pebble conglomerate of the Mozaan Group southeast of Amsterdam, Mpumalanga (Cole, 1998). • In quartz-pebble conglomerate of the Black Reef Formation, Transvaal SuperGroup, southwest of Kaapsehoop (Cole, 1998). The

	uranium is adsorbed onto leucoxene and goethite.
Collapse Breccia Pipe deposits (Dahlkamp, 1991)	
Intrusive deposits such as alaskite, quartz monazite, carbonatite, peralkaline syenite and pegmatite (Dahlkamp, 1991)	• Phalaborwa Alkaline Complex (AIEA and IAEA, 2000; Cole, 1998). • Glenover Carbonatite Complex (Cole, 1998). Uranium is present in apatite and monazite. • Pilansberg Alkaline Complex (AIEA and IAEA, 2000).
Phosphorites (Dahlkamp, 1991)	• Marine Phosphorites of the West and South Western coast off RSA (Cole, 1998). These are not however relevant to this project, since they are offshore. Of importance however is the Dwyka Group northwest of Upington, which was deposited in a marine environment.
Volcanic deposits (Dahlkamp, 1991)	
Metasomatized granites and metasediments (Dahlkamp, 1991)	
Lignite (Dahlkamp, 1991)	
Black and carbonaceous shales (Dahlkamp, 1991)	• Coal fields in the Warmbad-, and Turfpan Formations on the Springbok Flats (AIEA and IAEA, 2000; Cole, 1998). Uranium is present in coffinite, oyamalite, auerlite, and organo-metallic compounds. • The ferruginous mudrocks of the Whitehill, and Tierberg Formations of the Ecca Group in the Northern Cape (Cole, 1998). The uranium is adsorbed onto haematite surfaces. • Apatite in calcareous mudrocks of the Dwyka Group in the Northern Cape (Cole, 1998).

3.2 Distribution of Arsenic, Selenium and Uranium in South Africa

3.2.1 Arsenic and Selenium

Based on the geological models of mineralisation, potential target areas of arsenic and selenium mineralisation were identified based on the occurrence of sulphide mineralisation. Sulphide mineralistion is also associated with deposits of antimony, chromium, coal, copper, gold, molybdenum, phosphates, platinum, tin, iron, uranium, zinc, sulphur and manganese, and with Sedimentary exhalative deposits (SEDEX). These deposits were identified (Wilson Cole, 1998), and the lithologies in which they were located flagged on the 1:1 000 000 geological map of South Africa and are reproduced on the arsenic map. These lithologies are potentially arsenic and selenium rich due to documented sulphide mineralisation.

Based on antimony association

- Leydsdorp and Weigel Formations of the Gravelotte Group: These Formations are located in the loweveld of the Northern Province and extend form the foot of the Transvaal Drakensberg escarpment to the Kruger national Park. These Formations consist of massive schistose and carbonatised mafic lava, interbedded with ironstone, quartz chlorite schist and quartz porphyry, carbonates, with antimony-gold sulphide ores. These make up part of the Murchison Schist Belt, which have been altered by widespread hydrothermal activity. Mineralisation is along tectonically controlled bodies, which appear to be vertical shears and are located primarily in the Weigel Formation. Sulphide mineralisation is in fractures and quartz veins in schists that have been hydrothermally altered to a talc carbonate.

Based on chromium association

- In the Bushveld Igneous Complex: Croydon Subsuite Formation, Shelter Norite Formation, Dwars River Subsuite, Schilpadnest Subsuite, Vlakfontein Subsuite, Kolobeng Norite Formation of the Rustenburg Layered Suite. These are mafic and ultramafic stratiform deposits of igneous layering and the Subsuites can be classed as Mafic Igneous Sulphides. They form the lower part of the Bushveld complex, in which chrome is interstratified and associated with a number of lithologies. The norites comprise the base of the Suite and are known as the Marginal Zone. They rest on the floor rocks in a disconcordant manner. The Croydon, Vlakfontein and Zoetveld Subsuites are characterised by igneous layers and form the Lower Zone. They consist of mineralised bronzitite, pyroxene, chromitite and harzburgite. The Dwars River and Schilpadnest Subsuites form the Critical Zone and consist of pyroxenite, norite, chromite and the platiniferous Merensky Reef.

- In the Tugela Rand Complex: This basic intrusive complex in the Tugela valley of the Natal Metamorphic Belt is pseudostratified and consists of peridotite, pyroxenite, norite and gabbro. Sulphides are primarily associated with the peridotite core of the intrusion.

- In the Uitkomst Complex: This complex consists of harzburgite and has been subjected to widespread hydrothermal alteration. It cuts the Transvaal Supergroup in Mpumalanga

- In the Mount Dowe Group of the Beitbridge Complex: These rocks consist of metaquartzite and magnetite quartzite with interbeds of leucocratic gneiss and are located about 40 km SW of Messina. Sulphides exist as isolated bands.

Based on coal association

- In the Karoo Supergroup: Normandien Formation, Emakwezini Formation, Grootgeluk Formation, Irrigasie Formation, Letaba Formation, Madzaringwe Formation, Molteno Formation, Volksrust Formation, Vryheid Formation: Large deposits of coal occur in the northern Free State, South Rand, north eastern Natal. Mpumalanga and the Northern Province. The Coal is associated with carbonaceous shales of the Ecca Group, which is widespread in South Africa, and the Normandien and Molteno Formations of the Beaufort Group. Sulphides are also associated with the Pietermaritzburg Shale Formation at the base of the Vryheid, which consist of black shale. The Vryheid consist of sandstone with coal interbeds that originate as marsh, flood plain and delta plain deposits. The overlying Volksrust shale consists of black shale and can also be considered as sulphide rich. Coal is associated with the Vryheid and in the Vryheid, Witbank, Highveld, Ermelo, South Rand, Vryheid and Klip River coalfields. In the Free State and Vereeniging-Sasolburg coalsfields coal is associated with both the Vryheid and Lower Beaufort Normandien Formations. In the Kangwane coalfield stretching from the Crocodile river to the Swaziland border, coal is associated with the Vryheid and Volksrust Formations. The Madzaringwe Formation is a carbonaceous shale alternating with coal, siltstone and sandstone. It forms the basis of the Mopane, Pafuri and Tshipise coalfields of the Soutpansberg District. The Emakwezini Formation, which forms the lower part of the Beaufort Group in northeastern Natal. It consists of shale, mudstone, sandstone and coal, which is mined together with eth Vryheid Formation in the Nongoma and Somkele coalfields in northern Natal. The Molteno Formation consists of arkosic sandstone with carbonaceous shale between Molteno and Indwe. The Irrigasie Formation underlies the Springbok Flats and consists of mudstone, sandstone. In the Tuli coalfields west of Messina coal is mined from a succession of mudstone, shale and sandstone of the Volksrust Formation, however, it has no outcrop and has been mapped as Letaba and Clarens Formations, which are lithologically dissimilar. In the Ellisras coalfield, the coal bearing Grootgeluk Formation, equivalent to the Volksrust Formation is distinguished.

Based on copper association

- Barberton Supergroup: At Bein Venue SE of Kaapmuiden volcanogenic massive sulphides are hosted in tuffs, rhyolite and felsites.

- Bulai Gneiss: Copper mineralisation in veins in the granite and gneiss is widespread in the Messina area.

- Uitkomst Complex: This complex is an ultramafic to mafic intrusion N of Badplaas intruded between 2 NW striking fracture systems. It cuts through the Malmani dolomite and Timeball Hill shale.

- Koperberg Suite and Concordia Granite Formation: The Koperberg Suite near Okiep is not shown on the map as individual occurrences are too small There are over 1700 such bodies. It is intrusive into the Concordia granite and consists of pyroxenite, diorite, anorthosite, sulphides and other basic to intermediate rocks. In the Okiep District of the Northern Cape copper mineralisation covers over 3000 km^2 around Springbok. The sulphides are predominately pyrrhotite and chalcopyrite and are associated with the diorites.

- Malmani and Duitschland Formations and the Wolkberg Group of the Transvaal SuperGroup: Within the Wolkberg group copper, uranium and other sulphide metals occur near Zebediela and are hosted in shears and breccias. In the Duitschland Formation chalcopyrite mineralisation exists in the Potgiersrus area. In the Rooiberg area copper follows the contact between quartzite of the Magaliesberg Quartzite Formation and Rooiberg felsite. In the Malmani Formation from Abjaterskop near Derdepoort to Ramoutsa in Botswana copper sulphides are hosted in quartz and calcite veins in NW trending faults. Chalcopyrite is also found in massive bands in the pilgrims Rest and sabie areas in quartz veins in the Malmani dolomites. SW of Pretoria small dessminations of sulphides occur in quartz veins, brecciated pockets and black shale bodies in the Malmani dolomites.

- Goudplaats Gneiss: Copper mineralisation occurs SE of Pietersburg and near Messina in shear zones and veins within the gneiss

- Insizwa Complex: Four mafic to ultramafic intrusions with sulphide mineralisation occur near Mt Ayliff and have not be denoted on the 1:1000000 Geologicl map due to their small size.

- Jannelsepan Formation: Base metal massive sulphides in the Prieska, Areachap, Kielder, Boksputs and van Wyks Pan areas represent volcanic exhalatives. They are hosted in deformed gneisses that have a metasedimentary origin. The sulphides are both disseminated within the Formation and in bands of massive sulphides up to 35 m thick. They occur as pyrite, pyrrhotite, galena, chalcopyrite, spalerite, magnetite and arsenopyrite in a carbonate rich matrix. The disseminated sulphides are hosted in calc-silicates. The sulphide ores are also associated with an adjacent zone of pyretic quartzite and magnetite. The Areachap sulphide body NW of Upington is hosted in gneisses and schists. West of Areachap the Lutzputs deposits contain sulphides in hysrothermally altered sheared magnetite-haematite bodies with arsenopyrite rich zones. The Jacomyns Pan sulphides in the Kenhardt District are hosted in an ultramafic intrusive dyke body intruded into the gneisses in a broad shear zone.

- Khurisberg Subgroup of the Bushmanland Sequence: SE of Pofadder sulphides are present within siliceous gneisses. The sequence is considered to be of SEDEX origin.

- Lebowa Granite Suite: This suite includes all the granites of the Bushveld Complex. Significant belts of sulphide minerals exist near north and west of Marble Hall, Potgietersrus and Rooiberg. Veins of mineralisation also exist within the Nebo Granites, however mineralisation is patchy.

- Mkomazi Gneiss, Mzimkulu Group, undifferentiated MD granite gneiss Near Mfume SW of Durban contains disseminated chalcopyrite is found in gneisses intruded into Mapumulo Group rocks. Other sulphides in intrusive gneisses exist near Nindweni, S and SE of Vryheid and N of Melmoth.

- In Undifferentiated ZB pottasic granite gneiss: near the confluence of the Tugela and Mfongosi rivers sulphides occur in deformed lenses in a sodic granitoid. Another occurrence is found W of Empangeni.

- Natal Metamorphic Province: North of Greytown in Natal quartz-calcite veins in quartz mica schists contain pyrite sulphide mineralistion. NNE of Kranskop a sulphide rich layer is hosted in pelitic schists and gneisses.

- Mount Dowe Group of the Beitbridge Complex: Copper sulphides are associated with NE trending faults near Messina in the extreme north of the country, especially where faults intersect metaquartzite and geniss contacts.

- Hom and Aggeneys Subgroups: East and west of the town of Aggeneys SEDEX deposits formed from hydrothermal solutions discharged into a sedimentary basin are hosted as leucogneisses, quartzite, and schists. They consist of chacopyrite, galena, sphalerite and magnetite.

- In the Nzhelele, Sibasa and Tshifhefhe Formation of the Soutpansberg Group: Copper mineralisation occurs close to the southern contact of the Soupansberg Group near Louis Trichardt and is concentrated in joints faults and shears within the Sibasa basalts and the epidotite lava. At the northern contact of the Soutpansberg Group, mineralisation is in quartz veins and breccias of the Nzhelele Formation lavas and sediments

- Phalaborwa Complex: This ultramafic multi-intrusive complex on the western border of Kruger Park intrudes the Goudplaats Gneiss and consists of pyroxenite, magnetite, syenite, phosphate and carbonatite at the core of the intrusion. Porphyry copper, uranium, magnetite, chalcopyrite and phosphate are associated with the carbonatite, where chalcopyrite predominates a host of sulphide minerals (sphalerite, galena, pyrite, pyrrhoyite, mrcasite etc.)

- Roodekraal Complex: SE of Potchefstrroom fault controlled mineralisation occurs in the andesitic lavas.

- Rubbervale Formation of the Gravelotte Group: in the eastern lowveld of Northern Province near Gravelotte copper-zinc sulphides exist in banded quartz schists

- Schiel complex: This alkaline complex ESE of Louis Trichardt is intrusive into the Goudplaats gneiss. It consists of syenite emplaced as ring dykes in an ultramafic complex including magnetite. Chalcopyrite, pyrite and pyrrhotite are present within carbonatite north of Letaba dam

- Roossenkraal Subsuite, Bierkraal and Molendraai Magnetite, Gabbro, and Villa-Nora Gabbro-Anorthosite of the Rustenberg Layered Suite, Bushveld Igneous Complex: These represent the Upper Zone and contain magnetite in appreciable quantities, together with pyroxene. Sulphides constitute in excess of 5% of the rock mass, with chalcopyrite, pyrrhotite and lentlandite dominating. A number of ultrabasic pegmatite pipes also occur, which are rich in sulphides. Disseminated sulphides also occur at the contact with Transvaal Supergroup sediments

Based on gold association

- Bandelierskop Complex: North of Soekmekaar gold is hosted in quartz veins in gneisses.

- Giyani Group: In the Giyani greenstone belt near Klein Letaba gold with minor sulphides is found in quartz veins, banded iron formations, and carbonate veins in mafic and ultrafic rocks. The mineralistion is associated with shearing and pyrite, arsenopyrite and chalcopyrite are the principal sulphides, with arsenopyrite being predominate in the banded iron formations.

- Rooiwater Complex and Gravelotte Group: In the Murchison Greenstone or Schist belt between Tzaneen and Phalaborwa gold is associated with antimony and desiminated in sililceous carbonates, talcose and chloritic schists in shear zones in the Weigel and Mackop Formations. Gold is also associated with arsenopyrite and pyrites in chert and banded iron formations, and in quartz veins of the Rooiiwater igneous complex.

- Kraaipan Group: Gold is associated with pyretic quartz veins in banded iron formations in the Vryburg-Mafikeng area.

- Onverwacht. Fig Tree and Moodies Group of the Barberton Greenstone Belt. The Onverwacht Group consist of ultramafic and mafic rocks and is overlain by greywacke sandstones, mudstones and ferruginous shales of the Fig Tree Group. Mineralisation occurs in greenstones, greywackes, shales, banded ferruginous shales, quartzites and cherts. Gold is included within pyrites and arsenopyrites of hydrothermal origin and is associated with shears and fractures related to strike-slip faults. A large part of the mineralisation occurs at Bein Venue, within 15 km of Barberton.

- Nondweni Group: Quartz vein gold is hosted in this granite-greenstone remnant W of Melmouth.

- Pietersburg Group: In the volcano-sedimentary succession of Pietersburg greenstone belt gold is associated with shear zones and mafic and ultramafic volcanic. Gols is associated with pyrrhotite and arsenopyrite.

- Black Reef Formation: Malmani SubGroup and the Timeball Hill Formation: Within sedimentary rocks of the Transvaal Supergroup exposed along the Transvaal Drakensberg gold mineralisation occurs between Sabie, pilgrims Rest and Bourke's Luck. Gold exists primarily within stratiform gold-quartz-carbonate-sulphide veins in dolomitic rocks of the Malmani SubGroup, but also within the under lying Black Reef Formation and the lower layers of the overlying Timeball Hill Formation shales. Gold is associated with pyrites, arsenopyrites and chalcopyrite.

- Black Reef, Daspoort, Magaliesburg Formations: Throughout Northwest and Gauteng provinces sporadic gold is associated with hydrothermal mineralisation in the Black Reef conglomerates. The gold is hosted with pyrite, arsenopyrite, spahelrite and pyrrhotite. Mineralisation also occurs in quartz veins in N trending shears in the Malmani dolomites in the vicinity of Ottoshop, and quartzites and shales of the Timeball Hill Formation near Marabastad, and in the Daspoort shales. East of Silverton in Pretoria, gold is associated with quartz-carbonate veins in diabase and shale of the Magaliesberg Quatzite Formation.

- Dominion Group, Central Rand and West Rand Groups of the Witwatersrand Supergroup: The large gold-uranium-pyrite deposits of the Wits Basin consist of thin layers of quartz pebble conglomerate in a very thick succession, of which the Dominion group forms the base. Pyrite is contained in the matrix, together with arsenopyrite and other sulphides. In the Dominion Group Uranium predominates over gold. Pyrite is the most abundant of the heavy mineral constituents. Significant gold bearing carbonaceous reefs also exist.

- Black Reef Formation and Goudplaats Gneiss: SW of Haenertsburg gold is hosted in the lower portion of the Chuniespoort Group and the Goudplaats geniss and is associated with faulting. Gold is hosted in quartz veins intruded between the Black Reef and Chnuiespoort Group, and is also found in sheared black shales within the dolomites. Quartz veins are highly sulphidic. Further sulphidic mineralisation in quartz veins is found scattered throughout t the Black Reef Formation in the Northern Province.

- Hout River Gneiss: In this gneiss gold occurs in quartz veins NW of Pietersburg.

- Mfongozi Group: NW of Kranskop quartz veins in sheared mafic and pelitic schists is associated with remobilised massive sulphides.

- Nsuze and Mozaan Groups of the Pongola Supergroup: SE of Vryheid quartz reefs in shear zones are associated with pyrite and arsenopyrite in Mozaan metasediments. W of Nkandla conglomerates of the Nzuze contain pyritic gold.

- Mzimlilo Granites: Near Umzinto sulphide rich quartz veins are found in sheared granite-gneisses.

- Transvaal Group xenoliths found in the Bushveld Igneous Complex; NW of pretoir and near Cullinan pyroxenite and magnetite sills intrude into the Raton Formation of the Traansvaal Supergroup, which lie between gabbros of the Upper Zone and Lebowa Granites. The gold is associated with arsenopyrite. The shear zone between Rooiberg felsite and Bushveld granite near Cullinan is also arsenopyrite rich.

Based on molybdenum association

- Adelaide SubGroup of the Karoo Supergroup: The sandstone hosted uranium deposits of the SW part of the Karoo basin near Beaufort West contain molybdenum bearing minerals.

- Cape Granite Suite: Quartz veins and breccia bodies in Riviera Granites N of Piketberg contain molybdenum pyrites. NW of Darling hydrothermal pipe like breccias in granites contain arsenopyrite and chalcopyrite. Quartz veins occurring SW of Philedelphia also contain sulphide bearing ores.

- In the Hilda Formation of the Gariep Supergroup: At Geigas SE of Khubus dolomitic xenoliths encased within granite of the Kuboos pluton (Cape Granites) skarns bearing molybdenum and copper sulphides are developed.

- Khurisberg Formation of the Bushmanland Group, Concordia Granite and Spektakel Suites of the Namaqualand Complex: S, SE and SW of Springbok molybdenum is associated with pyrite and chaclopyrite in quartz veins and lenses and in pegmatite veins.

- Korannaland Supergroup: Quartz veins cut the gneisses of this Supergroup WSW of Upington.

- Lebowa Granite Suite: The Bobejaankop Granite NW of Potgietersrus is associetd with ore bearing arsenopyrites. W and SW of Dennilton and SW and NE of Groblersdal the Nebo Granites arsenopyrite is present in quartz veins.

- Meinhardskraal Granite Formation: Quartz veins in granite S of Pietersburg contain minor amounts of sulphide minerals.

- Tatasberg Formation of the Kuboos Bremen Suite: NW of Vioolsdrif syentic plutons contain veins of molybdenum sulphides.

Based on phosphate association

- Bierkraal Magnetite Gabbro and Villa Nora Gabbro Formations of the Rustenberg Layered Suite: In the Upper Zone of the Bushveld complex apatite and magnetite become significant minerals.

- Glenover Carbonatite Complex: This carbonatite contains disseminated apatite.

- Phalaborwa Complex: The carbonatite core and surrounding magnetite rich zone are apatite rich.

- Schiel Complex: This alkaline pluton between Lous Trichardt and Giyani intrudes the Southern Marginal Zone of the Limpopo Belt. Apatite is disseminated in pyroxenite, carbonatite and syenite.

- Spitskop Complex: This carbonatite contains disseminated apatite and is located NE of Grobblersdal.

Based on platinum group element association

- Schilpadnest, Dwarsrivier and Grasvally Norite-Anorthosite Subsuites, Croydon, Zoetveld and Vlakfontein Subsuites of the Bushveld Igneous Complex: PGE mineralisation is associated with base metal sulphides in the Critical Zone of the Bushveld Complex. Ultramafics in the Lower Zone S of Potgeietersrus also contain PGE bearing sulphides. PGE sulphides occur only sporadically in the Main Zone and are associated primarily with anorthosites. Small quatities are also associated with copper sulphides through much of the Upper Zone. PGEs are associated with dunite pipes in the Critical Zone of the Eastern Bushveld Complex .

- Uitkomst Complex: This massive sulphide deposit N of Badplaas consists of gabbro, harzburgite and pyroxenite.

- Dwarsfontein Complex: Sulphide mineralisation is associated with copper in the lower part of the Complex.

Based on lead association

- The Black Reef, Daspoort, Hekpoort, Magaliesberg, Silverton and Timeball Hill Formations: Sulphides are present NE of Zeerust quartz veins in the upper contact of Hekpoort lava. SW of Zeerust sparsely distributed sulphides occur in quartz veins in Timeball Hill shale. Lead bearing quartz veins occur shales of the Silverton Formation near Witbank. Near Waterval-Boven occurs in quartz veins in Daspoort quartzite and intrusive diabase. Galena occurs in the Black Reef near Krugersdorp. In the Pretoria-Witbank area galena and other sulphides occur in quartz veins in the Magaliesberg Formation.

- Malmani Subgroup: W to SE and NW of Zeerust sulphides are present in the upper beds of the Malmani Subgroup along its contact with shales of the Prtoria Group. North of Thabazimbi, galena is also hosted in bedding planes and veins of Lyttelton Formation dolomites.

- Campbell Rand and Asbestos Hills Subgroups: Sporadic minerlisation occurs in the vicinity of Griquatown, where the dolomite is intruded by thin basic

dykes. Between Griquatown and Prieska sulphides occur in banded iron of the Absbestos Hill Subgroup in quartz-carbonate veins. At Reivelo, breccia bodies in the dolomites also contain sulphides.

- Dsjate Subsuite, Norite Anorthosite, and Pyramid Gabbro Norite Formations of the Bushveld Igneous Complex: Near Potgietersrus galena is found in gabbronorites in gangue and vein quartz.

- De Hoop Formation of the Orange River Group: ESE of Stinkfontein prominent quartz veins are associated with calcite that intrude these volcanics.

- Gaamtoos Group: Dolomitc limestones near St Francis Bay contain sulphide bearing calcite veins.

- Halfway House Granites: SW of Centurion galena is associated with vuggy quartz veins associated with a mafic dyke in the granite

- Hilda and Kaigas Formations Gariep Supergroup: Galena occurs in quartz veins and Kaigas schists and hornfels of the Hilda Formation.

- Aggeneys Subgroup of the Bushmanland Group: Metasedimentary rocks of this subgroup have a limited surface exposure and appear only as inselbergs through the Quaternary cover. These SEDEX massive sulphides are located around Aggeneys, NE of Springbok. Rocks in a layer of pelitic schists and close to major quartzite formations hosted in gneisses of the Hom Subgroup. Galena is the dominant sulphide, followed by sphalerite, chalcopyrite and pyrite.

- Kuibis, Schwarzkalk Formations of the Nama Group: Sulphides occur in quartz veins near Modderdrift.

- Lebowa Granite Suite: Galena is common as an accessory mineral in sulphide ores hosted in the Bobbejaankop granite, where it has been associated with arsenic.

- Vioolsdrif Suite: Between Klein Helskloof and Rooiberg south of Moddersdrift quartz filled fractures in the Vioolsdrif granitoid.

- Vaalwater Formation of the Waterberg Group: NNE of Vaalwater quartz veins in the proximity of diabase dykes contain an appreciable volume of sulphides.

- Vyfbeker Metamorphic Suite of the Hartbees Rivier Complex: This deposit occurs between Kakamas and Kenhardt and sulphides are hosted in felsic rocks.

Based on tin association

- Biesje Poort and Riemvasmaak Formations SW of Upington hydrothermal quartz veins and pegmatites are hosted in gneiss

- Brulpan Group: Quartz veins in the Gordonia District near Springbok contain tin mineralisation.

- Cape Granite Suite: Sulphides containing arsenopyrite occur in quartz veins in plutons in the vicinity of Cape Town at Kuilsrivier, Durbanville, Helderberg and Vredehoek.

- Goudplaats Gneiss: East of Thohoyandou tin rich pegmatites are present in gneiss.

- Kwarriehoek, Leeuwpoort and Rooiberg Formations of the Pretoria Group: the Rooiberg rhyolite contains tin W of Naboomspruit and near Nylstrrom. The tin is associated with shales interbedded in the rhyolites. The Rooiberg Tin Field W of Warmbaths contains sulphide rich fractures in quartzites of the Leeuwpoort Formation. N of Marble Hall, tin is found in veins in low dipping faults in the Kwarriehoek Formation.

- Lebowa Granite Suite: Tin is emplaced within the granite and in the Rashoop Granophyre Suite, which is the surrounding host rock, in the Potgietersrus and Olifants Tin Fields. It occurs as pipe like bodies, flat lens and disseminations in the granite. These deposits have been associated with arsenopyrite.

- Mpuluzi Granites: Tin rich pegmataites are present at Oshoek on the Swaziland border.

- Richtersveld Complex: Pegmatites in granites of the Richtersveld Complex NW of Sprongbok contain tin.

- Tugela Group: large numbers of pegmatite dykes intruded into this Group near Umfuli east of Melmouth contain tin.

Based on zinc association

- Campbell Rand and Malmani Formations in the Transvaal Supergroup: SW of Vryburg splaerite and galena are concentrated in massive sulphide bodies in carbonates of the Campbell Rand, with minor traces of pyrite. South of Zeerust, zinc is associated with lead in the Malmani Formation near the contact with the Pretoria SubGroup.

- Jacomyns Pan Group: At Prieska a pyrite rich zinc body is present.

- Fig Tree and Onverwacht Groups: S of Kaapmuiden massive and disseminated sulphides are present with arsenides in the Fig Tree Group.

- Nondweni Group:Veins at the contact of Nondweni schist and granite intrusives contain sphalerite.

- Rubbervale Formation in the Gravelotte Group: NE and W of Gravelotte a spahelrite rich deposit is present.

3.2.2 Uranium

The uranium target geology was chosen on the basis of existing geological data:

- Dominion and Central Rand Groups of the Witwatersrand SuperGroup: The quartz-pebble conglomerates of the Wits basin contain the largest source of uraninite in South Africa. The uraninite deposit also extends to the Ventersdorp Conglomerate Formation, which caps the Central Rand Group. Pyrite is also associated with these strata.

- Black Reef Formation: The quartz pebble conglomerate of the basal part of this Formation is present in Klerksdorp, Carletonville, the West and Central and East Rand. The highest uranium concentration lie where this Formation unconformably overlies the Central Rand Group.

- Verena Porphyritic Granite and Klipkloof Granite: uranium bearing hydrothermal veins occur NNE of Bronkhorstspruit.

- Adelaide SubGroup: Uranium is present in the southwestern part of the Karoo from Beaufort West and extending almost as far as Cradock and Bloemfontein. The uranium is sandstone hosted, disseminated and in peneconcordant tabular bodies.

- Molteno and Elliot Formations: Uranium occurs between Clocolan and Qwa-Qwa, and between Ficksburg and Bethlehem.

- Cape Granite Suite: The granite of the George Pluton and granites of the south western Cape contain uranium, with the highest concentrations occurring in the youngest granites.

- Roodewal Suite of the Namaqualand Metamorphic Complex: At Steenkampsskraal N of Vanrhynsdorp uranium is found in monazite-apatite-rich veins in granite gneiss.

- Concordia Granite of the Spektakel Suite: granite gneiss of the Namaqualand Metamorphic Complex show high uranium contents over large parts of central Namaqualand. Thre most important deposits are near Kommaggas and Nooitgedacht SW of Springbok. Granite gneiss in this region is also intruded by uranium rich pegmatites, particularly near Gordonia and Kenhardt Distrtcts west of Upington.

- Surfical Deposits: Fluvial, lacustrine, pedogenic and ferruginous mudrock deposits occur south of the Orange River between Upington and the West Coast., and in the Ecca Group around Brandvlei. Fluvial

deposits are present in calcite cemented sediment near Kakamas. These rest on granite gneiss of the Namaqualand Metamorphic Complex. Lacustrine deposits are found over pans where outflow has been impeded, such as at E of Port Nolloth, NNE of Springbok and NNE of Upington. Pedogenic occurrences are common around Upington. In calcrete horizons. The ferruginous mudrock of the Whitehill Formation of the Ecaa Group contains uranium in a broad E-W belt from ENE-WSW of Brandvlei.

- Phalaborwa Complex: uranium occurs within carbonatite that forms the core of the complex.

- Glenover Complex: The carbonatites SW of Ellisras contain low grades of uranium.

- Irrigasie Formation: The coal and carbonaceous shale underlying the Springbok flats contains disseminated uranium.

- Waterberg group: Low grade mineralisation occurs in pebble conglomerates E of Thabazimbi.

- Mozaan Group and Nsuze Group: Sporadic occurrences exist within quartz-pebble conglomerates between Babanago and the Swaziland border and SE of Amsterdam.

- Pilansberg Alkaline Complex: Uranium occurs in green foyaite (Wydhoek Foyaite) of the Mankwe Formation and in syenite.

4. SOURCES OF DATA

The following sources of data were used in the compilation of the Arsenic, Uranium and Selenium Occurrence Maps:

- Water Management System of the Department of Water Affairs and Forestry
- National Groundwater Database of the Department of Water Affairs and Forestry
- National Groundwater Quality Monitoring Network Data of the Department of Water Affairs and Forestry
- An Electronic Atlas: An Assessment of Groundwater Quality at a National Scale in the Republic of South Africa (Simonic, 2001)
- The 1:1000000 Metallogenic Map of South Africa from the Council for Geoscience
- The 1:1000000 Geological Map of South Africa from the Council for Geoscience
- The Helicopter-Borne Stream Sediment Geochemical Sampling Survey data of the Council for Geoscience
- SAMINDABA - the South African minerals deposit database of the Council for Geoscience
- The Mineral Resources of South Africa (Wilson and Anhaeusser, 1998)

4.1 Description, Distribution and Limitations of Data in the Context of this Study

4.1.1 The Department of Water Affairs and Forestry Data

The Department of Water Affairs and Forestry (DWAF) is the current custodian of water data in South Africa, this data was gathered from sampling networks distributed nationally. This data consists of:

- the Water Management System (WMS) – formerly called the Water Quality Database (QualDB) (Simonic, 2000);
- the National Groundwater Database (NGDB) – also know as the borehole data, this is a description of all boreholes drilled by DWAF over the last three decades;
- the National Groundwater Quality Monitoring Network (ZQM) - a network of over 400 boreholes established for the purpose of monitoring groundwater quality.

The WMS data contains data from a number of monitoring networks, such as the NGDB and the ZQM, but database links to the other monitoring networks are in the process of being established, thus both surface and groundwater quality parameters are included in the WMS.

There are over 210000 borehole records in the NGDB. The DWAF data suffers from some limitations; the lack of GPS receiver location data due to technology unavailability during the drilling of most of these boreholes has led to boreholes

being assigned locations such as the centre of a farm in which they are found. In addition, geological logs are unreliable. Furthermore many duplicate records exist.

Many of the problems with the database can be attributed to a historic lack of policy regarding the licensing, drilling, sampling and proper logging of boreholes for water supply or monitoring purposes. Therefore, data entry has been ad hoc. As a result, aquifers in South Africa have been poorly delineated, the geological dimension is poorly understood, and the flow of groundwater is poorly characterised. This project was thus hindered by a lack of reliable data, which prevents boreholes being uniquely attributed to specific geological Formations.

Field parameters such as the pH and Eh are very important when performing hydrogeochemical modelling. With the DWAF data, Eh does not feature at all while the pH was mostly measured in the laboratory and is not representative of field conditions; therefore these cannot be reliably used for hydrogeochemical modelling or speciation prediction.

The pH data from the WMS was used after geostatistical treatment by Simonic (2001) and linked with the polygons defined by Vegter (1995) in his map of the groundwater resources of South Africa. However, these represent the range of pH conditions found during laboratory analyses.

Data on trace constituents occurs only in the ZQM, however, selenium and uranium are not amongst the determinands analysed for. Many of the boreholes are not located in geological regions where trace constituents are expected, and the laboratory analyses methods used had too high a detection limit to provide an accurate picture of trace constituent occurrence.

4.1.2 The Council for Geoscience data

The Council for Geoscience is the current custodian of national geological data. Other data exists that is owned mainly by mining houses. Due to confidentiality, much of the mining house data has either not been made available to the South African public, or its access via the Council for Geoscience is restricted and cannot be reproduced. Where mineralised occurrence only was of interest, much of the rock core was improperly logged or not archived properly resulting in it not being of much use in delineating the three dimensional geology of South Africa. The National Borehole Core Library of South Africa does however contain much useful core donated by certain mining houses and which in the future will form a source of data if any geological work or mapping in the third dimension is undertaken. Again as with the DWAF data, inaccuracy does occur as a result of the unavailability of GPS technology at the time of drilling.

The Council for Geoscience data utilised during this project consists of the national scale digital format 1:1000 000 Geological and Metallogenic maps and the helicopter Stream Sediment Geochemical Sampling survey, which is still a work in progress.

The geological and metallogenic maps are based on data from field mapping performed by staff members of the Council for Geoscience during the last century.

The Metallogenic map is based on SAMINDABA data, and identifies occurrences of economic commodities, and also of mineral lines and polygons representing provinces of element occurrence.

SAMINDABA is an abbreviation for the South African Mineral Deposits Database. It is a modern database continuously active in data acquisition, data capturing and updating all mineral commodities for the whole of South Africa. During the early nineties some 16 000 mineral occurrences were captured on the system. The SAMINDABA data is a database of mineral deposits described as commodities, with commodity one (com1) being a larger deposit then the minimum and much smaller commodity eight (com 8) deposit. This data is in the form of point data describing a deposit having a location as described by geographical coordinates. Arsenic occurrence is documented as a primary and lower order commodity (arsenic found in association with economic commodities). Selenium is not documented in this database.

The helicopter Stream Sediment Geochemical Sampling survey contains data for Arsenic and Uranium amongst other elements but not for Selenium. It is a very fine grid with sampling points spaced every 1 km. but the data does not cover the entire country; only about 15% of the country has been covered. This data has been extrapolated per geological unit to areas that are not covered to show a greater coverage using a geographical information system (GIS) ARCGIS 8 software (ESRI, 2001).

4.2 Sampling Studies

This study required verification sampling in areas of the country where predicted occurrence of arsenic, selenium and uranium could be verified. Two sets of data have been collected for the purposes of this study.

4.2.1 Field sampling data from the University of Pretoria, Department of Animal and Wildlife Sciences.

The data set consists of an analyses of groundwater samples for a broad range of trace constituents that are prevalent as potentially hazardous constituents. The samples were taken from sources used for drinking purposes in several rural communal areas (12 communities in 2 Provinces). Data was collected by Dr James Meyer of University of Pretoria during a study of the livestock health issues caused by livestock drinking groundwater containing potentially hazardous trace constituents. The data was obtained by sampling various water points such as boreholes, hand pumps, water tanks and drinking troughs, all having as their source groundwater. Analyses were primarily concerned with concentrations at intake by the host at point of use and speciation was not recorded. Chemical analyses of the water samples were conducted by ICP-AES techniques (inductively coupled plasma atomic emission spectrometry) by the Institute for Soil Climate and Water at the Agricultural Research Council, Pretoria, using full quantitative and semi-quantitative procedures.

The limitations of this data set for geochemical evaluation of aquifer water quality and natural hydrogeochemical conditions is that samples may not be representative of

hydrogeochemical composition as it occurs in the aquifer due to changes in Eh conditions that occur between the aquifer and point of use.

4.2.2 Field sampling data obtained by the project

Groundwater samples from 3 communities in the same areas as the first set of field sampling data (4.2.1) were obtained during the course of this study. These communities were located on geological units identified as being potentially arsenic and selenium bearing. The samples were obtained from water supply boreholes in rural areas and in the Pilanesberg National Park. The rural areas are north west of Pretoria in the District of Jericho, and in Capricorn District to the north of Pietersburg. Five duplicate samples were taken, two were from the Pilanesberg; two were from Jericho District and one sample was taken in Capricorn. Samples were taken to characterise natural geochemical conditions in the aquifer rather than intake concentrations by hosts.

Field sampling was carried out at all locations by first purging boreholes by pumping three borehole standpipe volumes to expel casing storage water which had equilibrated with atmospheric conditions and or conditions occurring in the borehole. The water table was allowed time to recover to the static water level. The water was then pumped into and sampled (duplicate samples) in a flow through cell, underwater, to ensure that atmospheric conditions could not alter Eh-pH conditions. Samples were collected in non-reactive sample bottles and no air was allowed to accumulate in these bottles. These sample bottles were stored on ice at a temperature of close to zero degrees Celsius. At the same time, continual measurements of the temperature, pH, Eh (redox potential), dissolved oxygen, conductivity and salinity were taken in the flow through cell to ensure that samples were collected under stable Eh-pH conditions. This sampling method thus gives an indication of the naturally occurring hydrogeochemical composition in the aquifer.

The duplicate samples were transported to two different laboratories within 48 hours continually kept on ice at a temperature close to zero degrees Celsius. The laboratories were the Agricultural Research Council (ARC) laboratory in Pretoria and the University of the Witwatersrand Department of Chemistry in Johannesburg. At the ARC laboratories the samples were analysed using an ICP – MS while at Witwatersrand University the samples were analysed by using ICP – OES – CCD to scan the metals as well as ion chromatography and voltametry to determine speciation of the elements arsenic, uranium and selenium.

Samples were only collected from only one sampling run, hence they do not represent a time series to show any potential seasonal and long term fluctuations.

5. PRODUCTION OF MAPS

The following methodologies were used to produce the accompanying maps.

5.1 Maps of the Geological Occurrence of Arsenic, Selenium and Uranium

5.1.1 Maps of predicted Arsenic, Selenium and Uranium occurrence

Very little documented evidence exists for the occurrence of arsenic and selenium. The presence of these elements was predicted based on the documented occurrence of associated economic commodities (3.2). In the case of arsenic and selenium minerals, these often form in association with metal bearing sulphides (antimony, chromium, coal, copper, gold, molybdenum, phosphates, platinum, lead, tin, uranium, zinc), therefore the possible associations between arsenic and selenium mineralogy and other metal sulphides were selected and used as potential indicators of the Formations in which arsenic is most likely to occur.

Uranium occurrence is well documented in South Africa, and is based on extensive exploration from the 1940s-1970s. Each documented occurrence was plotted in order to identify the geological Formation in which occurs.

All the Geological Units considered to be associated with arsenic or selenium bearing sulphide minerals, and Formations with known uranium mineralisation, were selected using ARCGIS 8 (ESRI, 2001) on the Digital South African Geological Map at 1:1000 000 scale and these units were extracted as separate shapefiles. Separate shapefiles were compiled for each of the elements arsenic, uranium and each of the individual associated sulphide minerals (antimony, arsenic, chromium, coal, pseudo-coal, copper, gold, iron, lead, manganese, molybdenum, phosphate, platinum, sulphur, tin, uranium, zinc). These were subsequently merged. The result of this process were three separate coverages or layers of target Geological Units for arsenic, selenium and uranium.

In some cases, the entire Unit is not associated with mineralisation, since mineralisation is related to hydrothermal alteration or other geological processes. For example, the uranium province of the Karoo is restricted to the southwest margin of the Beaunfort Group in the Karoo Supergroup. The Boundaries of the uranium province are not lithological and hence are not depicted on the geological map. The same situation can be said to apply to coal provinces; coal deposits do not necessarily occur across an entire mapped geological unit that is known to be coal bearing.

Where a limited mineralised domain was suspected for a unit, the target unit maps were clipped with mineralogical polygons created from the Metallogenic map of South Africa and the SAMINDABA commodity point data (5.1.2).

5.1.2 Map of Arsenic and Uranium occurrence based on the Metallogenic map of South Africa

The digital format 1:1000 000 scale Metallogenic Map of South Africa contains point data and spatial data on the distribution of various metals and elements occurring in

South Africa in the form of mineral lines and mineral provinces, and point data of known occurrences from the SAMINDABA database. Using ARCGIS 8, polygons were created from relevant mineral lines and mineral provinces (pseudo-polygons) displayed on this map for the elements arsenic and uranium, as well as for the constituents and elements associated with arsenic (antimony, arsenic, chromium, coal, pseudo-coal, copper, gold, iron, lead, manganese, molybdenum, phosphate, platinum, sulphur, tin, uranium, zinc). These lines and polygons were saved as polygons in shapefile format. Commodity point data for sulphide metals deemed to be in association with arsenic were separately converted into polygons by drawing lines around conglomerations of like commodity points. The uranium commodity points were also extracted from the SAMINDABA database to create polygons of uranium occurrence. These polygons were used to clip the map of target Geological Units produced in 5.1.1 so that only portions of a geological unit associated with relevant mineralisation were included in the target maps.

The polygons created from the metallogenic map were also produced as maps of documented occurrence of arsenic and uranium.

5.2 Map of Potential Arsenic Occurrence in Groundwater

The maps of predicted geological occurrence of arsenic, uranium and selenium represent regions of South Africa portray where these elements are likely to occur in elevated concentrations in the rock mass and soil. In these regions groundwater could potentially contain naturally occurring arsenic, uranium or selenium constituents, depending on redox conditions (2.4) and mobilisation processes (2.5).

These maps, therefore, do not suggest that arsenic, uranium or selenium occurs in the groundwater of the identified regions. They merely suggest that if these elements do occur in South Africa, they would most likely occur in areas where arsenic, uranium or selenium is found in the host geology and could be mobilised depending on Eh-pH conditions.

In order to compile a map of the risk of occurrence in groundwater, borehole data from National Groundwater Quality Monitoring Network (ZQM) was overlain with the map of predicted arsenic occurrence. Zones of High, Medium and Low Risk were defined as follows:

- High Risk: Predicted arsenic occurrence and arsenic concentrations of greater than 0.1 mg/l in ZQM boreholes.
- Medium Risk: Predicted arsenic occurrence but less than 0.1 mg/l of arsenic in ZQM boreholes.
- Low Risk: No predicted arsenic occurrence or detection in groundwater.

Similar maps could not be compiled for uranium and selenium, since no data is available in the ZQM.

5.3 Map of Sediment Sampling Surveys

The helicopter Stream Sediment Geochemical Sampling Survey of the Council for Geoscience contains data for arsenic and uranium, amongst other elements, but not for selenium. It is a very fine grid with sampling points spaced every 1 km, but the data covers only the northern portion of the west coast and the northern to northwestern portion of the country. The data points exceeding 40 ppm are shown as concentrations in raw sediment.

This data was overlain and merged with polygons of the South African 1:1000000 Geological Map using ARCGIS 8, permitting concentration data to be attributed to specific geological units. The distribution of concentration values in each unit was observed to be highly skewed. In order to derive an average value that would be representative for each polygon, the data was treated geostatistically to reduce the influence of extreme end member concentration values. This was done by exporting the ARCGIS 8 data table of concentration values for arsenic and uranium in each geological unit, as well as the unique key linking these concentration values to a particular unit of the South African Geological map, into the MATLAB program AD (Kijko, 2002). Since the distribution of data was highly skewed, the program AD first transformed all arsenic and uranium concentration values (occurring as points) using a square root transformation to eliminate the effect of extreme end members.

In the second step, for each unique key code representing a geological unit the arithmetic mean of the square root transformed values was calculated. In the third step, all the mean of the square root transformed data for each key code were squared to obtain the mean arsenic and uranium concentration of each geological unit.

This geostatistical treatment resulted in a more extensive coverage for arsenic and uranium, since the mean values were extrapolated to all lithologically identical geological units across the country. However, it must be stressed that in many cases arsenic and uranium concentrations may not be based on the primary lithology of a geological unit, but on secondary mineralisation, which may be highly localised in nature. Consequently, the mean of concentration values may not be representative of localised concentrations, and the extrapolation of data to identical lihologies in other areas of the country may not be valid.

6. FIELD EVIDENCE

6.1 National Groundwater Quality Monitoring Network (ZQM)

The map of potential arsenic occurrence in groundwater shows point measurements of arsenic derived from boreholes of the ZQM. In total 1514 boreholes in South Africa have been sampled for arsenic. Of these 252 contained measurable arsenic. Figure 6-1 shows the distribution of arsenic concentrations in these boreholes. 200 of these boreholes had concentrations exceeding the WHO limits (0.01 mg/l), and over 40 had concentrations exceeding 0.1 mg/l.

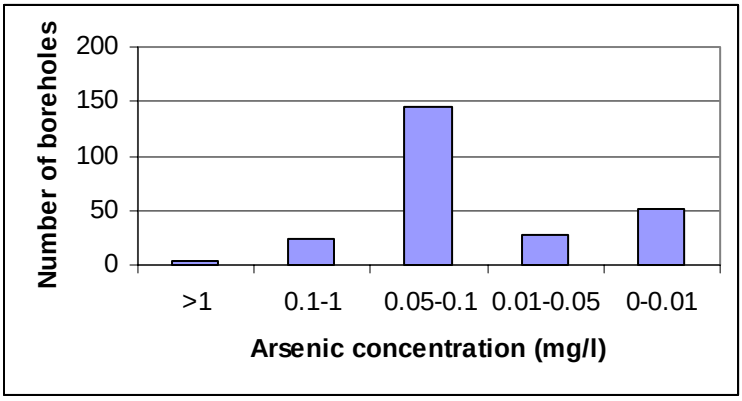

Figure 6-1 Distribution of Arsenic concentrations in boreholes sampled for arsenic in South Africa.

The geological units in which the arsenic bearing boreholes are located are shown in table 6-1. However, the poor borehole co-ordinates of the data may result in several inaccuracies in attributed geological units. The majority of the units observed to contain arsenic bearing boreholes were identified in Section 3 as being potentially As bearing. The exceptions that were not identified as being arsenic bearing were the Quaternary deposits and the Kirkwood Formation, which contain no known sulphide mineralisation. In these units the source of arsenic is believed to be the sorbed component on iron and manganese oxides in unconsolidated sediment. Rocks of the Table Mountain Group also contain an unknown source of arsenic. The source of arsenic may be related to the weathering of the ferric iron rich quartzites.

The results may also not be comprehensive, since many geological units contain no monitoring boreholes, have never been sampled for arsenic, or contain samples taken from localities not subjected to localised sulphide mineralisaton.

High concentrations of arsenic (observed concentrations >0.1 mg/l) are recorded in the following geological units:

- Tygerberg Formation of the Malmesbury Group: One borehole north of Cape Town records a concentration of 10 mg/l of arsenic. It has been intruded by Cape Granites, and as a result has been hydrothermally altered and may contain veins including copper tin and molybdenum sulphides.

- Timeball Hill and Rooihoogte Formation: One borehole west of Potchefstroom contains 7 mg/l of arsenic. Arsenic is associated with stratiform gold-quartz-carbonate-sulphide veins.
- Kirkwood Formation: Eight boreholes in the Algoa basin contain arsenic concentrations between 0.25-1.6 mg/l. No sulphide minerals exist in this Formation, however, the Formation is a marine shale with abundant organic material. Arsenic is believed to occur due to desorption from iron and manganese oxides following pumping induced oxidation.
- Kalahari Group: One borehole located north of Sishen contains 0.5 mg/l of arsenic. The arsenic is believed to be related to the underlying Dwyka group, which contains black shales.
- Adelaide Subgroup: Nine boreholes in the southwestern Karoo basin in the vicinity of Beaufort West contain arsenic concentrations between 0.13-0.3 mg/l. Arsenic is associated with roll front uranium deposits.
- Quaternary deposits: Four boreholes in the sands of the Cape Flats contain 0.11-0.14 mg/ of arsenic. The source of arsenic is unknown, but it may be related to the release of sorbed arsenic from the dissolution of arsenic-bearing hydrous oxides due to changes in Eh-pH.
- Volksrust Formation: 3 boreholes north of Calvinia contain between 0.14-0.2 mg/l of arsenic. The arsenic is believed to be associated with carbonaceous black shale.

Table 6-1 Geological Units in which arsenic above WHO limits has been documented in ZQM groundwater database.

SBGRP= Subgroup, SUI = Suite, FM= Formation, SPGRP = Supergroup, GRP = group

Unit		Predicted Arsenic association
ADELAIDE	SBGRP	Roll front uranium
BITTERFONTEIN	SBGRP	Sedimentary and volcanogenic exhalative deposits or sedimentary stratiform ore deposits
CAPE GRANITE	SUI	Porphyry copper, tin granophile, molybdenum
CERES	SBGRP	Black shale
ECCA	GRP	Rollfront uranium, black/ carbonaceous shales, peat and coal deposits
ENON	FM	Dependent on nature of source material of conglomerate matrix
GARIEP	SPGRP	Molybdenum, lead mineralisation
HOUT RIVER GNEISS	NONE	Gold bearing veins
IRRIGASIE	FM	Coal
KALAHARI	GRP	
KAMIESKROON GNEISS	NONE	
KAROO DOLERITE	SUI	
KIRKWOOD	FM	Desorption from iron and manganese oxides
KLIPRIVIERSBERG	GRP	Placer gold
LEBOWA GRANITE	SUI	Tin granophile, copper, gold, molybdenum and lead bearing hydrothermal veins
LETABA	FM	coal
MALALA DRIFT	GRP	Copper bearing veins

MALMANI	SBGRP	Hydrothermal copper, gold, lead
MOLENDRAAI MAGNETITE GABBRO	NONE	Hydrothermal copper
MOORREESBURG	FM	Black shales of the Malmesbury Group
NABABEEP GNEISS	NONE	Granite vein deposits
NARDOUW	SBGRP	
PENGE	FM	Hydrothermal copper and lead
PIKETBERG	FM	Molybdenum
PRETORIA	GRP	Tin, zinc
PRINCE ALBERT	FM	Black shale
QUATERNARY	SYS	
SILVERTON	FM	Black shale, lead
SUNDAYS RIVER	FM	Desorption from iron and manganese oxides
TABLE MOUNTAIN	GRP	
TIERBERG	FM	Carbonaceous shale
TYGERBERG	FM	Black shale, hydrothermal alteration related to Cape Granites
VOLKSRUST	FM	Coal

6.2 Field Sampling

Field sampling data exists from two sources. The first source of data is from the University of Pretoria and is data for arsenic and selenium from rural areas in four main areas to the north of Pretoria (4.2.1). The second source of data is the field sampling data that was obtained in the course of this study (4.2.2).

The first source of data desribed in 4.2.1 (University of Pretoria) occurs in four sampling location areas, where 12 rural community water supply schemes were sampled. The first sampling location area is in three villages to the north of Pietersburg located on the Matok Granite of the Bandolierskop Complex and in Hout River Gneiss. The area has been identified as potentially arsenic and selenium bearing due to gold associated with quartz veins (3.2.1). Of 6 samples recorded, 4 exceed the guidelines for As and 1 for Se. The recorded range is 0.002-0.09 mg/l for As and 0.01-0.09 mg/l for Se.

The second sampling location area is in the Immerpan resettlement district SE of Potgietersrus and is underlain by the Letaba and Irrigasie Formations, associated with coal and carbonaceous shale (3.2.1). Of 23 samples recorded, 10 exceed the guidelines for As and 7 for Se. The recorded range is 0.003-0.095 mg/l for As and 0.013-0.258 mg/l for Se.

The third sampling location consists of villages in the Jericho District north of Brits and is also underlain by the Irrigasie Formation. Of 18 samples recorded, 9 exceed the guidelines for As and 12 for Se. The recorded range is 0-0.288 mg/l for As and 0-1.526 mg/l for Se.

The fourth sampling location area is in the Pilanesburg National Park and is underlain by the Pilansberg Alkaline Complex and the Lebowa Granite Suite, known to be associated with uranium bearing foyatite and syenite and with copper mineralisation (3.2.2). Of 43 samples recorded, 32 exceed the guidelines for As and 39 for Se. The recorded range is 0.002-0.09 mg/l for As and 0.017-0.522 mg/l for Se.

Table 6.2 provides an indication of those water quality constituents (WQC) that are prevalent as potentially hazardous constituents (PHC). Potentially hazardous constituents occurring in all of the areas are designated as “High Incidence”, those in more than one area as “Medium Incidence”, whilst those for only a single area are designated as “Isolated Incidence”. Samples were obtained from the point of use, and whilst not affording an opportunity to determine speciation and aquifer specifics, do indicate relevant changes in water collection, distribution and storage, as they affect the user. The data indicates that arsenic and selenium concentrations in excess of accepted limits is widespread.

Table 6-2. Main potentially hazardous constituents recorded in groundwater in the communal areas. (Casey & Meyer, 2001)

WQC	PHC	COC	Average (mg/L)	Incidence
As	40	3	0.022	High
Be	87	0	0.0188	High
Br	130	0	1.192	High
Hg	56	3	0.0397	High
Se	91	2	0.1705	High
Ti	58	9	0.323	High
Sr	0	126	0.501	High
F	51	3	2.184	Medium
Te	56	6	0.0777	Medium
Mo	29	9	0.0307	Medium
Mn	66	0	0.16	Medium
Zn	0	21	0.158	Medium
V	1	21	0.014	Medium
Sb	28	0	0.037	Isolated
Cd	30	3	0.023	Isolated
Cr	4	15	0.039	Isolated
Tl	22	0	0.016	Isolated
Pb	28	1	0.026	Isolated

PHC = observed value exceeds guideline limit.

COC = observed value within 10% of guideline limit.

The second source of data is the results of field sampling carried out during the course of this study. The field sampling points were undertaken at the some of the same villages as those from the University of Pretoria survey. These locations are at the Village of Sekakene to the north of Pietersburg (two sample points), in the Pilanesberg National Park (two sample points) and in the Jericho district at the Kalkbank Village (one sample point). These represent samples collceted at one moment in time only and may not be representative of long term average

concentrations. The analytical data is shown in Appendix 1 and summarised in table 6-3. The University of Witwatersrand results based on ion chromatography appear suspect since a poor ion balance is evident. The ARC laboratory results produce an ion balance.

Although arsenic and selenium concentrations are below WHO guidelines in boreholes SP1 and SP2, antimony exceeds WHO guidelines (0.005 mg/l). Antimony (Sb) is often associated with gold, indicating that the boreholes are in contact with gold bearing quartzitic veins. In borehole SP3 antimony, gold and molybdenum exceed WHO guidelines. In boreholes SP4 and SP5, antimony and bismuth concentrations exceed WHO guidelines. The presence of antimony and molybdenum in water samples indicates that the boreholes do strike zones mineralised with sulphide metals.

The results show that As occurs primarily as As+5 when oxidising conditions are present, such as in SP1 and SP2. In borehole SP3 strongly reducing and alkaline conditions, hence As+3 is expected to be the dominant species (figure 2-2.). Thee As+5:As+3 ratio is closer to 1, as expected. Boreholes SP4 and SP5 are mildly reducing and As+3 is predicted to be dominant.

All measured As concentrations are below the 0.01 mg/l WHO standard. Concentrations are generally lower than those indicated by the University of Pretoria study. This can be attributed to the University samples being taken at the point of ingestion, which allows for sufficient standing time for samples to equilibrate with atmospheric conditions and for metals to desorb from oxides according to the oxidation model of arsenic desorption.

The low arsenic concentrations from this study imply that weathering of sulphides has not taken place to a significant extent, or arsenic released by weathering has sorbed onto ferrous oxides that form from the weathering of pyrites. The occurrence of arsenic bearing minerals in lithological units does therefore not necessarily imply that arsenic will be present in groundwater. The maps of predicted arsenic occurrence must therefore be interpreted as regions where there is a risk of arsenic being mobilised into groundwater.

Table 6-3 Summary of data from field verification studies

Village	**Sekakene**		**Pilansberg**		**Kalkbank**
Sample	SP1	SP2	SP4	SP3	SP5
Geological Unit	Matok Granite	Matok Granite	Lebowa Granite	Pilansberg Complex	Irrigasie
Eh (mV)	138	237	30	-243	51
PH	7.39	7.14	6.85	10.5	7.2
Predicted As phase	$H_2AsO_4^-$ (As+5)	$H_2AsO_4^-$ (As+5)	H_3AsO_3 (As+3)	AsS_2^- (As+3)	H_3AsO_3 (As+3)
Predicted U phase	$UO_2(CO_3)_2^{2-}$	$UO_2(CO_3)_2^{2-}$	$UO_2(HPO_4)_2^{2-}$	$UO_2(CO_3)_3^{4-}$	$UO_2(HPO_4)_2^{2-}$
Predicted Se phase	$HseO_3^-$	$HSeO_3^-$	Se	Se_2^{2-}	Se
Predicted As risk	Medium	Medium	High	Medium	Medium
Predicted U risk	Low	Low	Low	Medium	Medium
Predicted Se risk	Medium	Medium	Medium	Medium	Medium
Total As (mg/l)	0.0035	0.002	0.005	0.005	0.003
As+3 (mg/l)	0.0015	0.0005	0.00167	0.0025	0.00134

As+5 (mg/l)	0.0020	0.0015	0.00333	0.00275	0.00166
As+5:As+3 ratio	1.33	3	1.99	1.1	1.19
UO_2^{2+} (mg/l)	0.00046	0.0006	0.0005	0.00625	0.00668
Se+4 (mg/l)	0.0026	0.004	0.0038	0.0032	0.0052
Total As (mg/l) U. of Pretoria	0.006-0.018		0-0.08		
Se+4 (mg/l) U. of Pretoria	0.01-0.09		0.04-0.52		
As risk from Drinking Water standards	None	None	Low	Low	None
U risk from Drinking Water standards	None	None	None	None	None
Se risk from Drinking Water standards	None	None	None	None	None

6.3 Conclusions

The study found that little documentation on the geological occurrence of arsenic and selenium exists for South Africa, however, the wealth of literature on economic mineralisation permits a regional prediction of the possibility of occurrence of arsenic and selenium bearing minerals. This information has been used to derive maps of predicted arsenic and selenium geological occurrence. By comparison, uranium occurrence in South African geology is well documented.

An understanding of the extent of mobilisation of arsenic, uranium and selenium into groundwater occurrence is problematical for the following reasons:

- The occurrence of arsenic in groundwater is unknown in many geological units suspected to contain arsenic, since many geological units contain no monitoring boreholes, have never been sampled for arsenic, or contain samples taken from localities not subjected to localised sulphide mineralisaton.

- Little or no data exists to verify the extent of selenium and uranium in groundwater on a national scale since the National Monitoring Network (ZQM) does not monitor these parameters

- Boreholes of the ZQM are not necessarily sited to monitor trace constituents

- The lack of Eh data and the poor quality of most pH data prevents an identification of regions where redox and pH conditions are suitable for mobilisation of trace constituents.

- Their mobilisation is dependent on Eh and pH conditions, which may vary over time, especially in surroundings experiencing water level fluctuations due to pumping, consequently trace constituent concentrations may vary in time.

- The potential difference in trace constituent concentration over time in boreholes after drilling and its dependence on pumping regimens, suggests long term monitoring is required

Field studies in 12 localities in 4 Districts identified as being potential arsenic and selenium bearing due to sulphide mineralisation found that arsenic and selenium incidence is high when sampled at point of use. However, 5 samples taken from purged boreholes in these localities found that arsenic is not necessarily present in the dissolved phase in groundwater above WHO guideline concentrations. Nationwide, 200 boreholes of 1514 boreholes sampled nationally for arsenic have been found to contain arsenic concentrations above WHO standards.

6.4 Recommendations

Due to the lack of national scale long term monitoring of trace constituents in groundwater, it has not been possible to verify whether trace constituents occurred in the dissolved phase in the identified target zones. As an alternative, it is recommended that livestock, blood chemistry, and other health related data be used to provide clinical biochemistry information for the purpose of validating predicted high-risk areas and communities.

A generic level risk assessment (using fixed tabulated guideline values) is recommended as the first step in determining baseline hazardous exposures for various trace constituents in the geochemical environment that may contribute to adverse effects on health, productivity, and product quality. Any potential hazards identified would then require further site-specific investigation regarding the water chemistry, soil composition, animal and human health.

In high risk areas, a water quality monitoring programme is essential in order to assess dose and intake levels from water borne pathways. Monitoring of pumping boreholes in geological units suspected of containing arsenic, uranium and/or selenium should therefore be initiated.

The use of geochemical speciation models may also play a role in providing further information on the dissolution and mobilisation of trace constituents. The use of a predictive model in areas where naturally-occurring and industry-related hazardous constituents are known or suspected to occur a vital component to understanding expected concentration trends and to:

- Prevent adverse effects on human and animal users of groundwater,
- Improve the sustainability of animal production in communal systems,
- Provide meaningful and scientifically founded risk-management strategies.

The study has identified regions where naturally occurring As, Se and U are present, hence has identified regions where monitoring can be focused in future.

It is recommended that:

- Monitoring of pumping boreholes in geological units suspected of containing arsenic, uranium and/or selenium as well as other trace constituents should be initiated
- A comprehensive analysis of the full spectrum of trace constituents be initiated

- Clinical data from health and agricultural sources, such as blood chemistry of livestock and other toxicity tests, be used to supplement geological data on the occurrence and mobility of trace constituents and identify problem areas
- Sampling be undertaken both at source (borehole) and point of use of water (tap) to identify mobilisation and transport pathways, as well as risk of exposure.
- A follow up study be undertaken to verify the occurrence of trace constituents in areas identified as being at risk, and to clarify policy issues as a basis to safeguard people and livestock against harmful constituents ingested through drinking water.

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APPENDIX 1

SP 1			
Parameters	**Field**	**ARC Laboratory**	**Witwatersrand University Laboratory**
pH	**7.39**	**8.07**	
Lab Conductivity (mS/m) at 25 ºC		**236**	
Field Conductivity (mS/cm)	**2.430**		
Temp (° C)	**22.7**		
ORP Ag/AgCl (mV)	**138**		
Salinity (% wt)	**1.1**		
Dissolved Oxygen (mg/l)	**1.3**		
Dissolved Oxygen (% sat.)	**16.0**		
X-Coordinate	**29,7002**		
Y-Coordinate	**23,5191**		
Total Alkalinity ($CaCO_3$) titrant 0.01341M H_2SO_4 **(mg/l)**			**571.76**
Alkalinity		**395**	
Temporary Hardness		**395**	
Permanent Hardness		**80.76**	
Total Dissolved Solids		**1505.05**	
Undissociated Ions (mg/l)	**Field**	**ARC Laboratory**	**Witwatersrand University Laboratory**
Sodium Carbonate		**0**	
Sodium Bicarbonate		**0**	
Anions (mg/l) measured using Ion Chromatography	**Field**	**ARC Laboratory (mg/l)**	**Witwatersrand University Laboratory (mg/l)**
Fluoride (1.5)		**4.19**	**3.51**
Nitrite (4.0)		**0**	**0.36**
Nitrate (44.0)		**344.64**	**1665.575**
Chloride (250)		**297.74**	**1290.705**
Sulphate (500)		**175.73**	**437.4**
Phosphate		**0**	**nd**
Carbonate (20.0)		**0**	**571.76**
Bicarbonate		**481.9**	
Cations measured using Inductively Coupled Plasma Spectrometry	**Field**	**ARC Laboratory (mg/l)**	**Witwatersrand University Laboratory (ug/l)**
Sodium (400)		**283.27**	
Potassium (400)		**10.99**	
Calcium (200)		**83.29**	
Magnesium (100)		**64.22**	
Boron (1.5)		**0.25**	
Uranium(VI) UO_2^{2+}			**0.46**
Selenium(IV)			**2.6**
Arsenic (total)			**3.5**
Arsenic (III)			**1.50**
Arsenic (V)			**2.00**
Additional Metals (mg/l) measured using Inductively Coupled Plasma Spectrometry detection limit 10 ug/l	**Field**	**ARC Laboratory**	**Witwatersrand University Laboratory (mg/l)**
Li			**0.0256**
Be			**0.0086**
B			**0.0565**
Na			**34.27**
Mg			**75.9**
Si			**1.22**
P			**0.023**
K			**22.13**
Ca			**93.4**
Fe			**0.0839**
Ni			**0.0368**
Zn			**0.1033**
Ga			**0.2331**
Sr			**1.16**
Sb			**0.69**
Ba			**0.1176**
Ir			**0.023**

SP 2			
Parameters	**Field**	**ARC Laboratory**	**Witwatersrand University Laboratory**
pH	7.14	7.3	
Lab Conductivity (mS/m) at 25 ºC		195	
Field Conductivity (mS/cm)	1.953		
Temp (° C)	23.8		
ORP Ag/AgCl (mV)	237		
Salinity (% wt)	0.8		
Dissolved Oxygen (mg/l)	2.81		
Dissolved Oxygen (% sat.)	37.3		
X-Coordinate	29,6941		
Y-Coordinate	23,4638		
Total Alkalinity ($CaCO_3$) titrant 0.01341M H_2SO_4 **(mg/l)**			604.64
Alkalinity		410	
Temporary Hardness		370.15	
Permanent Hardness		0	
Total Dissolved Solids		1244.9	
Undissociated Ions (mg/l)	**Field**	**ARC Laboratory**	**Witwatersrand University Laboratory**
Sodium Carbonate		0	
Sodium Bicarbonate		66.95	
Anions (mg/l) measured using Ion Chromatography	**Field**	**ARC Laboratory (mg/l)**	**Witwatersrand University Laboratory (mg/l)**
Fluoride (1.5)		2.13	1.465
Nitrite (4.0)		0	0.37
Nitrate (44.0)		328.93	1293.77
Chloride (250)		180.87	381.975
Sulphate (500)		113.72	164.12
Phosphate		0	nd
Carbonate (20.0)		0	604.64
Bicarbonate		500.2	
Cations measured using Inductively Coupled Plasma Spectrometry	**Field**	**ARC Laboratory (mg/l)**	**Witwatersrand University Laboratory (ug/l)**
Sodium (400)		234.77	
Potassium (400)		15.79	
Calcium (200)		77.59	
Magnesium (100)		41.53	
Boron (1.5)		0.39	
Uranium(VI) UO_2^{2+}			0.6
Selenium(IV)			4
Arsenic (total)			2
Arsenic (III)			0.5
Arsenic (V)			1.5
Additional Metals (mg/l) measured using Inductively Coupled Plasma Spectrometry detection limit 10 ug/l	**Field**	**ARC Laboratory**	**Witwatersrand University Laboratory (mg/l)**
Li			0.0302
Be			0.0076
B			0.083
Na			21
Mg			53.5
Si			0.457
P			0.0391
K			21.34
Ca			83.6
Ni			0.0313
Cu			0.0393
Zn			0.0982
Ga			0.2412
Sr			1.044
Sb			0.4451
Ba			0.0791
Ir			0.022

SP 3			
Parameters	**Field**	**ARC Laboratory**	**Witwatersrand University Laboratory**
pH	**10.5**	**10.42**	
Lab Conductivity (mS/m) at 25 ºC		**181**	
Field Conductivity (mS/cm)	**1.868**		
Temp (° C)	**22.8**		
ORP Ag/AgCl (mV)	**-243**		
Salinity (% wt)			
Dissolved Oxygen (mg/l)	**0.21**		
Dissolved Oxygen (% sat.)	**2.7**		
X-Coordinate	**27,2255**		
Y-Coordinate	**25,2333**		
Total Alkalinity ($CaCO_3$) titrant 0.01341M H_2SO_4 **(mg/l)**			**697.25**
Alkalinity		**560**	
Temporary Hardness		**3.69**	
Permanent Hardness		**0**	
Total Dissolved Solids		**967.25**	
Undissociated Ions (mg/l)	**Field**	**ARC Laboratory**	**Witwatersrand University Laboratory**
Sodium Carbonate		**302.1**	
Sodium Bicarbonate		**455.81**	
Anions (mg/l) measured using Ion Chromatography	**Field**	**ARC Laboratory (mg/l)**	**Witwatersrand University Laboratory (mg/l)**
Fluoride (1.5)		**86.19**	**65.619**
Nitrite (4.0)		**0**	**nd**
Nitrate (44.0)		**1.01**	**0.035**
Chloride (250)		**138.44**	**226.445**
Sulphate (500)		**58.35**	**50.89**
Phosphate		**0**	**nd**
Carbonate (20.0)		**171**	**697.25**
Bicarbonate		**335.5**	
Cations measured using Inductively Coupled Plasma Spectrometry	**Field**	**ARC Laboratory (mg/l)**	**Witwatersrand University Laboratory (ug/l)**
Sodium (400)		**338.85**	
Potassium (400)		**5.42**	
Calcium (200)		**0.49**	
Magnesium (100)		**0.16**	
Boron (1.5)		**0.13**	
Uranium(VI) UO_2^{2+}			**6.25**
Selenium(IV)			**3.2**
Arsenic (total)			**5**
Arsenic (III)			**2.25**
Arsenic (V)			**2.75**
Additional Metals (mg/l) measured using Inductively Coupled Plasma Spectrometry detection limit 10 ug/l	**Field**	**ARC Laboratory**	**Witwatersrand University Laboratory (mg/l)**
Li			**0.0146**
Be			**0.0091**
B			**0.0395**
Na			**119.4**
Mg			**0.0074**
Si			**1.14**
K			**16.29**
Ca			**0.4735**
Fe			**0.0389**
Ni			**0.0137**
Ga			**0.2709**
Sr			**0.0787**
Mo			**0.0422**
Sb			**0.93**
Ba			**0.0077**
W			**0.1268**
Au			**0.0845**

SP 5			
Parameters	**Field**	**ARC Laboratory**	**Witwatersrand University Laboratory**
pH	**7.20**	**8.2**	
Lab Conductivity (mS/m) at 25 ºC		**165**	
Field Conductivity (mS/cm)	**1.694**		
Temp (° C)	**23.7**		
ORP Ag/AgCl (mV)	**51**		
Salinity (% wt)	**0.7**		
Dissolved Oxygen (mg/l)	**4.49**		
Dissolved Oxygen (% sat.)	**54.1**		
X-Coordinate	**27,9905**		
Y-Coordinate	**25,2894**		
Total Alkalinity ($CaCO_3$) titrant 0.01341M H_2SO_4 **(mg/l)**			**695.23**
Alkalinity		**430**	
Temporary Hardness		**211.7**	
Permanent Hardness		**0**	
Total Dissolved Solids		**955.7**	
Undissociated Ions (mg/l)	**Field**	**ARC Laboratory**	**Witwatersrand University Laboratory**
Sodium Carbonate		**0**	
Sodium Bicarbonate		**366.75**	
Anions (mg/l) measured using Ion Chromatography	**Field**	**ARC Laboratory (mg/l)**	**Witwatersrand University Laboratory (mg/l)**
Fluoride (1.5)		**1.82**	**1.03**
Nitrite (4.0)		**0**	**nd**
Nitrate (44.0)		**134.04**	**1339.405**
Chloride (250)		**177.93**	**1660.48**
Sulphate (500)		**61.11**	**69.66**
Phosphate		**0**	**nd**
Carbonate (20.0)		**0**	**695.23**
Bicarbonate		**524.6**	
Cations measured using Inductively Coupled Plasma Spectrometry	**Field**	**ARC Laboratory (mg/l)**	**Witwatersrand University Laboratory (ug/l)**
Sodium (400)		**232.98**	
Potassium (400)		**18.56**	
Calcium (200)		**42.38**	
Magnesium (100)		**24.84**	
Boron (1.5)		**0.26**	
Uranium(VI) UO_2^{2+}			**6.68**
Selenium(IV)			**5.2**
Arsenic (total)			**3**
Arsenic (III)			**1.34**
Arsenic (V)			**1.66**
Additional Metals (mg/l) measured using Inductively Coupled Plasma Spectrometry detection limit 10 ug/l	**Field**	**ARC Laboratory**	**Witwatersrand University Laboratory (mg/l)**
Li			**0.0346**
Be			**0.0028**
B			**0.0589**
Na			**43.58**
Mg			**26.12**
Si			**0.72**
K			**29.24**
Ca			**49.24**
Fe			**0.0572**
Ni			**0.026**
Zn			**0.1213**
Ga			**0.2707**
Sr			**1.4**
Rh			**0.0515**
Sb			**0.568**
Ba			**0.0764**
Bi			**0.71**

SP 4			
Parameters	**Field**	**ARC Laboratory**	**Witwatersrand University Laboratory**
pH	6.85	6.94	
Lab Conductivity (mS/m) at 25 ºC		32	
Field Conductivity (mS/cm)	0.308		
Temp (° C)	24.1		
ORP Ag/AgCl (mV)	30		
Salinity (% wt)	0		
Dissolved Oxygen (mg/l)	1.8		
Dissolved Oxygen (% sat.)	32.1		
X-Coordinate	27,1405		
Y-Coordinate	25,2605		
Total Alkalinity ($CaCO_3$) titrant 0.01341M H_2SO_4 **(mg/l)**			194.6
Alkalinity		147.5	
Temporary Hardness		39.02	
Permanent Hardness		0	
Total Dissolved Solids		141.03	
Undissociated Ions (mg/l)	**Field**	**ARC Laboratory**	**Witwatersrand University Laboratory**
Sodium Carbonate		0	
Sodium Bicarbonate		182.24	
Anions (mg/l) measured using Ion Chromatography	**Field**	**ARC Laboratory (mg/l)**	**Witwatersrand University Laboratory (mg/l)**
Fluoride (1.5)		2.24	0.379
Nitrite (4.0)		0	0.2
Nitrate (44.0)		0.04	0.45
Chloride (250)		2.02	0.135
Sulphate (500)		0.15	0.18
Phosphate		0	nd
Carbonate (20.0)		0	194.6
Bicarbonate		179.95	
Cations measured using Inductively Coupled Plasma Spectrometry	**Field**	**ARC Laboratory (mg/l)**	**Witwatersrand University Laboratory (ug/l)**
Sodium (400)		28.41	
Potassium (400)		4.04	
Calcium (200)		12.5	
Magnesium (100)		1.89	
Boron (1.5)		0	
Uranium(VI) UO_2^{2+}			0.5
Selenium(IV)			3.8
Arsenic (total)			5
Arsenic (III)			1.67
Arsenic (V)			3.33
Additional Metals (mg/l) measured using Inductively Coupled Plasma Spectrometry detection limit 10 ug/l	**Field**	**ARC Laboratory**	**Witwatersrand University Laboratory (mg/l)**
Li			0.0047
Be			0.0069
B			0.0075
Na			3.492
Mg			1.91
Si			0.609
P			0.1399
K			5.02
Ca			14.12
Mn			0.0266
Fe			0.1981
Ni			0.0126
Zn			0.0363
Ga			0.2202
Sr			2.46
Rh			0.042
Sb			0.58