A GEOHYDROLOGICAL ASSESSMENT OF ARSENIC AS A CONTAMINANT IN THE JAGERSFONTEIN AREA AND REMEDIATION OPTIONS

By

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DECLARATION

I, Famah Fortunata Immaculata Bijengsi, hereby declare that this thesis submitted to the Institute for Groundwater Studies, Faculty of Natural and Agricultural Science, University of the Free State, Bloemfontein, South Africa, as a fulfilment for the degree of Magister of Scientiae, is my own work. This thesis has not been submitted to any other institution of higher education. I further declare that all sources cited have been acknowledged by means of a list of references.

FIB FAMAH

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A Geohydrological Assessment of Arsenic as a Contaminant in the Jagersfontein area and remediation options

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1 General Introduction

Providing clean and safe water to a community is one of the world's most alarming issues (Claesson and Fagerberg, 2003). Jagersfontein; South Africa's oldest diamond-mining town located in the south western part of the Free State province is not an exception. This town is well known for the high quality diamonds that was produced from the now decommissioned mine in the 1870s to 1900s. The diamond mine was first worked from an open pit because the presence of a dolerite sheet made the walls much more stable, underground mining commenced in the1900s. It is now known as the deepest hand excavated hole in the world. Water from this open pit (mine shaft) is being supplied to the community but lately this water's quality has been a call for concern with its high concentration of arsenic.

Arsenic is a metalloid found in the environment and earth's crust. It's presence in groundwater is as a result of natural processes (weathering and dissolution of minerals from rock materials in the aquifer) or artificial or anthropogenic processes (mining activities, use of arsenic containing pesticides and herbicides).

Arsenic in ground water is found in organic and inorganic forms. The organic form of arsenic is associated with carbon, oxygen, and nitrogen, while the inorganic form is present in pyrite. The inorganic form of arsenic is widely dispersed and is more poisonous than the organic form.

Arsenic toxicity has no known effective medicine for treatment, but drinking of arsenic free water can help the arsenic affected people to get rid of the symptoms of arsenic toxicity (Ahmed, 2001). The long-term exposure to arsenic in drinking water causes skin lesions, lung, bladder, and kidney cancers, neurological disorder, muscular weakness, loss of appetite and nausea.

The presence of arsenic in drinking water has adverse effects both on health and social. The only way to shun the toxicity of arsenic in drinking water is to use arsenic-free water source or to get rid of the arsenic from the water.

There are several methods available for removal of arsenic from water in large conventional treatment plants. The most commonly used technologies include oxidation, co-precipitation and adsorption onto coagulated flocs, lime treatment, adsorption onto sorptive media, ion exchange resin and membrane techniques (Cheng *et al.*, 1994; Hering *et al.*, 1996, 1997; Kartinen and Martin, 1995; Shen, 1973; Joshi and Chaudhuri, 1996 cited in Ahmed, 2001).

This study goes to address the issue of the arsenic contamination in the groundwater of Jagersfontein. Therefore to achieve this goal certain objectives must be set and reached.

1.1 Aims and objectives

In order to assess and quantify the extent of arsenic contamination in the Jagersfontein area certain aims and objectives must be met. They include;

- ➢ Carrying out a literature review in order to be enlightened on the degree of arsenic contamination, its sources and impacts worldwide.

- ➢ Studying previous data collected from the study site (by DWA and Bloemwater) for the past years to be able to understand changes occurring in the groundwater.

- ➢ Characterising the groundwater based on macro elements, trace elements, specific element (arsenic) and isotopes (^{18}O, ^2H, ^3H).

- ➢ Assessing the concentration of the arsenic and degree of contamination by means of hydrocensus and sampling.

> ➢ Discuss the efficiency of treatment processes employed in treating water in Jagersfontein and hence propose feasible remediation techniques.

1.2 Dissertation outline

The dissertation is structured in a manner which will address the aims and objectives of this study.

Chapter 1 establishes the general introduction, aims and objectives of the study, thesis outline and background information of study area.

Chapter 2 addresses the literature review on arsenic contamination

Chapter 3 explains how field work was carried out and the description of instruments used.

Chapter 4 follows with the interpretation and discussion of the results of the chemical analysis including the worthiness of treatment processes carried out.

Chapter 5 brings forth the description of the treatment processes currently being used in Jagersfontein to treat arsenic and other possible techniques that could be more effective in treating arsenic contaminated water.

Chapter 6 integrates all the chapters to bring forth suitable conclusions and recommendations.

1.3 Site background information

1.3.1 Location

Jagersfontein; South Africa's oldest diamond-mining town is situated in the southern Free State, about 110 km southwest of Bloemfontein (Figure 1-1).
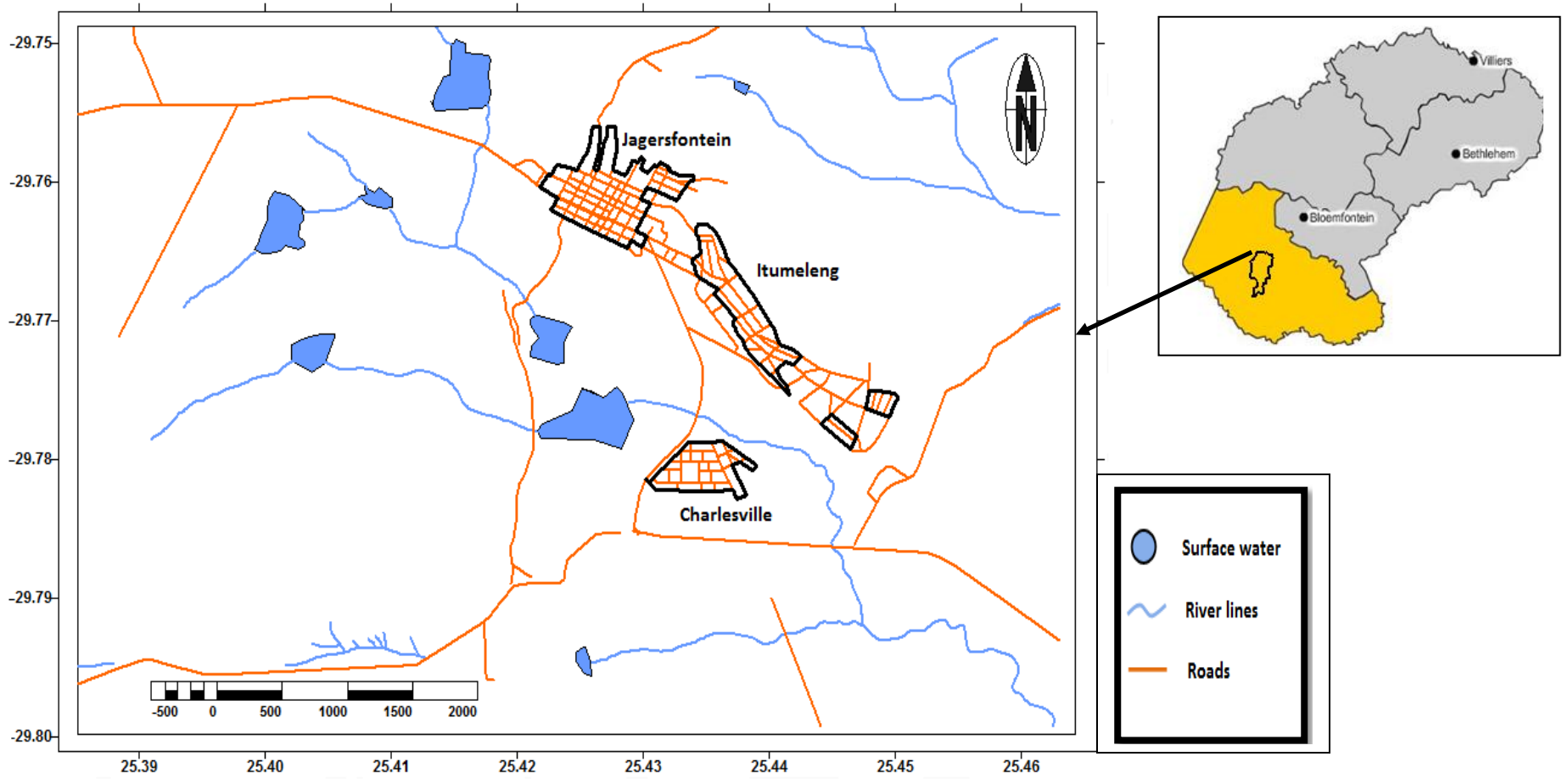
Figure 1-1: Location map of study area

1.3.2 Climate

Rainfall in Jagersfontein is about 278 mm/yr with most occurring during summer. Average rainfall is lowest in June (1 mm) and highest (54 mm) in March (Figure 1-2). Average midday temperatures for Jagersfontein ranges between 16 ^{o}C in June and 30 ^{o}C in January (Figure 1-3). The region is the coldest during July when the temperature drops to 0 °C usually during the night (Figure 1-4).
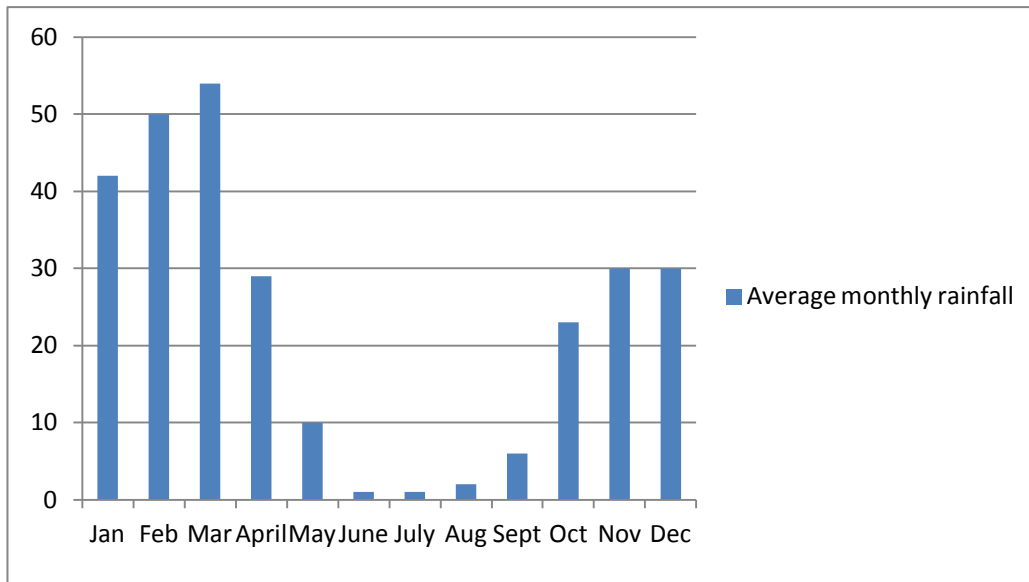
Figure 1-2: Average monthly rainfall (source:
http://www.saexplorer.co.za/southafrica/climate/jagersfontein_climate.asp)
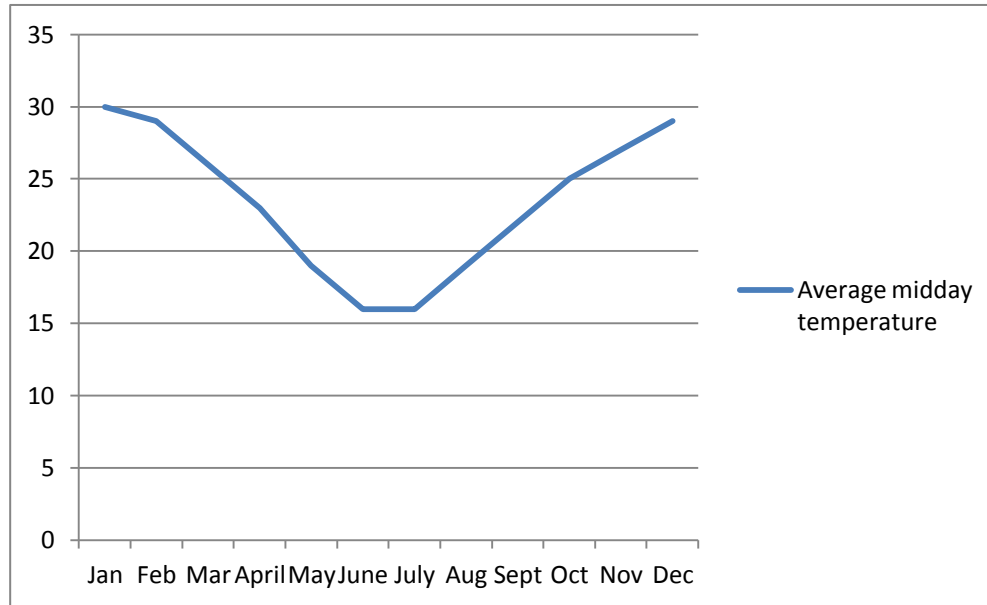
Figure 1-3: Average midday temperature (source: http://www.saexplorer.co.za/southafrica/climate/jagersfontein_climate.asp)
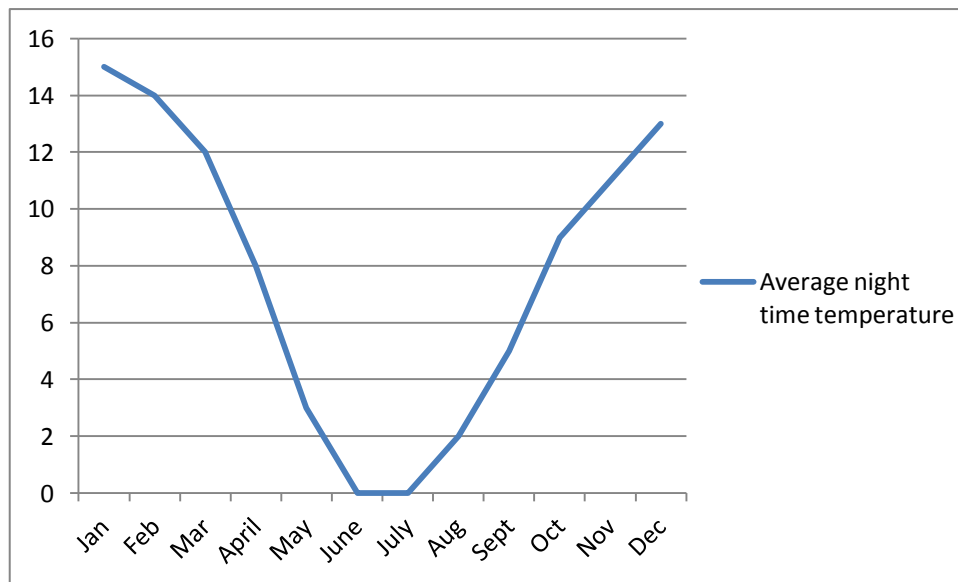
Figure 1-4: Average night time temperature (source: http://www.saexplorer.co.za/southafrica/climate/jagersfontein_climate.asp)

1.3.3 Topography and drainage

The study area is located in the north-western part of the quaternary catchment C51H (Figure 1-5), of the Upper Orange Water Management Area. The topography of the study area is shown in Figure 1-6 with surface elevations varying between 1 400 to 1 500 m.

Jagersfontein and the plains south of it are drained by the Proses Spruit a tributary of the Riet River. The catchment area of Proses Spruit is due east of Jagersfontein, covers approximately 864 km^2 of landscape with gentle slopes though ridges and isolated hills are common. North of Jagersfontein is a mountainous area, but most parts of the runoff flow into the Proses Spruit. Other tributaries of the Riet River are Van Zyl Spruit in the south west and Kromellenboog Spruit in the north of Jagersfontein (Figure 1-5). In Figure 1-7 is presented the vector map of quaternary catchment C51H showing general water flow direction.
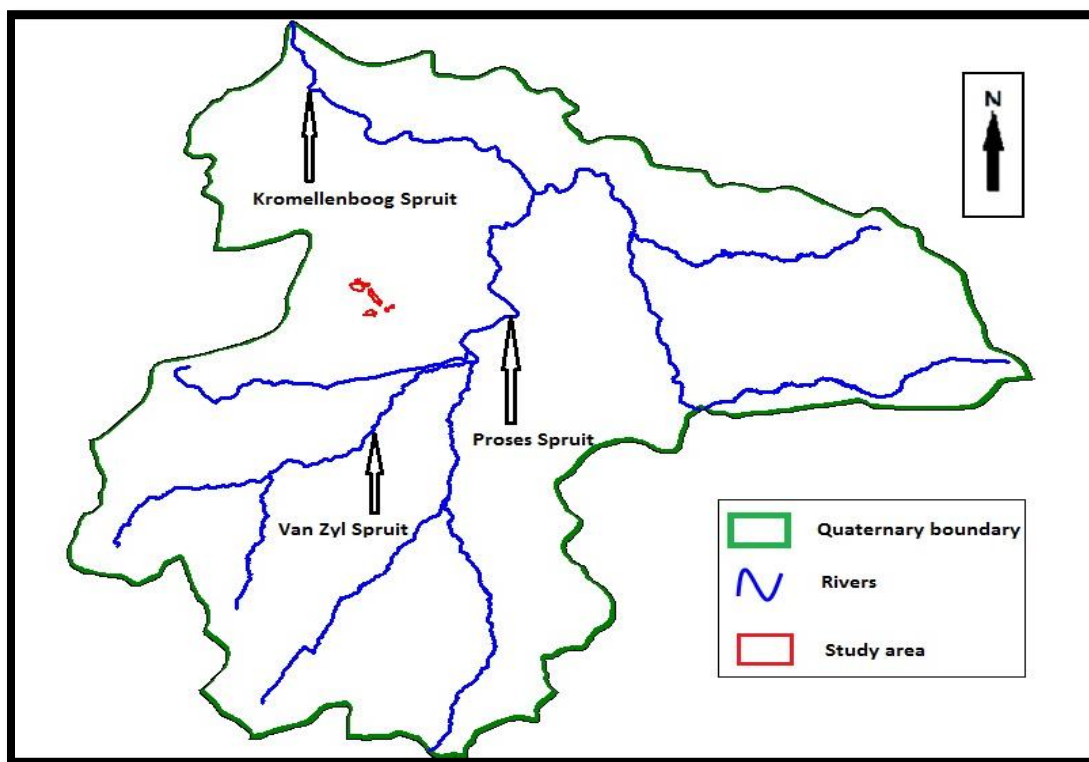
Figure 1-5: Quaternary catchment C51H showing location of study area and rivers
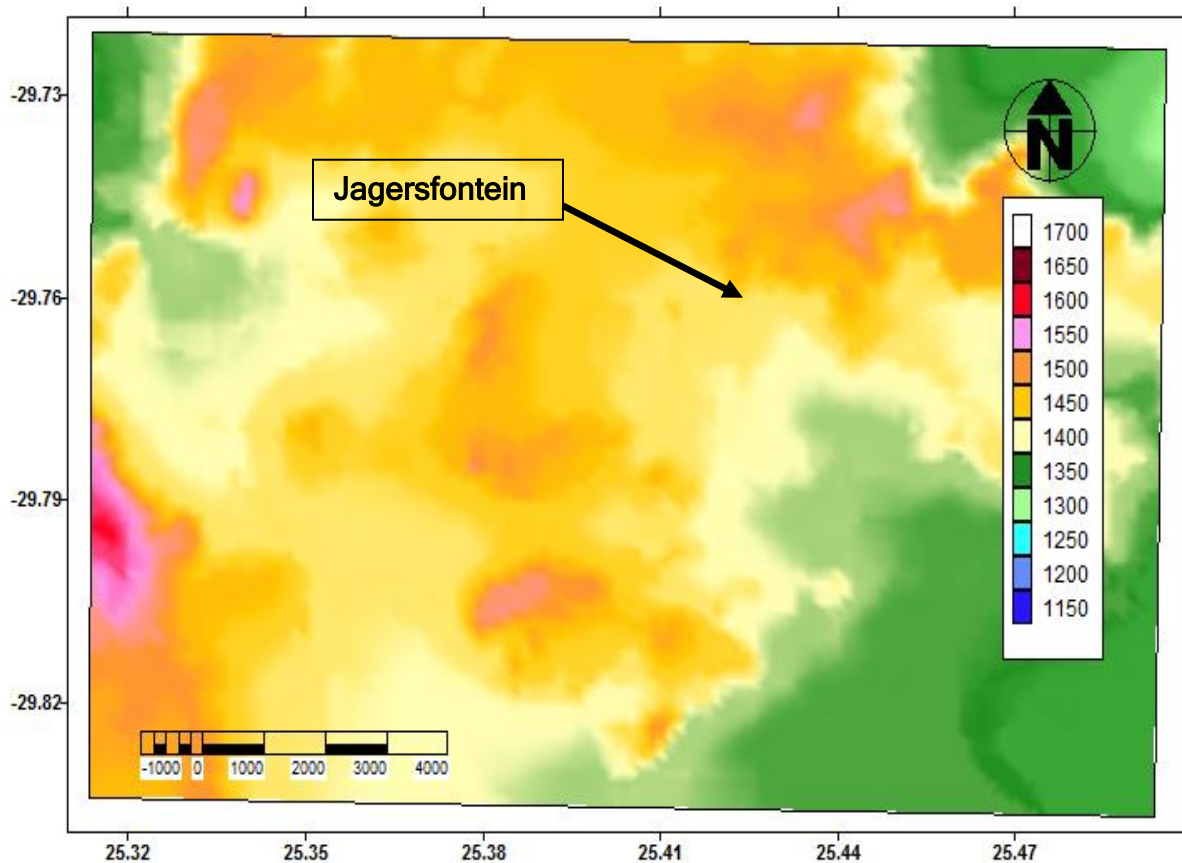
Figure 1-6: Topographic map of study area showing stream lines
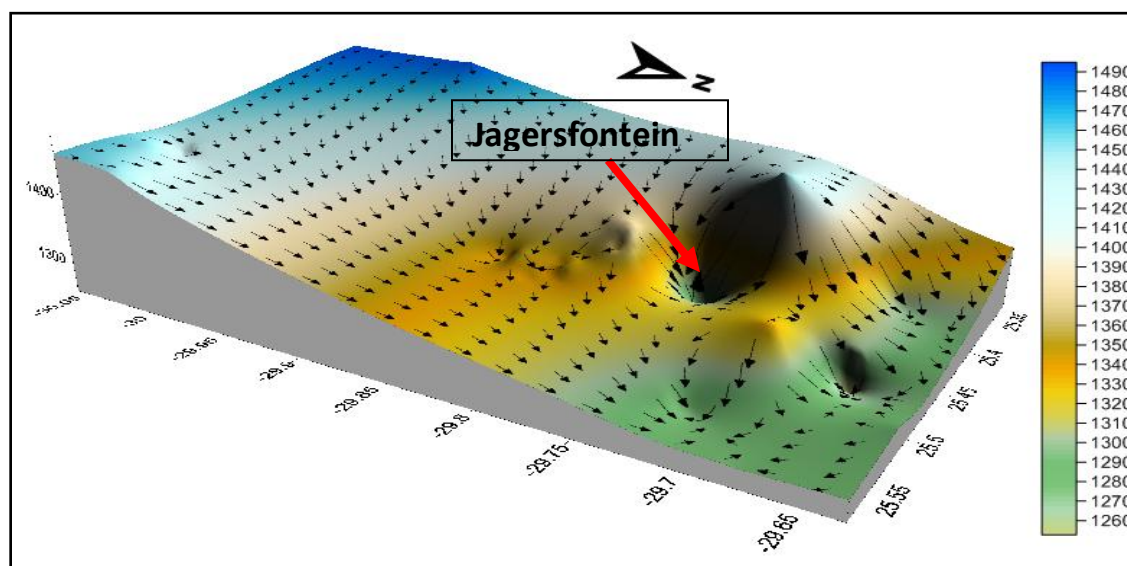
Figure 1-7: Vector map of C51H showing general water flow direction

1.3.4 Geology

The geology of the study area (Figure 1-8) is predominantly sandstones, shale and mudstones of the Dwyka and Ecca group and argillaceous and arenaceous rocks of the lower Beaufort group (Adelaide subgroup) of the Karoo Supergroup infringed by dolerite and Kimberlite pipes in which diamonds can be found.

Ecca Group

The Prince Albert (cherty shale beds), White Hall (white-weathering, carbonaceous mudstones) and Tierberg (dark basinal clastone) Formations make up the Ecca Group which overlies the glaciogenic Dwyka Group. The thickness of the group together makes up 340 to 360 m. The Prince Albert formation maintains a relatively constant thickness of between 34 to 46 m. It consists of black carbonaceous shale and dark bluish-green to grey massive micaceous shale. An iron-rich concretion horizon is followed by grey to olive-green micaceous shale/mudstone. The thickness of the White Hill Formation varies between 10 to 18 m but regional thinning northwards has been recorded (Xhariep District Municipality Integrated Development Plan (draft) 2010/2011).

The unit consists mainly of thinly laminated carbonaceous shale which is white in colour due to weathering of pyrite (sulphide) at surface to sulfate (gypsum). (Branch *et al*, 2007).

The uppermost Tierberg Formation attains a thickness of approximately 300 m. This unit consists of mudstone, light-green to greenish-grey shale with concretional horizons. Shale with interbedded siltstone and fine-grained sandstone comprises the upper portion of this unit (Xhariep District Municipality Integrated Development Plan (draft) 2010/2011).

Beaufort group

The Beaufort Group comprises the Adelaide and Tarkastad Subgroups.

The Adelaide Subgroup attains a maximum thickness of 400 m. It consists of 10 to 15 m thick marker sandstone at the base, followed by siltstone and grey to reddish mudstone with subordinate lenses of sandstone. The topmost part of the unit consists of bluish to greenish-grey shales and red to purple mudstone (Xhariep District Municipality Integrated Development Plan (draft) 2010/2011).

The Tarkastad Subgroup consists of cream to khaki coloured, medium grained, feldspatic sandstones with interbeds of red, purple and green mudstones. The sandstone horizons are thicker and more prominent than those of the underlying Adelaide Subgroup. The Sandstone layers are particularly well developed at the bottom and towards the top of the unit (Xhariep District Municipality Integrated Development Plan (draft) 2010/2011).
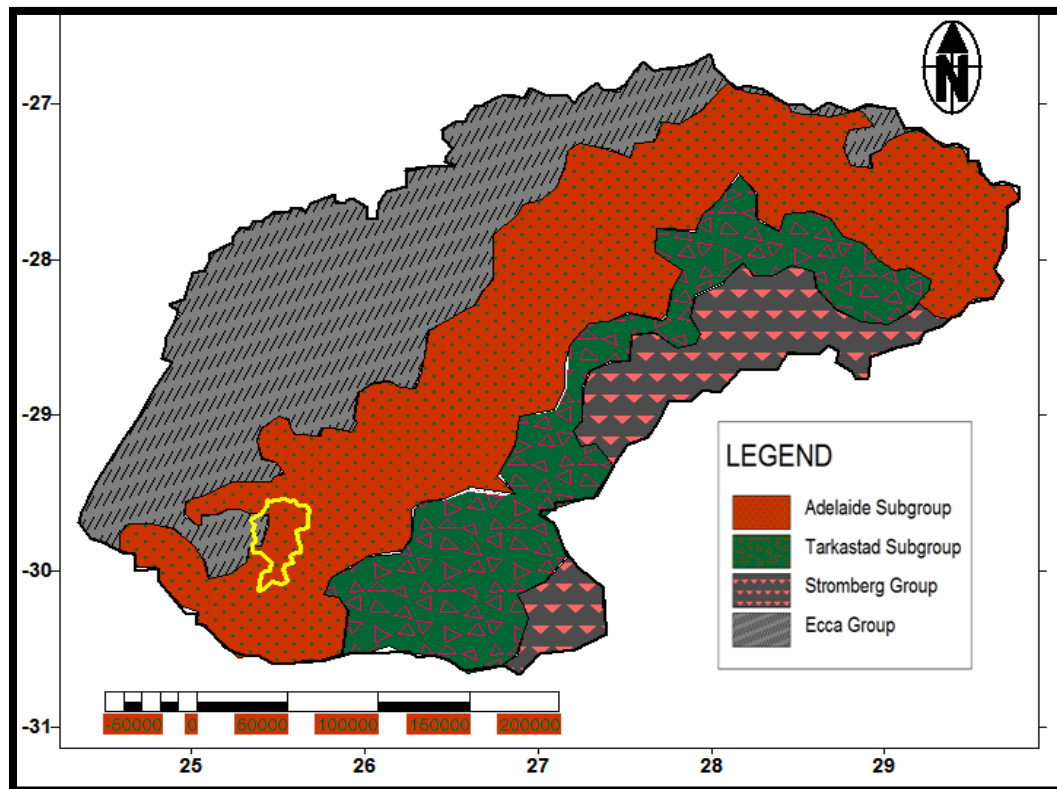
Figure 1-8: Geology Map (study area in yellow) (modified from Rutherford, 2009)

1.3.5 Kimberlite Pipes

The definition of Kimberlite by Skinner and Clement (1979) underlines the complex nature of this rock type and for the sake of absoluteness, it is repeated word for word: "Kimberlite is a volatile-rich, potassic ultrabasic igneous rock which occurs as small volcanic pipes, dykes and sills. It has a distinctive inequigranular texture resulting from the presence of macrocrysts set in a fine grained matrix. This matrix contains as prominent primary phenocrystal and/or groundmass constituents, olivine and several of the following minerals: phlogopite, carbonate (commonly calcite), serpentine, clinopyroxene (commonly diopside), monticellite, apatite, spinels, perovskite and ilmenite. The macrocrysts are anhedral, mantle-derived, ferromagnesian minerals which include olivine, phlogopite, picroilmenite, chromian spinel, magnesian garnet, clinopyroxene (commonly chromian diopside) and orthopyroxene (commonly enstatite). Olivine is extremely abundant relative to the other macrocrysts, all of which are not necessarily present. The macrocrysts and relatively early-formed matrix minerals are commonly altered by deuteric processes, mainly serpentinization and carbonatization. Kimberlite commonly contains inclusions of upper mantle-derived ultramafic rocks. Variable quantities of crustal xenoliths and xenocrysts may also be present. Kimberlite may contain diamond but only as a very rare constituent". Most of the known Kimberlite pipes are in South Africa and Siberia, but there are also many in North America, Australia, Brazil.

According to Wagner 1914, there are two types of diamond-bearing Kimberlite pipes in South Africa which he referred to as "basaltic" and "lamprophyric" Kimberlites. The theory behind the formation of Kimberlite pipes can be divided into two main disciplines, namely those that favour the role of juvenile gases as the main driving force, and those that favour the interaction between magma and near-surface water as the main process.

In Jagersfontein area, the main Kimberlite pipe intrudes sedimentary rocks of the Karoo Supergroup and a Stormberg-aged dolerite sill of 245 m thickness. The

pipe is slightly inclined to the east (Wagner, 1914 cited in Field *et al.*, 2008). Wagner 1914 noted the presence of extensive breccias derived from Karoo sediments above the current erosion level. Williams 1932 (cited in Field *et al.*, 2008) referred to these breccias as "grey-ground" and had very low diamond grades. Williams stated that these breccias consisted of abundant red and grey mudstone fragments, which in places contained little or no Kimberlitic matrix. This "grey-ground" occurred from the surface to the greatest depths of the mine. Jagersfontein was also noted as a key location where Stormberg basalts were preserved as down-rafted fragments. The remainder of the Kimberlite was termed "blue-ground". No modern studies have been carried-out on this Kimberlite since the mine closed in 1971. Hawthorne (1975) published the first model of a Kimberlite pipe, in which he depicted this lithological zonation. His model has been widely quoted and used since, and is shown in Figure 1-9. It also illustrates the stratigraphy through which most of the Cretaceous-aged Kimberlites of Southern Africa were emplaced (Field *et al.*, 2008).

Kimberlite fissures are 0.4 to 4 m wide and often show strong up warping of the surrounding Karoo beds. In projection the Kimberlite intrusion is often inconspicuous and only visible as stringers of highly decomposed Kimberlite (green ground) or micaceous calcrete (yellow ground). Fresh hypabyssal Kimberlite is usually encountered after drilling through 12 to 60 m of weathered zone. Parallel regional jointing often accompanies the fissures. They do not contain any igneous material, except for a few indicator minerals or traces of mica. Kimberlite fissures are discerned from dolerite dykes on aerial photographs as regularly spaced, narrow, co-linear features with relatively denser vegetation growth along the fissure (Woodford *et al.*, 2002).
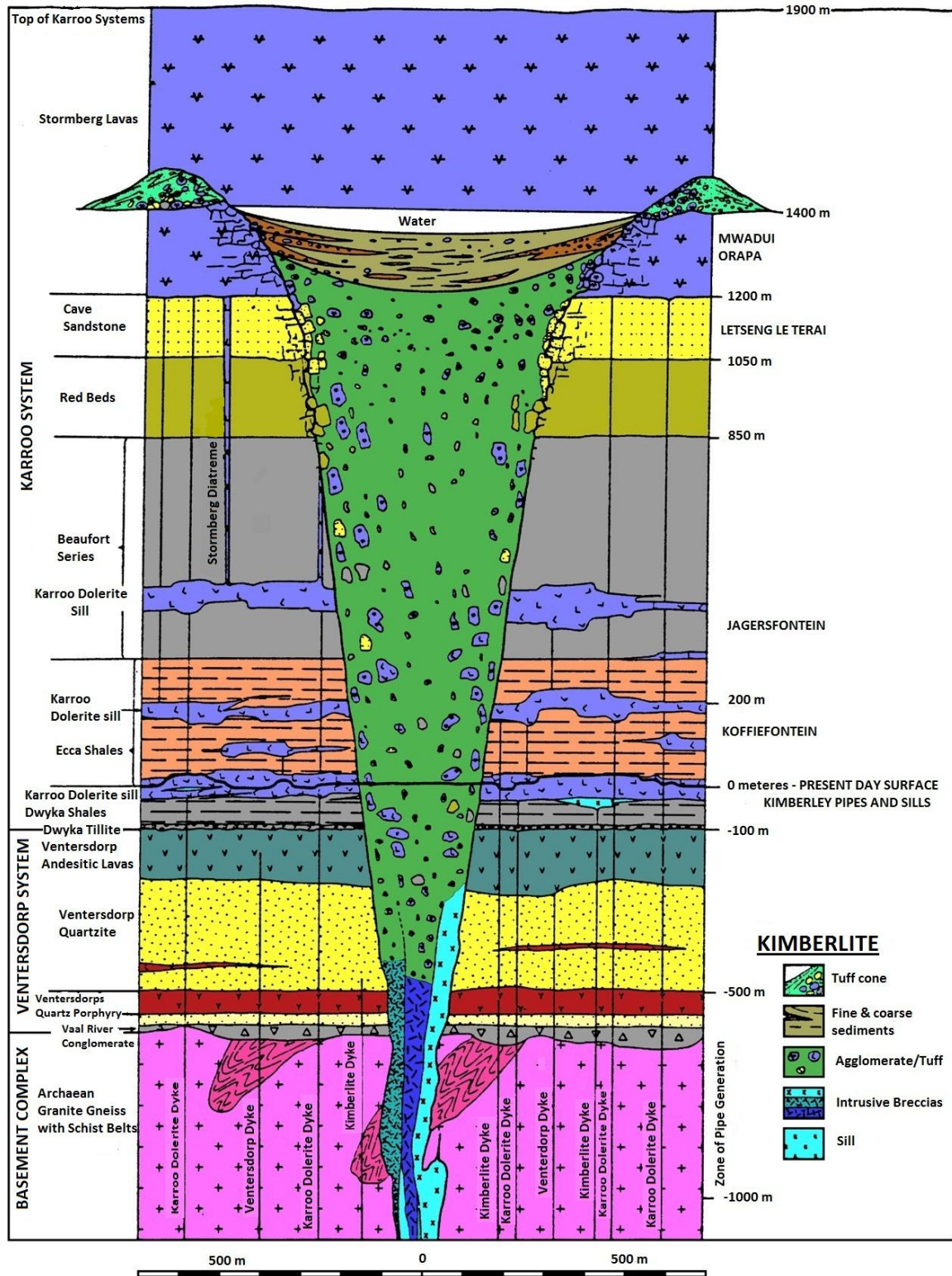
Figure 1-9: Model of a Kimberlite pipe (modified from Field *et al.*, 2008)

Kimberlite diatremes are unevenly distributed. They are not very common and vary in diameter from only 10 to 400 m in the western Karoo, Sutherland, Victoria West, Britstown, Prieska and East Griqualand areas. Both the fresh and weathered hypabyssal Kimberlite can form positive-relief hills or negative-relief, calcrete, calcrete-rich depressions. They contain a large amount and a wide variety of mantle and crustal xenoliths as well as megacrysts (Woodford *et al.*, 2002).

1.3.5.1   Hydrological Properties of Kimberlite pipes

Intrusion of Karoo sediments by Kimberlites did not result in to intensive thermal metamorphism as did the dolerites, and they did not significantly alter the hydrological properties of the sediments. On a regional scale however, clusters of Kimberlites may represent important fractured domains. On a local scale, the thin Kimberlite dykes (< 3 m) are generally only weakly jointed and thus have a very low permeability, especially within the highly decomposed upper section of the dyke. However, the emplacement of Kimberlite groups may be important for the occurrence and movement of groundwater. Large Kimberlite pipes and diatremes are more heterogeneous and brecciated. There is thus a possibility that high-yielding boreholes can be sited alongside or within these features similar to the breccia plugs (Woodford *et al.*, 2002).

The Department of Water Affairs (DWA) drilled five exploration boreholes into and alongside Kimberlite dykes (Loxton Kimberlite dyke and Nuweland Kimberlite dyke) in the Loxton area (Chevallier *et al.*, 2001). The Loxton Kimberlite dyke is 3 m wide, trends in the NNE (North-northeast) direction and intersects a N-W (northwest) dolerite dyke. Three boreholes were drilled around this intersection as follows:

1. In the middle of the dyke,
2. In the Kimberlite dyke at the intersection zone, and
3. Approximately 1 m from the dyke contact (150 m north of the Kimberlite/dolerite dyke intersection).

Boreholes 1 and 2 intercepted highly decomposed Kimberlite (yellow-ground) to a depth of 11 to 12 m and weathered Kimberlite (green-ground) from 12 to 14 m, subsequently the Kimberlite was fresh (blue-ground). The only seepage recorded was at the transition zone between the weathered and fresh Kimberlite (Woodford *et al.*, 2002).

The Nuweland Kimberlite dyke which forms part of the narrow N-S trending corridor of intense fracturing and Kimberlite intrusion, has two diatremes and a number of blow-pipes mapped. The fissures and blow-pipes contain Kimberlitic material (mainly yellow-ground) while the diatremes contain fresher Kimberlite and breccias. Most of the other fissures and parallel joints are barren of contain micaceous, calcretized material (Woodford *et al.*, 2002). Two exploration boreholes were drilled as follows:

i.   In the centre of the main Kimberlite fissure to a depth of 162 m, and
ii.   Into a parallel, but 'barren' fissure to a depth of 150 m. Some 22 m east of borehole i.

Borehole i only intercepted seepage inflow at 47 m, despite the heterogeneity, textural and structural complexity of the dyke. Borehole ii struck a water bearing fissure at 65 m that yielded 4 l/s (Chevallier *et al*, 2001).

DWA also drilled a borehole into a diatreme at Carnarvon. It is intruded along a system of north fissures. It has a diameter of 300 m and is oval in shape. This borehole was drilled into the centre of the structure to a depth of 240 m. It was evident that the Kimberlite was highly decomposed (yellow-ground) to 16 m below surface, weathered (green-ground) from 17 to 83 m and fresh (blue-ground) from 84 to 140 m (Woodford *et al.*, 2002). The borehole intercepted water in the weathered Kimberlite at 26 m which yielded 1.5 l/s and the jointed/weathered-fresh Kimberlite transition zone at 83 m which yielded 1.5 l/s (Woodford, unpublished data cited in Woodford *et al.*, 2002).

Jagersfontein Kimberlite Diatreme

The diamond mining operation on Jagersfontein Kimberlite diatreme extended to a depth of 750 m below the surface. Some 64 000 m^3/month of groundwater had to be extracted continuously at a rate of 25 l/s in order to keep the waterlevel below 750 m (Figure 1-10).

Groundwater was being extracted from the mine and supplied to the municipality for 9 years after mining ceased. During this period the piezometric level in the open-pit and shafts recovered from 750 to 183 m below ground-level (bgl). Over the period January 1980 to February 1982, the Municipality abstracted a total of 497 308 m^3 of groundwater via a pump installed in an abandoned shaft, with a maximum waterlevel drawdown of 0.66 m. The pump inlet was installed at 220 m and the pump rate was set at 17.5 l/s. The waterlevel and chemical information point to the existence of two separate aquifers, namely:

- A shallow, more 'typical' Karoo fractured-rock aquifer (Figure 1-10 well 1, showing a waterlevel of 4.8 m.bgl), containing recently recharged water.

- Deeper aquifer (intercepted in the mine, piezometric level 183 m.gbl) containing older water (Woodford *et al.*, 2002).
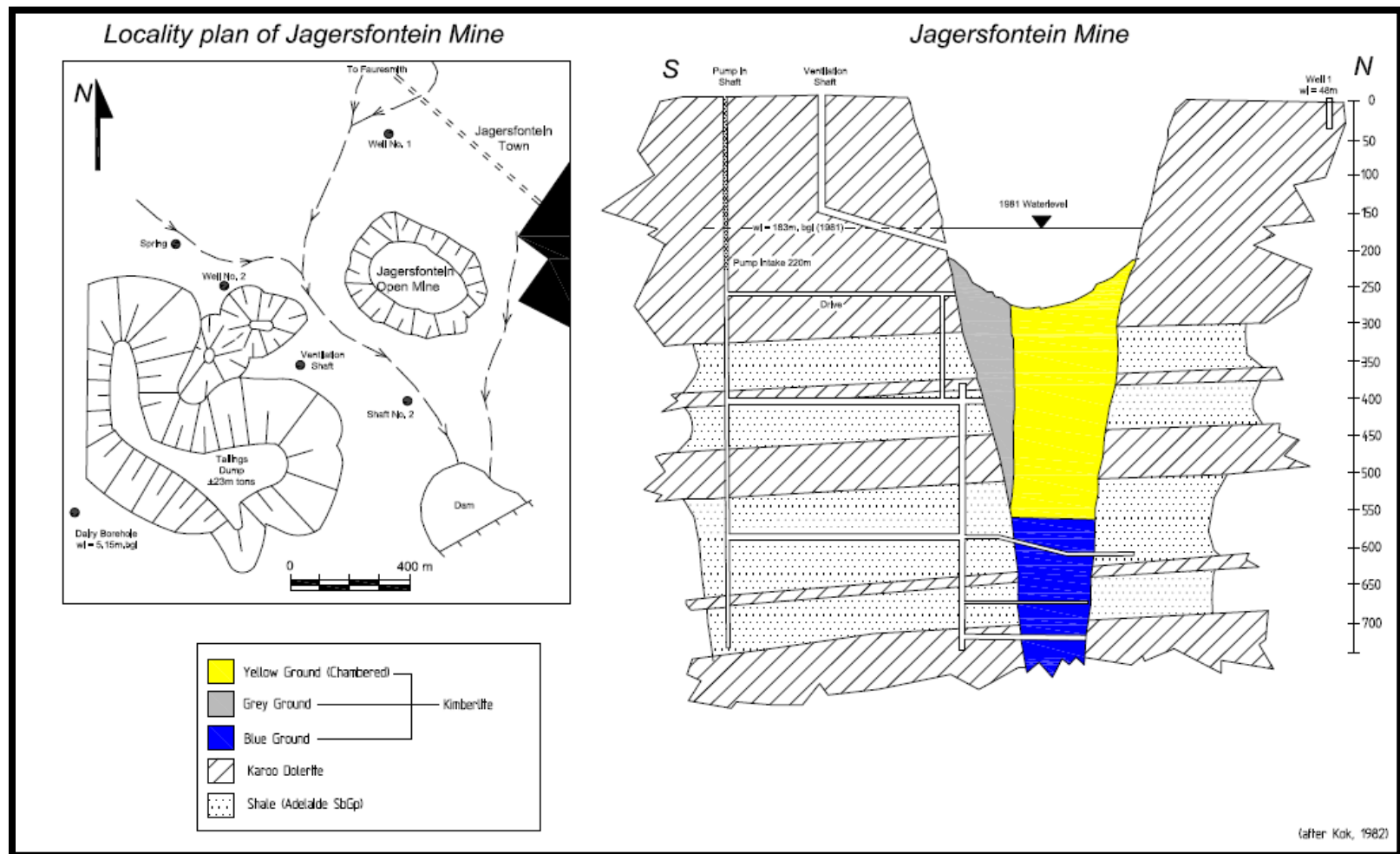
Figure 1-10: Geohydrology of the Jagersfontein Kimberlite diatreme (modified from Woodford *et al.*, 2002)

1.3.6 Geohydrology

The study area is characterised by Karoo intergranular and fractured-rock aquifers, which are the most extensive type of aquifer in South Africa. The Karoo aquifers occur within the Karoo Supergroup which consists of different groups of sediments each with its own physical properties. Low permeability is the main characteristic of the Karoo Supergroup aquifers. The majority of boreholes drilled in Karoo formations therefore have very low yields (Usher *et al.*, 2006)

The Dwyka group constitutes a very low-yielding fractured aquifer and water is confined within narrow discontinuities like jointing and fracturing (Woodford *et al.*, 2002). They therefore tend to form aquitards rather than aquifers. Since the Dwyka sediments were deposited mainly under marine conditions, the water in these aquifers tends to be saline. In general the Dwyka Group is thus not an ideal unit for the large-scale development of groundwater. Since the shales of the Ecca group are very dense, they are often disregarded as significant sources of groundwater. However as illustrated in Figure 1-11, their porosities tend to decrease from 0.10 % north of latitude 28 °S to < 0.02 % in the southern and south-eastern parts of the Karoo Basin while their bulk densities increase from 2 000 to > 2 650 kg/m^3. The possibility thus exists that economically viable aquifers may exist in the northern parts of the Basin underlain by the Ecca shale. It is therefore rather surprising to find that there are areas even in the central parts where large quantities of water are pumped daily from the Ecca formations. One should thus not neglect the Ecca rocks as possible sources for groundwater especially the deltaic sandstone facies. Roswell and De Swardt (1976) report that the permeabilities of these sandstones are usually very low the main reason being, the sandstones are usually poorly sorted, and that their primary porosities have been lowered considerably by diagenesis (Woodford *et al.*, 2002).

The sedimentary units in the Beaufort Group usually have very low primary permeabilities. The geometry of these aquifers is complicated by the lateral migration of meandering streams over a floodplain. Aquifers in the Beaufort group

will thus not only be multilayered, but also multi-porous with variable thicknesses. The contact plane between two different sedimentary layers will cause a discontinuity in the hydraulic properties of the composite aquifer; the pumping of a multi-layered aquifer will thus cause the piezometric pressure in the more permeable layers to drop faster than in the less permeable layers. It is therefore possible to completely extract the more permeable layers of the multi-layered Beaufort aquifers, without materially affecting the piezometric pressure in the less permeable layers. This complex behaviour of aquifers in the Beaufort Group is further complicated by the fact that many of the coarser and thus more permeable, sedimentary bodies are lens-shaped. The life-span of a high-yielding borehole in the Beaufort Group may therefore be limited, if the aquifer is not recharged frequently (Woodford *et al.*, 2002).
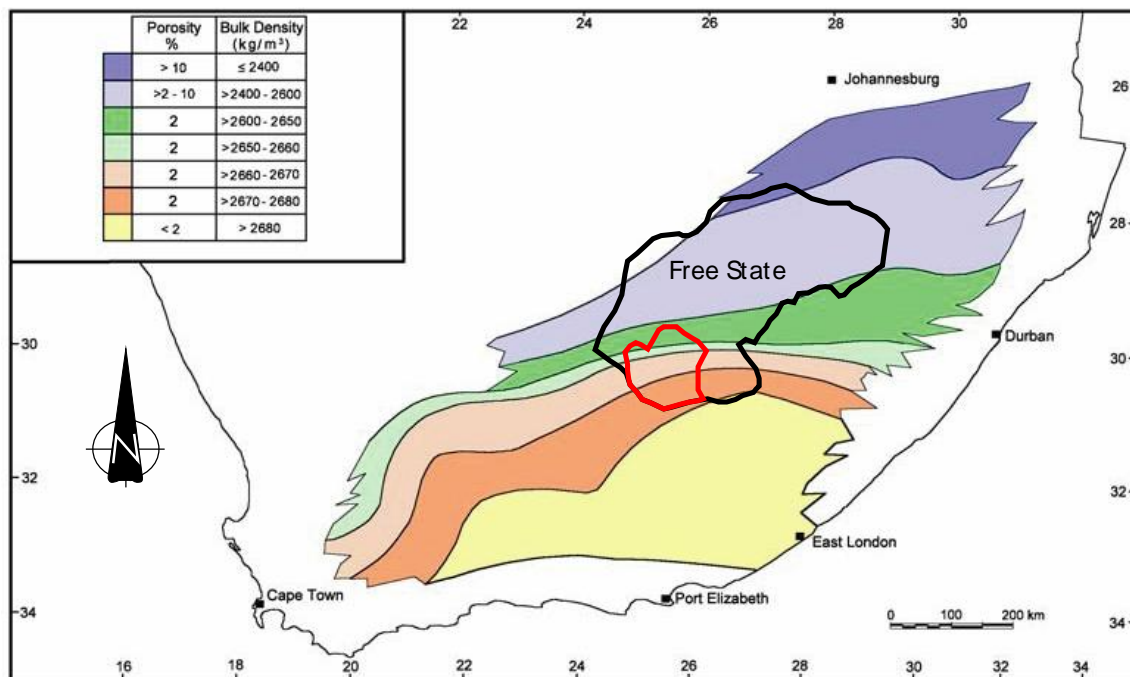
Figure 1-11: Porosity and bulk density variations in shales of the Karoo Basin (modified from Woodford *et al.*, 2002)

1.3.6.1 General aquifer information

Jagersfontein is underlain by predominantly argillaceous rocks (shale, mudstone and subordinate siltstone) of the Ecca group and argillaceous and arenaceous

rocks (approximately equal proportion) of the Beaufort group infringed by basic intrusive rocks (dolerite and norite). This comprises the intergranular and fractured aquifers. Average borehole yield is in the range 0.5 to 2.0 l/s (Figure 1-12). There is a large scale abstraction of groundwater at the rate of 0.1 to 1.0 million m^3/a for municipality use.

Yields of >2 l/s can be obtained in the joints and on bedding planes in shale and interbedded sandstone of the Ecca Group (Pe) and the Beaufort Group (P-Trb), even in the absence of dolerite intrusions.

Jointed and fractured contact zones between sedimentary rocks and dolerite dykes can be targeted for groundwater development. Groundwater strikes have also been obtained by drilling into the narrow dolerite dykes, rather than engaging contact zones.

Unsuccessful results can be anticipated where boreholes penetrate thick dolerite bodies. Decomposition is generally absent at depths exceeding 30 m, and few, if any water-bearing fractures can be expected at the deep lower contact of dolerite with underlying sedimentary rocks. (Hydrogeological map series of the Republic of South Africa 2924 Bloemfontein, 2002).
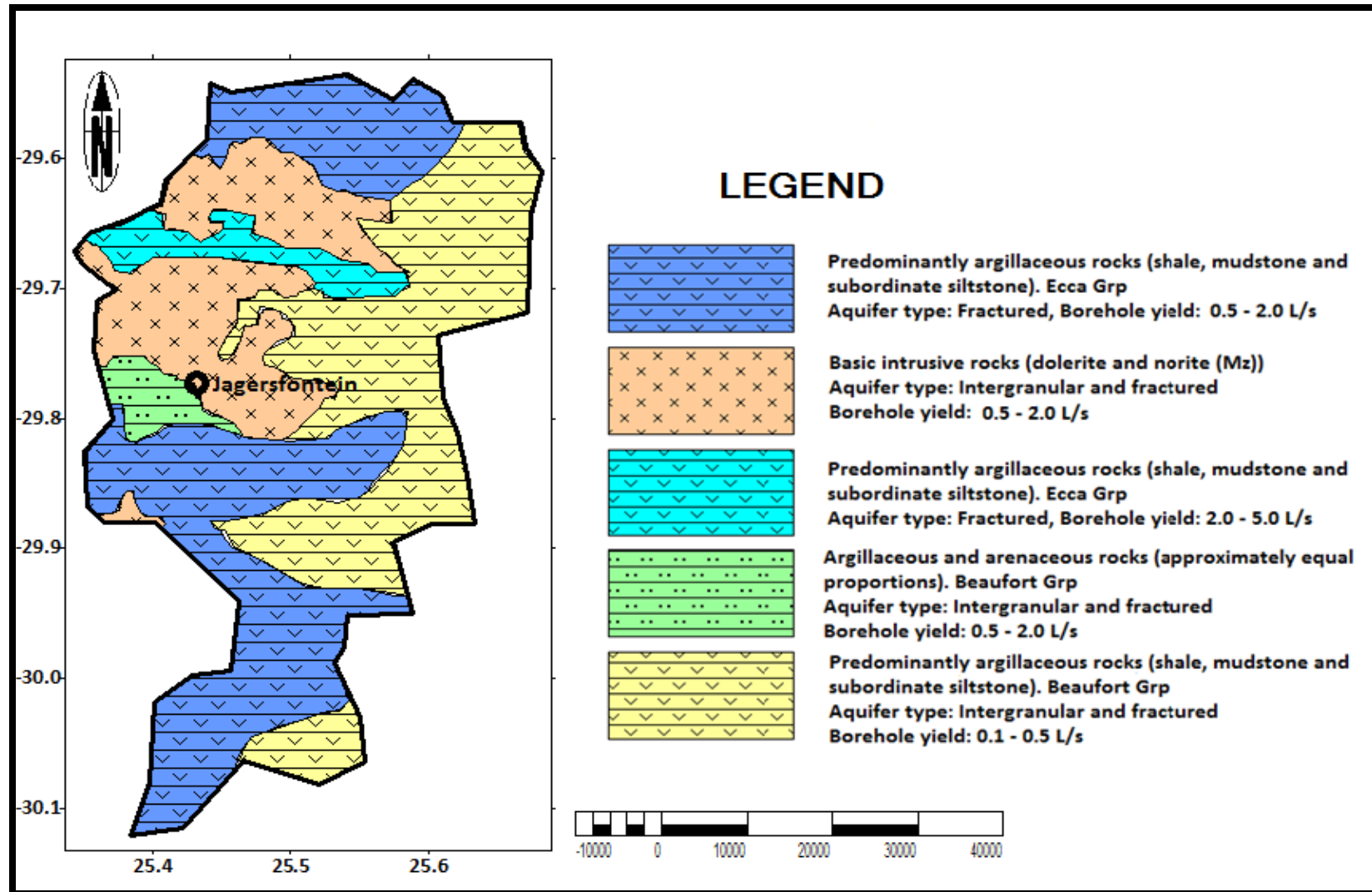
Figure 1-12: Geohydrology and aquifer information of Jagersfontein

1.3.7 Biome and Vegetation

Eastern Mixed Nama Karoo is the Biome of the study area (Figure 1-13). It is an extensive transition area between the Grassland Biome in the east and the Nama Karoo Biome to the west.

The vegetation is a complex mix of grass- and shrub-dominated vegetation types, which are subject to dynamic changes in species composition dependent on seasonal rainfall events. Common shrubs include Bitterkaroo *Pentzia incana, Kapokbush Eriocephalus ericoides,* Thornkapok *E. spinescens and Hermannia spp.,* while grasses, such as *Aristida spp., Eragrostis* spp. and Redgrass *Themeda triandra,* may dominate the landscape after good summer rains, especially in the north-east. Trees are not abundant, except along the dry river beds where Sweet Thorn *Acacia karroo* is a common element. This type has the highest cover of herbs of all the Nama Karoo types, as well as numerous geophytes (Nama Karoo Biome, key reference Acocks, 1988).
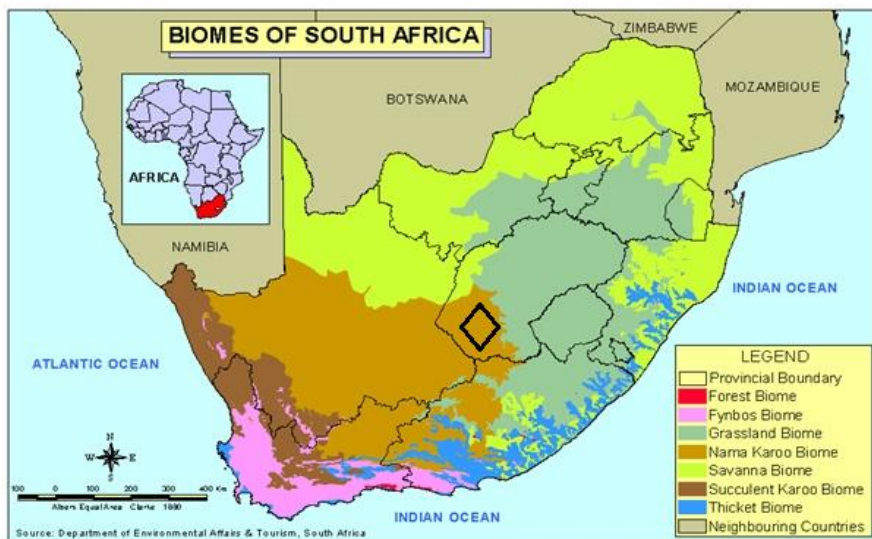
Figure 1-13: Biomes of South Africa (study area in black square) (source: http://www.ngo.grida.no/soesa/nsoer/general/about.htm)

1.3.8 Soil type

The soil of the study area (Figure 1-14) has the sandy clay loam to sandy clay texture. Clay content of the soils is appreciably high as a result of the intrusion of the sedimentary rocks by plagioclase rich dolerite during the Jurassic age.
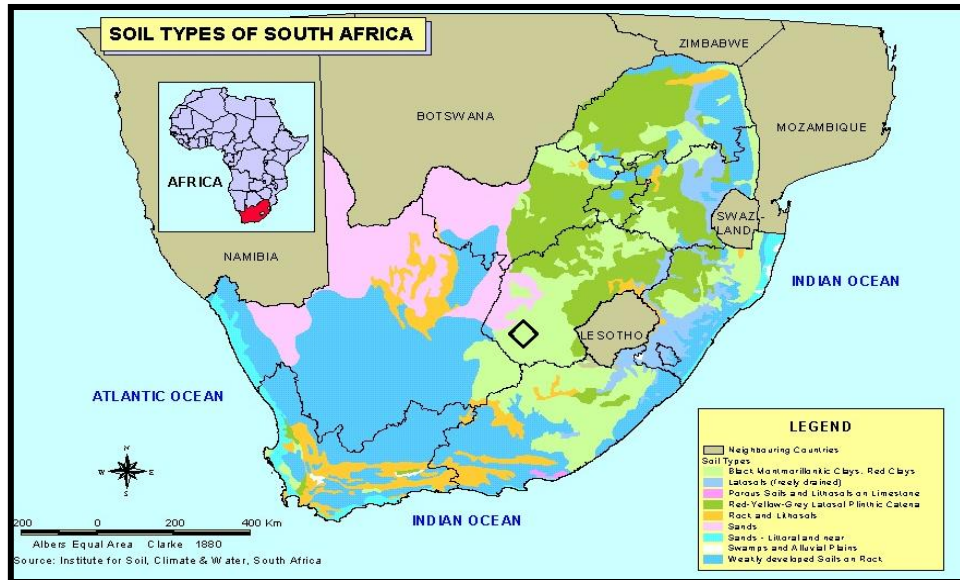
Figure 1-14: Soil types of South Africa (study area in black square) (source: http://www.ngo.grida.no/soesa/nsoer/general/about.htm)

2 Literature Review

Arsenic is an omnipresent metalloid found in the atmosphere, organisms, rocks, soil and natural waters. Its mobilization is as a result of natural processes (weathering and dissolution of minerals from rock materials in the aquifer) likewise artificial or anthropogenic activities (mining activities, use of arsenic containing pesticides and herbicides) (Smedley and Kinniburgh, 2001).

Arsenic contamination of groundwater is a global problem and affects many countries in the world. Level of arsenic in groundwater differs from country to country as well as the source of the arsenic. Some might be as a result of mining activities; some are from the aquifers or are geothermal. The World Health Organization (WHO) guideline of arsenic in drinking water is 0.01 mg/l, which many countries have adopted. However, many other countries have held on to the previous guideline of 0.05 mg/l as their national standards or target. Table 2-1 shows the accepted national standards for arsenic in drinking water in some selected countries. According to the World Health Organization (WHO) 2001, 130 million people worldwide were estimated to be exposed to arsenic concentrations above 0.05 mg/l (50 µg/l). Affected countries include Bangladesh (>30 million exposed people), India (40 million), China (1.5 million) and the United States (2.5 million) (van Halem *et al.*, 2009). Table 2-2 gives an overview of worldwide arsenic concentrations (WHO, 2001). Aquifers of Bangladesh, India, China as well as Argentina, Chile and Mexico are well documented and well known for the severe arsenic contamination in groundwater. The presence of arsenic in Argentina is related to volcanic ash found dispersed in the sediments (Claesson and Fagerberg, 2003). Highest concentrations of arsenic reach over 100 times the World Health Organisation (WHO) limit of arsenic in drinking water (0.01 mg/l). In the case of Jagersfontein South Africa, arsenic contamination is presumed to be as a result of mining activities. Figure 2-1 shows distribution of arsenic in groundwater all over the world alongside the main sources of the arsenic.

Table 2-1: Accepted national standards for arsenic in drinking water in some selected countries (Sombo *et al.,* 2009).

Standards	Country (year adopted) limit mg/l
Countries whose standard is lower than 0.01 mg/L	Australia (0.007 mg/L, 1996)
Countries whose standard is 0.01 mg/L	European Union (1998), Japan (1993), Jordan (1991), Laos (1999), Laos, Mongolia (1998), Namibia, Syria(1994)
Countries whose standard is lower than 0.05 mg/l but higher than 0.01 mg/l	Canada (1999) 0.025 mg/l
Countries considering to lower the standard from 0.05 mg/L	United States (1986*) , Mexico(1994)
Countries whose standard is 0.05 mg/l	Bahrain, Bangladesh (unknown), Bolivia (1997), China (unknown), Egypt(1995), India (unknown), Indonesia (1990), Oman, Philippines (1978), Saudi Arabia, Sri Lanka (1983), Viet Nam(1989), Zimbabwe
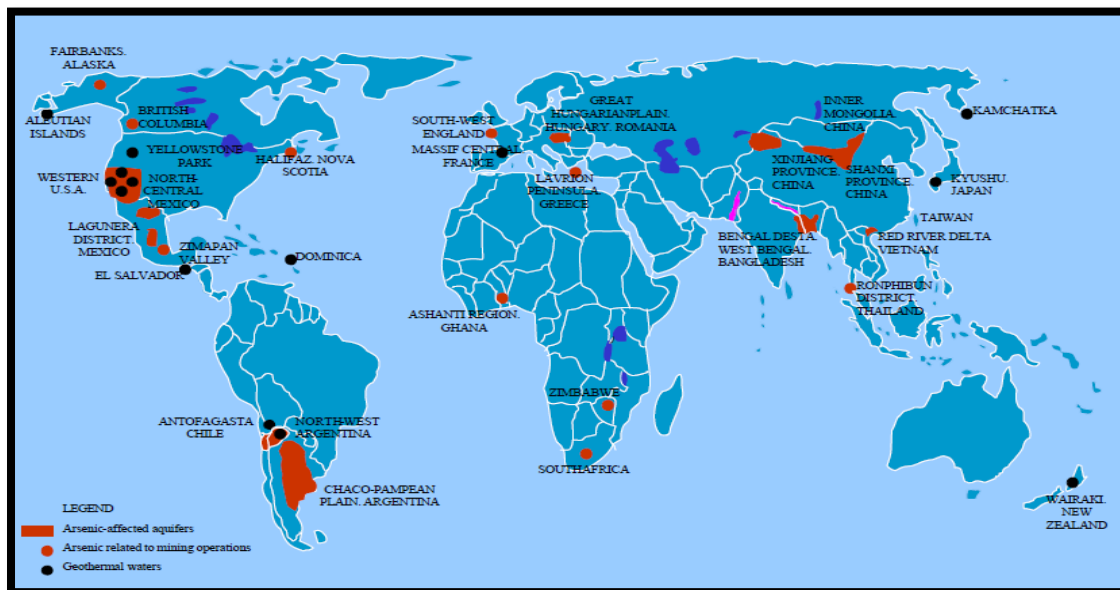
Figure 2-1: Locations of documented arsenic- effected aquifers, mining operations and geo-thermal systems. Areas in blue are lakes (Ahmed, 2004)

Table 2-2: Arsenic occurrence (modified from WHO, 2001)

Source of Arsenic	Example of country found	Arsenic concentration (mg/l)
Arsenic-rich sediments	Bangladesh, India, Vietnam, China	0.01-5
Groundwater contaminated by mining activities	Ghana	0.05-5
Geothermal influenced water	USA, Argentina,	<0.01-50

2.1 Sources of Arsenic

Arsenic is a semi-metallic element and ranks 20th in natural abundance of the earth crust. It consists of about 0.0005 % of the earth's crust (Gebreyowhannes, 2009).

The source of arsenic in groundwater is usually geogenic, although anthropogenic arsenic pollution does occur. Anthropogenic sources may also have an impact on the level of arsenic which can take any form including organic arsenic species (Teclu, 2008).

2.1.1 Natural sources

In nature, arsenic usually occurs as a major constituent in over a hundred minerals including elemental arsenic, arsenides, sulphides, sulfosalts, silicates e.t.c. According to Thornton (1996), 60 % of arsenic bearing minerals (Table B 2) consist of arsenates, 20 % are sulphides and sulfosalts and 20 % are arsenides, arsenites, oxides, silicates and native arsenic. Arsenic is also often found under reducing conditions. Such conditions are found in organic rich sedimentary environment such as black shales and coal bearing beds. Minerals containing arsenic in this form are not stable in aerobic systems; they oxidize resulting to the release of sulphate, acidity and associated trace constituents. This mechanism (oxidation) is one of the causes of the release of arsenic into groundwater. 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 (Sami and Druzynski, 2003).

Arsenic occurs in most igneous and sedimentary rocks but in negligible concentration (Sami and Druzynski, 2003). However there are a few sedimentary rocks with high concentrations of arsenic. These include argillaceous deposits containing a huge proportion of sulphide minerals formed under reducing environments (Sami and Druzynski, 2003), for example, reduced marine sediments such as marine black carbonaceous shales. Arsenic is known to be adsorped to clay mineral surfaces.

The geology of Jagersfontein is made up of sedimentary rocks (mudstone, sandstone and siltstone of the Prince Albert Formation and black carbonaceous shale of the Whitehill Formation) infringed by dolerite and Kimberlite pipes. These rocks are rich in silicate minerals such as quartz, pyroxene, plagioclase (mixture of albite and anorthite), feldspar, clay with traces of carbonate such as dolomite and calcite. These minerals may contain arsenic. According to Sami and Druzynski (2003), arsenic concentration in such minerals varies communally from 0.089 to 6 ppm but are not important contributors of arsenic to the whole rock geochemistry.

2.1.2 Anthropogenic sources

Arsenic is often found as a by-product of both acid mine drainage and of neutral pH leaching of mining waste from many precious and base metal ore deposits, for example sulphide ores (Facts sheet, 2003). Arsenopyrite (FeAsS) is the most common arsenic mineral in ores but it is usually found as a by-product associated with copper, gold, silver, and lead/zinc mining (Facts sheet, 2003). Arsenic is also released to the environment in the production of ceramics, application of wood preservatives and from landfills, application of arsenic compounds in agriculture as pesticides and insecticides, co-disposal of arsenical wastes with municipal wastes. Swine and poultry wastes, where the feed contained arsenic, might contaminate groundwater (Teclu, 2008).

The chemical nature of arsenic is dominated by its behaviour of changing its oxidation states or chemical form due to chemical or biological reactions that are common in the environment. The following chemical structures (Figure 2-2) show the differences in molecular structure between arsenite and arsenate that are the most common forms of arsenic in groundwater (Teclu, 2008).
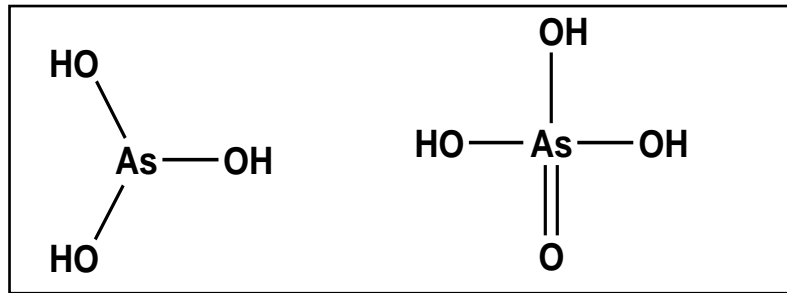
Figure 2-2: Molecular structures of arsenite and arsenate respectively (Teclu, 2008)

2.2 Uses of Arsenic

Arsenic is very poisonous to most life and there are only a few species of bacteria that are able to use arsenic compounds safely. Here are some of the most common uses for arsenic in the world today.

- The main use of metallic arsenic is for strengthening alloys of copper and lead to use in car batteries.
- It is also used as an n-type dopant in semi conductive electronic devices.
- Arsenic is also used in numerous pesticides, herbicides and insecticides though this practice is becoming less common as more of these products are banned.
- It is used as a wood preserver because of its toxicity to insects, bacteria and fungi. The product is chromated copper arsenate (CCA) which is an effective wood preservative that is hard to replace. A number of countries have banned its use (e.g., USA), but, it is still widely used in different regions, including Africa (Teclu, 2008).
- Arsenic is added to animal food to prevent disease and to promote growth. The products, Arsanilic acid and roxarsone (3-nitro-4-hydroxyphenyl arsenic acid) were added to increase rate of weight gain and improve feed efficiency in chickens and swine, and to control swine dysentery (Teclu, 2008).
- Arsenic is used in the medical treatment of cancers such as acute promyelocytic leukemia.
- It is also used in medical solutions such as Fowler's solution for psoriasis
- Arsenic-74 an isotope is being used as a way to locate tumours within the body. It produces clearer pictures than that of iodine.
- Arsenic is added in small quantities to alpha-brass to make it resistant to leaching zinc. This grade of brass is used to make plumbing fittings or other items which

are in constant contact with water (Source: http://wanttoknowit.com/uses-of-arsenic).

2.3 Speciation of Arsenic

Toxic effects of arsenic depend on its oxidation states therefore speciation of arsenic is of importance. The biological activity, mobility, bioavailability and also the toxicity of an element also depend on the chemical form in which the element is (Hedegaard and Sloth 2011).

Speciation of an element is the distribution of an element amongst defined chemical species in a system (Hedegaard and Sloth 2011). However, the identification of element species presents many analytical challenges (Beauchemin *et al.*, 1989 cited in Teclu, 2008). Some of the challenges include contamination and loss of the species during sample preparation (Burguera and Burgurea, 1997 cited in Teclu, 2008). Presented in Figure 2-3 are the chemical formulae for some of the different arsenic species occurring in the environment.
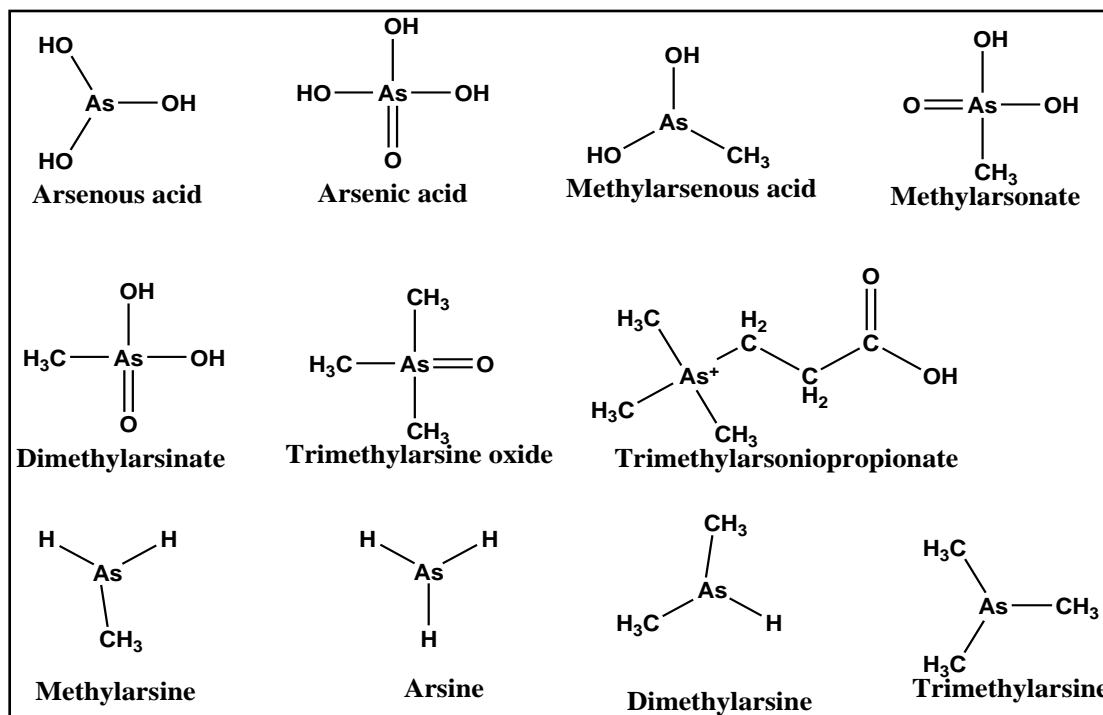
Figure 2-3: Environmental arsenic compounds (modified from Teclu, 2008).

The double bond in arsenate (Figure 2-2) influences its ability to be ionised through the loss of hydrogen ions. The pKa constants (tendency for ionisation) for arsenate and arsenite are as follows (O'Neil, 1995 cited in Teclu, 2008):

Arsenate: H_3AsO_4 $pK_1 = 2.2$ $pK_2 = 7.0$ $pK_3 = 11.5$

Arsenite: H_3AsO_3 $pK_1 = 9.2$ $pK_2 = 12.1$ $pK_3 = 13.4$

These ionisation steps occur at different pH values for arsenate and arsenite. The following diagrams (Figure 2-4) show the occurrence of arsenate and arsenite as a function of pH (Teclu, 2008).
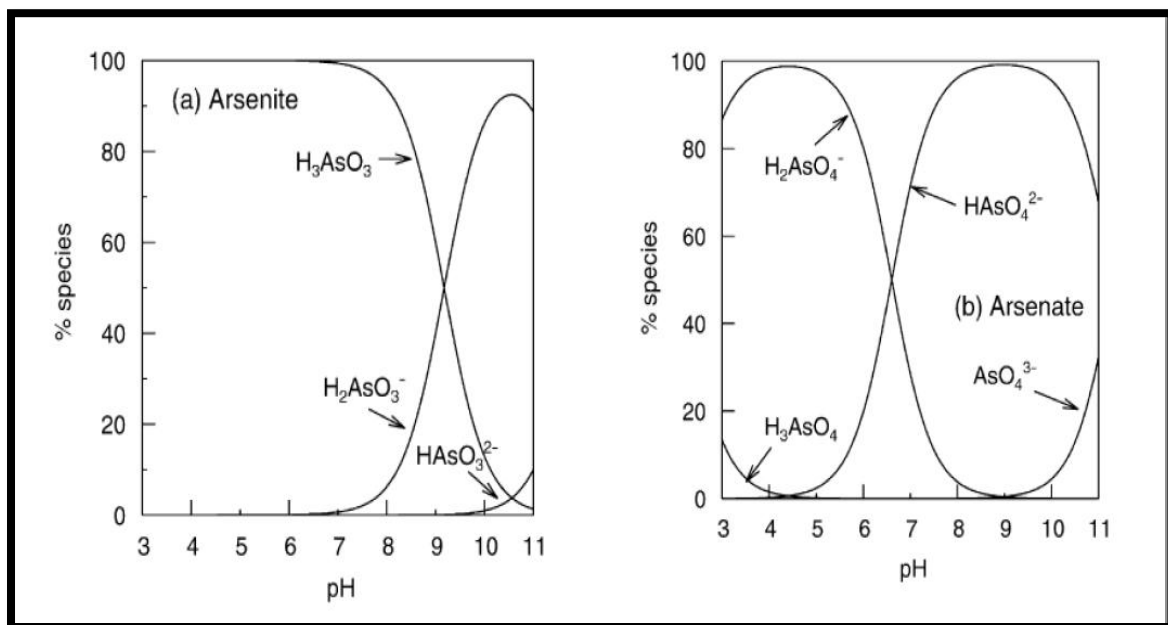
Figure 2-4: (a) Arsenite and (b) arsenate speciation as a function of pH (ionic strength of about 0.01M). Redox conditions have been chosen such that the indicated oxidation state dominates the speciation in both cases (Smedley and Kinniburgh, 2002)

Redox potential (Eh) and pH are the most important factors controlling arsenic speciation. Under oxidising conditions (low pH<6.9), $H_2AsO_4^-$ is dominant, whilst at higher pH, $HAsO_4^{2-}$ becomes dominant ($H_3AsO_4^0$ and AsO_4^{3-} may be present in extremely acidic and alkaline conditions respectively). Under reducing conditions at pH less than about pH 9.2, the uncharged arsenite species $H_3AsO_3^0$ will predominate (Figure 2-5; Brookins, 1988; Yan *et al.*, 2000 cited in Smedley and Kinniburgh, 2002).
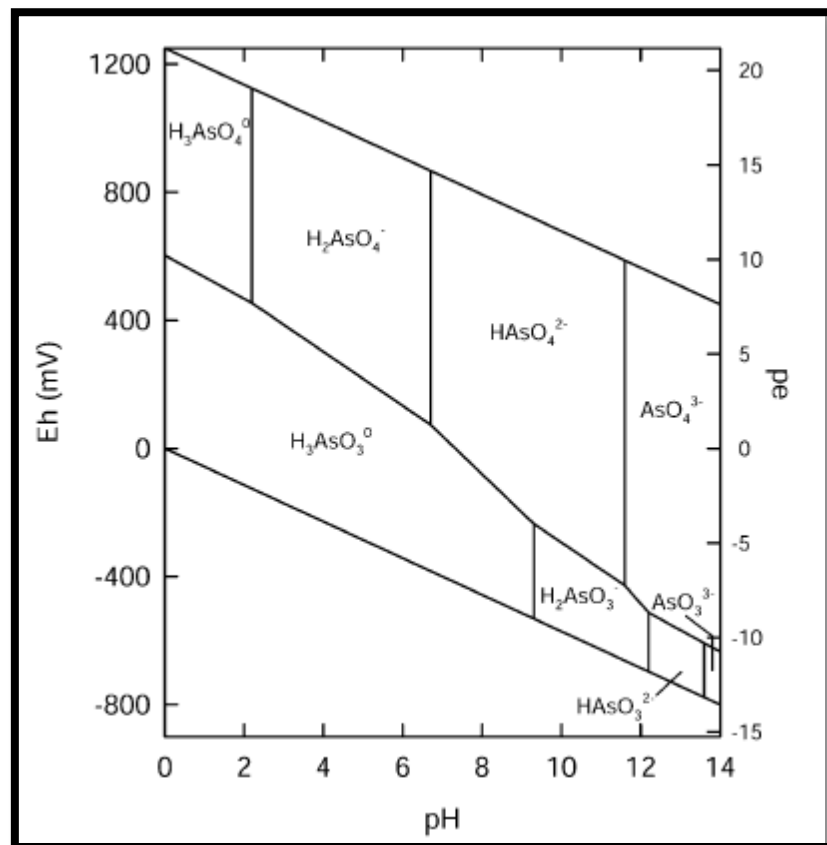
Figure 2-5: Eh-pH diagram for aqueous As species in the system As–O$_2$–H$_2$O at 25°C and 1 bar total pressure (Smedley and Kinniburgh, 2002).

In the presence of extremely high concentrations of reduced sulphur, dissolved As-sulphide species can be significant. Reducing, acidic conditions favour precipitation of orpiment (As$_2$S$_3$), realgar (AsS) or other sulphide minerals containing coprecipitated arsenic (Cullen and Reimer, 1989 cited in Smedley and Kinniburgh, 2002). Therefore high-arsenic waters are not expected where there is a high concentration of free sulphide (Moore *et al.*, 1988 cited in Smedley and Kinniburgh, 2002).

2.4 Geochemical Processes Controlling Arsenic Mobility

Geochemistry of arsenic determines the fate and transport of arsenic in the environment. Arsenic as an element is insoluble in water. The oxidized forms, or compounded forms, are usually more soluble in water. The two processes that chiefly control arsenic mobility in aquifers are; adsorption and desorption and solid-

phase precipitation and dissolution processes. Figure 2-6 illustrates the processes that enhance arsenic mobility in the atmosphere, soil and water.
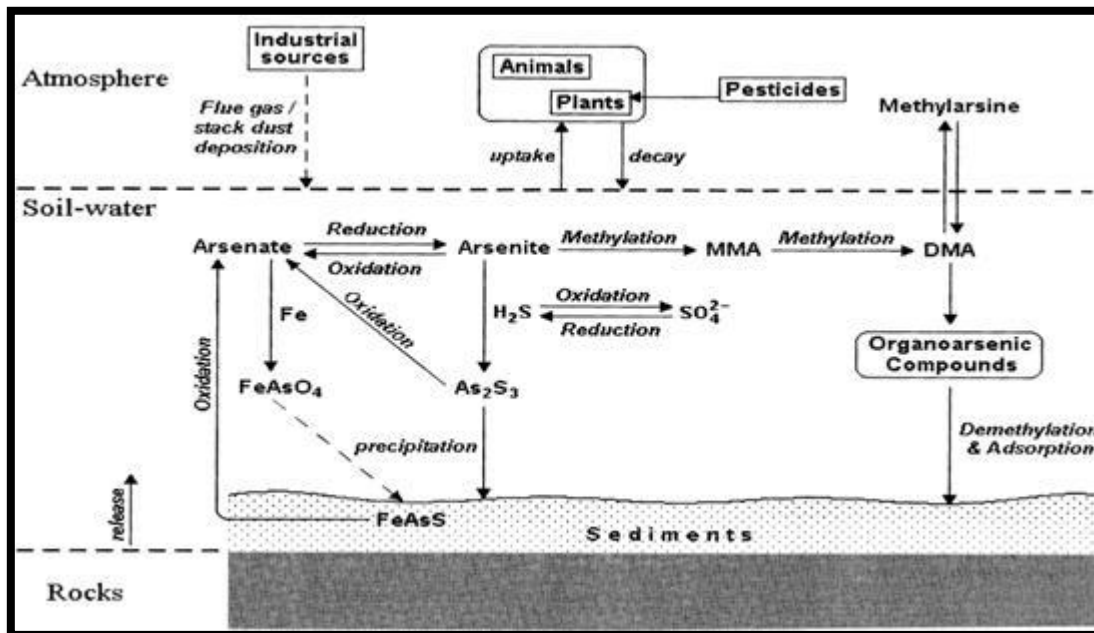
Figure 2-6: Mobilization of Arsenic in the environment (source: World Health Organization (WHO), 1999)

Arsenic adsorption and desorption reactions are influenced by changes in pH, occurrence of redox (reduction/oxidation) reactions, presence of competing anions, and solid-phase structural changes at the atomic level. Solid-phase precipitation and dissolution reactions are controlled by solution chemistry, including pH, redox state, and chemical composition (National Institute of Hydrology New Delhi, 2010).

2.4.1 Adsorption and Desorption Processes

There are two inorganic types of arsenic that usually occur in groundwater, As(III) mainly as arsenite or arsenous acid (H_3AsO_3) or As(V) in the form of arsenate or arsenic acid minus one or two of its protons ($H_2AsO_4^-$ and $HAsO_4^{2-}$).

□   Effect of pH

In natural pH range of groundwater As(V) exists with a negative charge and As(III) is neutral. Consequently As(V) compounds tend to sorb readily on the aquifer material (such as oxides or hydroxides of Fe, Al and Mn) as well as on clay minerals and organic matter. Since arsenite is neutral, it undergoes no sorption or exchange

processes hence it is 4 to10 times more mobile than arsenate. As the pH is raised, the compounds will tend to become more and more negatively charged as the arsenic and arsenous acid lose H^+ groups. So the charge of these arsenic compounds depends on pH.

As the pH increases, the charge on the arsenic compounds becomes more negative. One might tend to think that the arsenic compounds should bind more on the aquifer materials which are more positive. The problem is as the pH increases, the water becomes more basic and the OH^- ions tend to bind on the aquifer materials (positive sites) and neutralize them, hence they are no longer attractive to the arsenic compounds The solubility of metals in water is also affected by pH, so if at a pH that dissolves the mineral phase, it will result in the release of anything bound to it. So instead of decreasing in concentration, the As concentration in high pH water can actually rise.

☐ **Effect of Redox state**

Another factor affecting the form of As in solution is the reduction and oxidation (redox) state of the environment. As is redox sensitive, it losses electrons in the redox reactions resulting in a variety of redox states. The most stable soluble form of inorganic As under reducing conditions is arsenous acid (As(III)) and under oxidizing conditions is As(V) as arsenic acid. Just as pH affects binding sites, so is redox potential. Oxides or hydroxides of Fe, Al and Mn make up the binding sites for As and these metals can be reduced releasing them into solution hence releasing the As bound to them in to solution. Under reducing conditions there are two independent factors that are likely to increase the mobility of As;

- Reduction of As(V) to As(III), which is more mobile
- Reduction of binding sites, releasing bound As

Sulphides can also affect mobility of As under reducing conditions. If the sulphide is present in water containing arsenic, it precipitates out from the water phase with arsenic (MacRae, 2012).

☐ **Effect of Bacteria**

There are some bacteria that can endure and grow in the groundwater environment. They can affect As mobility directly by speeding the reduction of As(V) to As(III) and indirectly by reducing the binding sites for instance they can reduce Fe(III) on rock surfaces to Fe(II), which is released into water coupled with any As that was attached to the Fe(III) on the rock surface. But this can be limited by the amount of organic carbon present in the groundwater environment. Organic carbon serves as the "food" for the bacteria and acts as a reductant reducing the redox potential and fueling the reduction of As(V) to As(III) and Fe(III) to Fe(II) hence increasing mobility of As in water. Bacteria can also speed the oxidation of sulphides to sulphates which are soluble in water and hence releases arsenic. Oxidation of suphides can occur when minerals are exposed to oxygen due to excessive lowering of the water table.

2.4.2 Precipitation and Dissolution Processes

The various solid phases (minerals, amorphous oxides, volcanic glass, and organic carbon) of aquifer material can exist in a variety of thermodynamic states. Solid-phase precipitation is the formation of a solid phase from components present in aqueous solution. Precipitation of the mineral calcite, from calcium and carbonate present in groundwater, is an example of solid-phase precipitation. Dissolution of volcanic glass within an aquifer is an example of solid-phase dissolution. At any given time, some aquifer solid phases undergo dissolution, whereas others precipitate from solution. Arsenic contained within solid phases, either as a primary structural component or an impurity in any of a variety of solid phases, is released to groundwater when those solid phases dissolve. Similarly, arsenic is removed from groundwater when solid phases containing arsenic precipitate from aqueous solution. As an example, arsenic often co-precipitates with iron oxide; iron oxide, in such case, may act as an arsenic source (case of dissolution) or a sink (case of precipitation) for groundwater. Solid-phase dissolution contributes not only arsenic contained within that phase, but also any arsenic adsorbed to the solid-phase surface (National Institute of Hydrology New Delhi, 2010).

2.5 Impacts of Arsenic contamination

2.5.1 Health impacts

Arsenic is very toxic and affects animals, plants and humans after prolonged exposure. The toxicity of arsenic in water is dependent on the form, type of compound, and concentration in water. Inorganic arsenic is more toxic than organic arsenic.

Long term exposure of humans to arsenic could cause several diseases like skin lesions (igure 2-7). Table 2-3 presents a summary of infections caused by arsenic poisoning.

Table 2-3: Arsenic infection (Source: World Health Organization (WHO), 1999)

Organ System	Problems
Skin	Symmetric hyperkeratosis of palms and soles, melanosis or depigmentation, bowen's disease, basal cell carcinoma and squamous cell carcinoma
Liver	Enlargement, Jaundice, cirrhosis, non-cirrhotic portal hypertension
Nervous System	Peripheral neuropathy, hearing loss
Cardiovascular System	Acrocyanosis and Raynaud's Phenomenon
Hemopoietic System	Megalobastosis
Respiratory System	Lung Cancer
Endocrine System	Diabetes mellitus and goiter

Figure 2-7: Signs and symptoms of Arsenicosis (source: World Health Organization (WHO), 1999)

2.5.2 Social impacts

People are being ostracized due to skin diseases caused by long term exposure to Arsenic contaminated water. Figure 2-8 gives a summary of the various problems faced by individuals suffering from arsenicosis in Bangladesh.
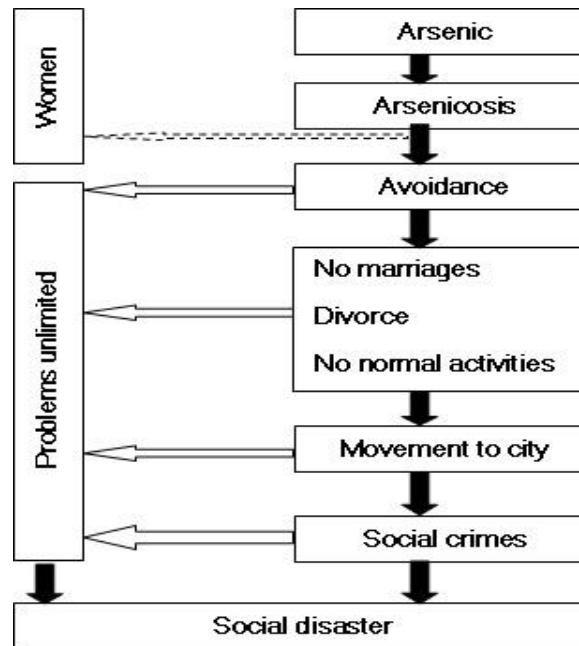
Figure 2-8: Social Implications of Arsenicosis Bangladesh. (modified from: **World Health Organization (WHO),1999)**

3 Field investigation: Methodology and Procedures

3.1 Introduction

The field work carried out was aimed at getting water samples from boreholes and surface water bodies in the Jagersfontein mine and the environs for chemical analysis. Historical data narrowly provides sufficient information on the availability of boreholes, water quality, and water use within a study area. Therefore it is often important to gather additional information from individuals within the study area. This can be achieved by carrying out a hydrocensus.

3.2 Hydrocensus and Groundwater sampling

Hydrocensus involves the collection of field data to develop an absolute understanding of the hydrological systems within a study area. Data collected usually involves borehole coordinates or coordinates of surface water bodies, groundwater levels, water samples for chemical analysis and typical water use in the study area.

In this study, the hydrocensus was aimed at

- Getting coordinates of boreholes and surface waters
- Measuring groundwater levels
- Collecting water samples for chemical and isotopic analysis and
- Finding out from the inhabitants, what the water is being used for.

3.2.1 Materials

GPS (Global Positioning System)

It is a device that can give a 3 dimensional (Longitude (X), Latitude (Y) and Elevation (Z)) position of a point. The model used during the field work was etrex Garmin and it enabled the taking of coordinates of boreholes and surface water where water samples were taken.

Multi-parameter Tester

This tester can measure up to five parameters. The model used was PCS Testr 35 (P stands for pH, C for electrical conductivity, S for salinity and T for temperature) and was used to measure the pH and Electrical conductivity of the water samples on site.

Water samples were collected for hydrochemical and isotopic analysis. The following determinants were required for this analysis:

Table 3-1: Physical and chemical determinants measured

Group	Determinants
Physical determinants	EC, pH, temperature
Major cations	K, Na, Ca, Mg
Major anions	Cl, SO_4, HCO_3^-
Main element monitored	As
Other elements	F, Br, Si, Fe, Al, Mn, Ba, Zn, Mo
Isotopes	$\delta^{18}O$, δD, ^3H

Temperature, EC and pH were measured in the field using PCS. This was done for the following reasons:

➢ These are parameters which can change after removal of water from the sampling point and are best measured as soon as possible. EC and pH are temperature dependent parameters and are influenced by precipitation of salts out of solution or sample degassing.

➢ These parameters provide a preliminary overview of the water quality which can be used to decide the extent of sample collection necessary.

➢ They provide a check on laboratory data. (Lloyd and Heathcote, 1985, cited in Weaver *et al*, 1999).

Water quality monitoring is the most effective way to ensure the fitness of use of the groundwater resource for the intended use(s). Regular water quality monitoring of indicator components of a water resource will give an early warning if water quality is

deteriorating over time (Usher *et al.*, 2006). In this light, Bloemwater, a water board established in 1991 whose vision is assuring sustainable provision of quality water services for life, conducts monthly sampling and analysis of their boreholes in Jagersfontein in order to monitor the water quality. Water quality monitoring is pursued internally at plant level and externally with the University of Free State. Internal plant monitoring involves testing on a two hourly to eight hourly basis. Externally, through the University of Free State, bio-monitoring takes place quarterly. Chemical monitoring and microbial monitoring takes place weekly, bi-monthly and monthly. Hence data was obtained from Bloemwater and will be included in the discussion of results.

For the purpose of this study, two sampling runs were carried out, the first in October 2011 and the second in April 2012. All the boreholes have pumps already installed and connected to a tap and so the water samples were collected from the tap using 500ml sample bottles, airtight and well labelled.

Three samples were collected from each borehole (500 ml each) from which one was sent to the IGS lab for general hydrochemical analysis with specific element Arsenic (As), the second was sent to School of Bioresources Engineering and Environmental Hydrology, University of KwaZulu-Natal for isotope (Oxygen-18 and Deuterium) analysis and the third to iThemba Labs in Gauteng for Tritium analyses. Other boreholes were located but were not available for sampling either because the owners were not around to give access or the boreholes were dry. Table 3-2 shows list of boreholes sampled and Figure 3-1 illustrates their positions.

Table 3-2: Boreholes sampled

Site name	Latitude	Longitude	Comments
Mine Shaft	-29.76778	25.41942	Sampled
Jagersfontein Borehole 1 (JBH 1)	-29.75795	25.42779	Sampled
17 Weil street (17 Wstr)	-29.76024	25.42391	Sampled, used for gardening

11 Fauresmith Street (11 Fstr)	-29.762203	25.42391	Sampled, domestic uses
Palmerston street (Pstr)	-29.76169	25.42805	Sampled, used irrigation.
Itumeleng	-29.77412	25.43794	Sampled
Charlesville (Cv) (surface water)	-29.78575	25.44497	Sampled
Fauresmith Borehole 1 (FB 1)	-29.75618	25.34821	Sampled
Fauresmith Borehole 1 A (FB1A)	-29.75627	25.34839	Sampled
10 Voottrekker street (10 Vstr)	-29.75786	25.42536	Sampled, adds chlorine to soften water. Used for gardening and domestic use.
6 Ried street (6 Rstr)	-29.75918	25.42500	Sampled, used for gardening.
20 Ooskloof street (20 Ostr)	-29.75603	25.42687	Sampled
9 Ooskloof street (9 Ostr)	-29.75840	25.42740	Sampled, domestic use and gardening
10 Ooskloof street (10 Ostr)	-29.75796	25.42744	Dry
11 Ooskloof street (11 Ostr)	-29.75790	25.42748	Sampled, domestic use
35 Harrington street (35 Hstr)	-29.75994	25.43072	Sampled, used for irrigation
6 Wekstreet (6 Wstr)	-29.76171	25.42292	Sampled, used for irrigation
TPB (Tswelang Pele Bomme)1	-29.79617	25.41904	Sampled, used for irrigation
TPB 2	-29.79657	25.42054	Sampled, used for irrigation
NG Kerk	-29.75877	25.42313	Sampled
Municipal Water (Mw)	-29.762145	25.426412	Sampled
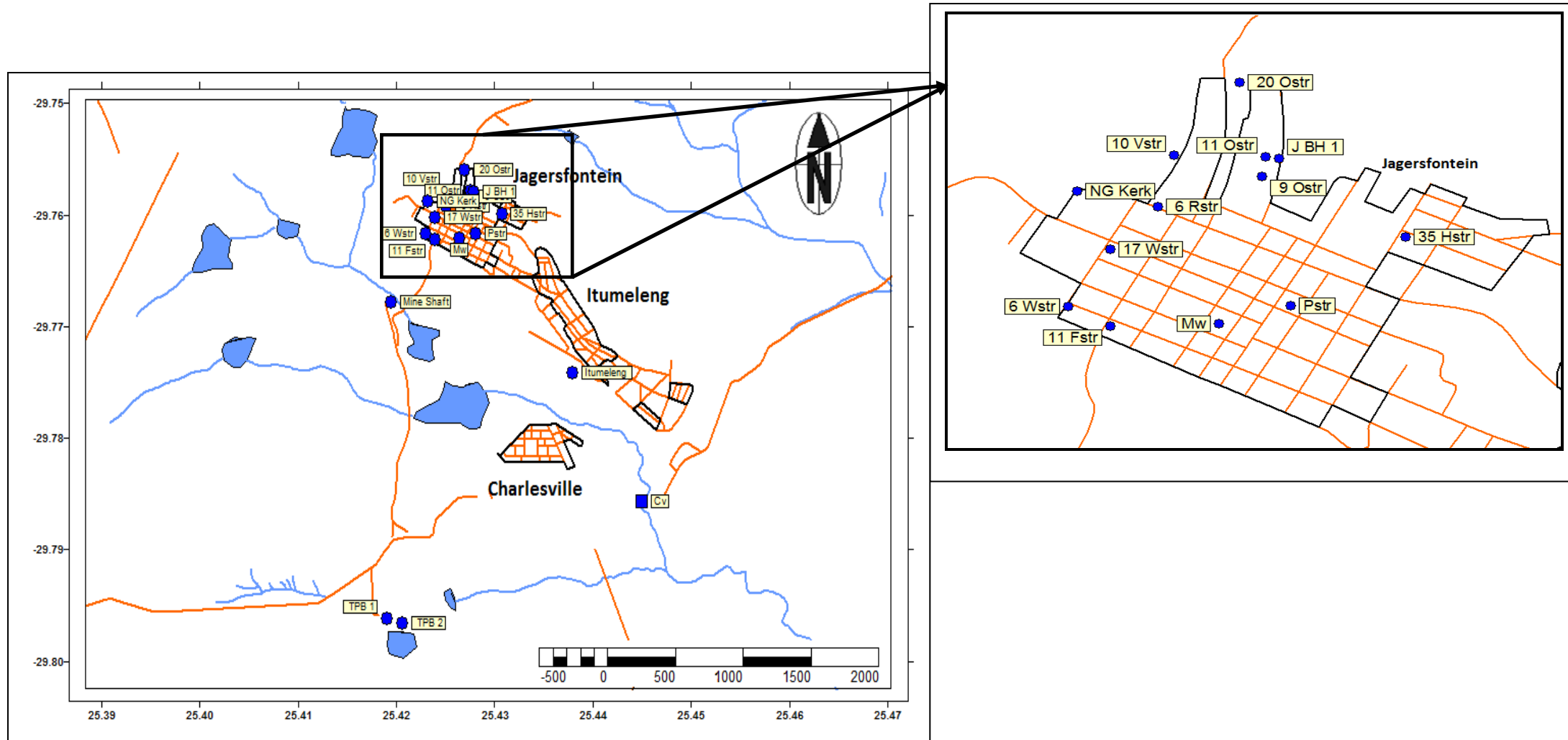
Figure 3-1: Position of Boreholes sampled

3.3 Laboratory analysis procedure

3.3.1 Hydrochemical analysis

The concentrations of the major cations for the samples were measured by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) on a Perkin Elmer DV 3000 system and the process is as follows;

Representative sample sub-aliquots (50 mL for waters) are taken and digested with mineral acids using microwave digestion procedures or beaker/hot plate digestion procedures using mineral acids and hydrogen peroxide. These digestion procedures are designed to insure that as much of the analytes that are available for recovery (i.e. total recoverable) are rendered soluble and relatively stable in aqueous acidic medium.

The resulting solutions are peristaltically pumped and pneumatically aspirated into aerosol mists which are conveyed in an argon gas stream through an inductively RF coupled region whereby a plasma is formed. Within the plasma, final desolvation, ionization, excitation and characteristic radiative emission for the analytes take place. The resultant emitted radiation is directed through the optics of the spectrometer where it is dispersed via a grating into component wavelengths that are indicative of specific elements present in the plasma. The intensity of the characteristic radiation is measured using a Charge- Coupled solid-state Detector (CCD).

The plasma can be viewed radially (from the side) and axially (down the central channel). If sample concentrations are expected to be low, axial, with a longer path length, will yield greater sensitivity. If concentrations are expected to be high, radial views will extend the linear range to greater concentrations. Since most elements have multiple analytical lines in this method, some were chosen to have one or more lines with axial view for sensitivity, but with a line viewed radially to extend the concentration range.

The Perkin Elmer Optima ICP optics is purged with nitrogen which should always be used when conducting an analysis with this analysis method. The sample concentration values are processed using the Perkin Elmer ICP WinLab software, typically using first order regression analysis calculations.

The concentrations of the major anions were measured using Dionex DX-120 Ion Chromatography system. Process is as follows;

Sample preparation

Eluent Solution: For anions, a 0.5712 g of sodium bicarbonate and 0.7632 g of sodium carbonate, dissolved in water and dilute to 4 L is used as eluent solution. This gives a reliable baseline and a multiple anion analysis. Eluent is degassed before use by purging with helium for 10 minutes.

Standard anion solution: Standard anion solutions are prepared by weighing the indicated amount of salt, dried to a constant weight at 105 ^{o}C, and diluted to 100 mL with distilled/deionized water.

Standards and solution are filled in vials and put in the autosampler.

Sample Analysis

If the sampler is collected with an autosampler that does not have filter samples, particulates are removed by filtering through a prewashed pore membrane. With either manual or automated injection, loop is flushed with several volumes of sample. Care should be taken to prevent carryover of analytes from samples of high concentration. After last peak has appeared and detector signal has returned to base line, another sample can be injected (Eaton *et al.*, 2005).

3.3.2 Deuterium and Oxygen-18 analysis

Sample preparation

Samples were shaken to equilibrate and 1.5ml of each sample was pipetted into marked autosampler vials with a fresh pipette tip. The samples were then capped with septa and stacked into the autosampler tray. A set of three standards was placed in the autosampler tray before every 5 samples to be analysed as well as after the last 5-sample set.

The standards used have been prepared by calibration against the following known standards: LGR2 (δ2H -117.00, δ18O -15.55), VSMOW2 (IAEA) (δ2H 0.0, δ18O 0.0) and IA-RO53 (IAD) (δ2H -61.97, δ18O -10.18). The accuracy of the standards calibration is presented in Appendix A.

Sample measurement

The spectrum of the analyzer was verified and the sub-sampling of the autosampler programmed. Each sample and standard was sub-sampled and analysed 6 times using a Los Gatos Research (LGR) DT-100 Liquid Water Isotope Laser Analyser.

Sample analysis

The LGR DT-100 analyser does not report δ values on a V-SMOW scale, but as ^{2}H/H and ^{18}O/^{16}O ratios. Post processing therefore requires determining these ratios for the standards, developing a relationship between the known V-SMOW δ values and the measured ratios of the standards (Figure C 4, appendix C) and then applying the relationship to the sub-sample measured ratios. Post processing checks included:

- Temperature variation (rate of change was less than 0.3oC/hour and standard deviation for each measurement less than 0.004oC),
- Sub-sample density (the density was between 2 to 4x1016 molecules/cm3 and standard deviation between measurements less than 1000 times smaller than the injected density),
- Deviation of the ^{2}H/H and ^{18}O/^{16}O ratios (Standard deviation of ^{2}H/H ratio was less than 1000x smaller than measured ratio; ^{18}O/^{16}O was less than 3000x smaller than measured ratio).

Each sub-sample result is reported as the average and standard deviation of injections 3-6 of the 6 sub-sample determinations. The standard deviation of the ^{2}H results was less than 2 permil and for the ^{18}O samples, less than 0.3 permil.

3.3.3 Tritium analysis

The samples were distilled and subsequently enriched by electrolysis. The electrolysis cells consist of two concentric metal tubes, which are insulated from each other. The outer anode, which is also the container, is of stainless steel. The inner cathode is of mild steel with a special surface coating. Some 500 ml of the water sample, having first been distilled and containing sodium hydroxide, is introduced into the cell. A direct current of some 10-20 ampere is then passed through the cell, which is cooled because of the heat generation. After several days, the electrolyte

volume is reduced to some 20 ml. The volume reduction of some 25 times produces a corresponding tritium enrichment factor of about 20. Samples of standard known tritium concentration (spikes) are run in one cell of each batch to check on the enrichment attained.

For liquid scintillation counting samples are prepared by directly distilling the enriched water sample from the now highly concentrated electrolyte. 10 ml of the distilled water sample is mixed with 11 ml Ultima Gold and placed in a vial in the analyser and counted 2 to 3 cycles of 4 hours. Detection limits are 0.2 TU for enriched samples.

4 Results and Interpretation of Hydrocensus Data

Interpretation of the hydrocensus data was done in sections which involved hydro-chemically characterising the water samples and determining the arsenic concentration level in the water samples; including assessing the water quality attained after treatment processes were carried out. Carcinogenic risk was calculated to ascertain the risk population stand when exposed to this water. Cross plots and correlations were done not leaving out degree of hardness and isotopic characterisation.

4.1 Hydrochemical characterisation

Groundwater in this area is characterised by pH between 7 and 8.66, designating an insignificant influence of anthropogenic contamination. The dominant cation is Magnesium (Mg) while the dominant anion is sulphate (SO_4).

Piper Diagram

Presented in Figure 4-1, is piper diagram of samples collected during the two sampling runs including Bloemwater's data. The chemical characteristics of the samples show different types or water characters and can be differentiated into three groups (Table 4-1).
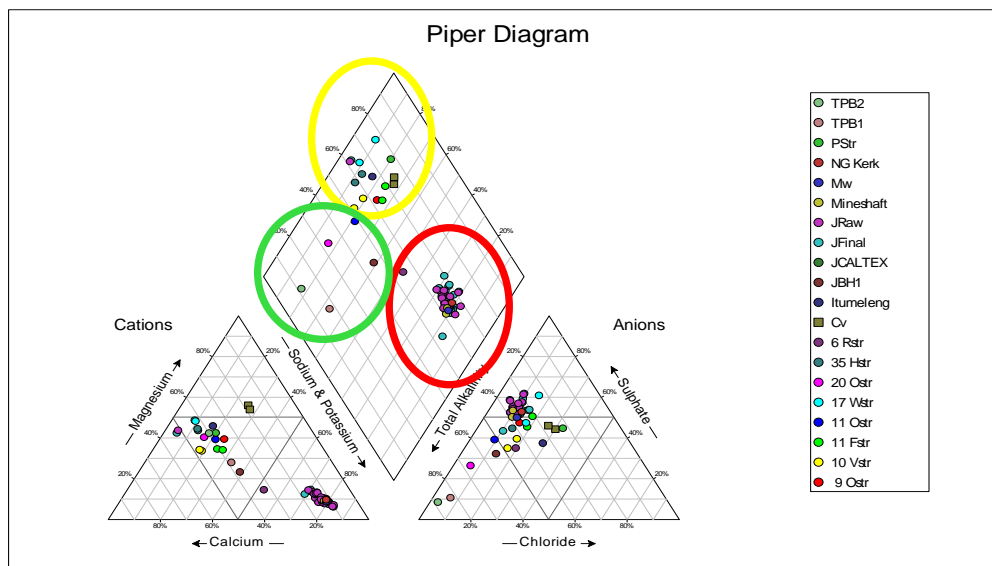
Figure 4-1: Piper diagram of samples

Table 4-1: Water character type from piper diagram

Water character type	Water samples
Sodium/Potassium-Sulphate (red circle)	Mine shaft, NG Kerk, Mw, 6 Rstr, Jfinal and Jraw
Magnessium-Sulphate (yellow circle)	Cv, 9 Ostr, Pstr, 11 Fstr, 17 Wstr, 10 Vstr, 6 Wstr, Itumeleng and 35 Hstr
Magnessium-Bicarbonate (green circle)	TPB1, TPB2, 20 Ostr, J BH 1 and11 Ostr

Expanded Durov Diagram

By referring to Figure C 1 (appendix c), water samples can be classified as presented in Table 4-2.

The macro element ion content of the majority of the boreholes is dominated by Magnesium cation and Sulphate anion. Some two samples JRaw and JFinal collected on the 25th of June 2012 plots on the $CaSO_4$ block. This is quite unusual compared with the other samples. This could either be an analytical error for some chemical parameters were not analysed. Figure 4-2 shows expanded durov diagram of samples collected in both sampling runs, Bloemwater data included.
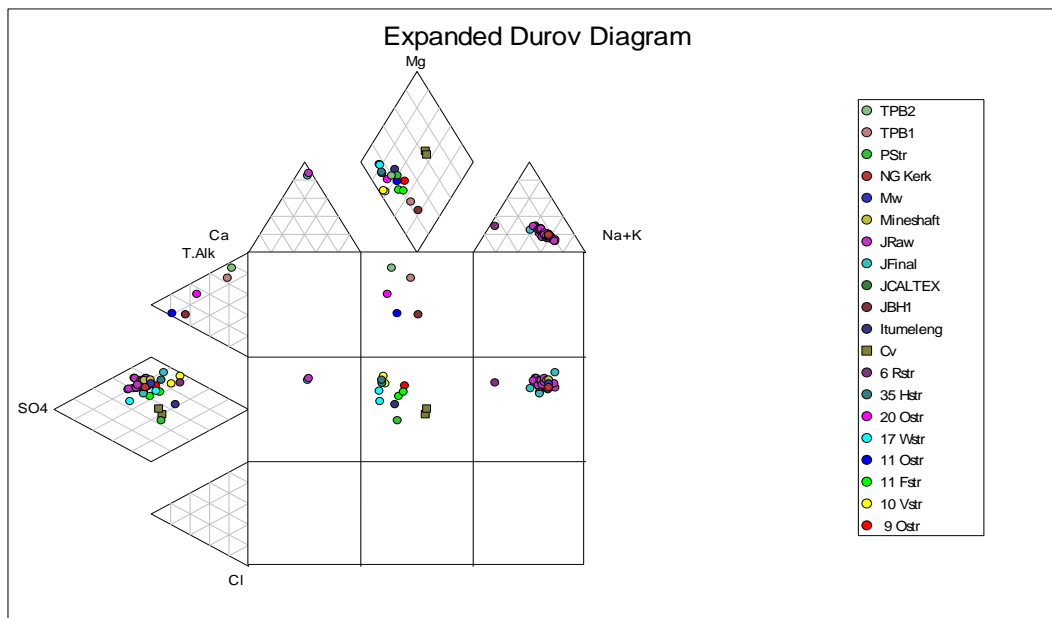
Figure 4-2: Expanded Durov diagram of samples

Table 4-2: Classification with respect to Expanded Durov

Water quality signature type	Water samples
Groundwater from field 5 that has been in contact with a source rich in Na or old stagnant NaCl dominated water that resides in Na rich host rock / material.	Mine shaft, NG Kerk, Mw, 6 Rstr, Jfinal and JRaw
Groundwater that is usually a mix of different types – either fresh water from fields 1 and 2 that has undergone SO4 and NaCl mixing/contamination or old stagnant NaCl dominated water that has mixed with clean water.	Cv, 9 Ostr, Pstr, 11 Fstr, 17 Wstr, 10 Vstr, 6 Wstr, Itumeleng and 35 Hstr
Fresh, clean, relatively young groundwater that has started to undergo Mg ion exchange, often found in dolomitic terrain.	TPB1, TPB2, 20 Ostr, J BH1 and 11 Ostr
Fresh, recently recharged groundwater with HCO_3 and CO_3 dominated ions that has been in contact with a source of SO_4 contamination or that has moved through SO_4 enriched bedrock	JRaw and JFinal analysed on the 25th of June 2012

Stiff Diagrams

The Stiff diagrams relates and agrees well with the piper and expanded Durov diagrams because, the diagrams all look different signifying that the water types are chemically different and most probably have different sources.

Two water samples from same aquifer have a general shape but different sizes portraying the different concentrations of the chemical species. This is the case of water samples TPB1 and TPB2. This implies they are chemically similar and have

same source. Mw, NG Kerk, mineshaft, JCaltex, JRaw, JFinal are all samples of same source because their geometry looks more or less the same. The only difference is that the data for JRaw and JFinal analysed on the 25th of June 2012 show low Na and K concentrations and by referring to the data, it was noticed Na cation was not analysed for these samples. In Figure 4-3, is presented the stiff diagrams and generally looking at the geometries of the water samples, they can be classified as presented in Table 4-3.

Table 4-3: Classification of water with respect to stiff diagram

Water samples	
Jfinal, Jraw, Mw, NG Kerk and Mine shaft	Mine water
6 Rstr	Fresh water mixed with mine water
TPB 1, TPB 2, 20 Ostr, JBH1, 11 Ostr and FB1	Freshly recharged water
Cv, 9 Ostr, Pstr, 11 Fstr, 17 Wstr, 10 Vstr, 6 Wstr, Itumeleng. 35 Hstr and FB1A	Fresh water slightly mixed
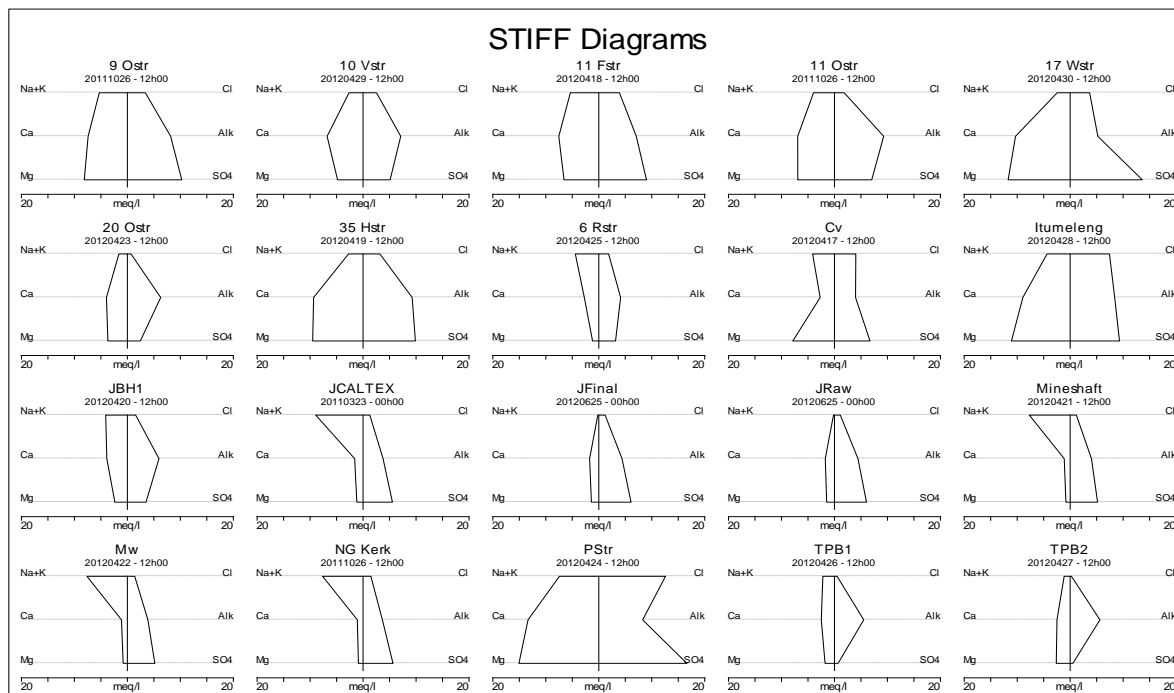
Figure 4-3: Stiff diagram for samples

Saturation index analysis

In Table 4-4, the saturation indices of some selected minerals calculated by PHREEQC with the wateq4f database is presented, using analytical data from boreholes with dissimilar arsenic concentration. The samples are generally under saturated with most of the minerals (negative saturation index) implying there is still chance for dissolution for most of these minerals. However samples with high arsenic concentrations are saturated (positive saturation index) with calcite, quartz and talc. Table 4-5 also presents calculated saturation indices of some selected minerals for the April 2012 samples. The groundwater shows saturation with respect to iron minerals such as hematite (Fe_2O_3), magnetite (Fe_3O_4) and goethite (FeOOH). On the other hand, it is under saturated with aluminium, manganese and zinc minerals. However, it is saturated with respect to diaspore (AlOOH).

Table 4-4: Saturation indices for selected minerals (October 2011 samples)

Mineral	Mineshaft As : 0.153mg/l	JBH 1 As: 0.058 mg/l	NG Kerk As:0.015mg/l	20 Ostr As: <0.006 mg/l	6 Wstr As:<0.006 mg/l

Anhydrite ($CaSO_4$)	-1.93	-1.43	-1.98	-1.87	-1.05
Arsenolite (AsO_3)	-35.62	-30.48	-33.55	-31.15	-28.30
As_2O_5 (Cr)	-34.53	-33.11	-33.94	-33.81	-32.61
As native	-43.02	-37.66	-40.87	-37.96	-35.31
$Ca_3(AsO_4)_2$:4w	-10.03	-12.24	-11.81	-13.47	-13.93
Calcite ($CaCO_3$)	0.43	0.42	-0.01	0.20	0.12
CO_2	-3.09	-1.89	-2.75	-1.95	-1.47
Diopside ($CaMgSi_2O_6$)	-1.18	-3.39	-2.69	-3.40	-4.08
Dolomite ($CaMg(CO_3)_2$)	0.84	0.76	0.02	0.50	0.39
Epsomite ($MgSO_4$:$7H_2O$)	-4.31	-3.87	-4.29	-4.11	-3.25
Gypsum ($CaSO_4$:$2H_2O$)	-1.71	-1.21	-1.76	-1.65	-0.83
Halite (NaCl)	-6.79	-6.89	-6.64	-7.69	-6.71
Hydromagnesite ($Mg_5(CO_3)_4(OH)_2$:$4H_2O$)	-11.02	-12.58	-13.27	-12.64	-13.34
Magnesite ($MgCO_3$)	-0.17	-0.25	-0.56	-0.27	-0.31
O_2 (g)	-33.79	-37.51	-35.27	-37.55	-39.19
Quartz (SiO_2)	0.22	0.35	0.23	0.42	0.62
Talc ($Mg_3Si_4O_{10}(OH)_2$)	2.68	-0.61	0.52	-0.25	-1.02

Table 4-5: Saturation indices of some selected minerals (April 2012 sampling)

Mineral	Chemical formula	Municipal water As:0.070mg/l	Mineshaft As:0.087mg/l	JBH1 As:<0.006mg/l	Pstr As:<0.006mg/l
Al(OH)$_3$(a)	Al(OH)$_3$	-2.85	-3.15	-3.13	-2.51
AlAsO$_4$:2H$_2$O	AlAsO$_4$:2H$_2$O	-10.73	-11.2	-11.69	-9.98
Albite	NaAlSi$_3$O$_8$	-1.8	-1.98	-2.4	-2.22
AlumK	KAl(SO4)$_2$:12H$_2$O	-21.33	-22.02	-22.12	-18.43
Anhydrite	CaSO$_4$	-2	-2	-1.67	-0.84
Arsenolite	As$_2$O$_3$	-35.98	-36.82	-36.55	-31.75
As_native	As	-43.08	-43.89	-42.76	-38.41
Ba$_3$(AsO4)$_2$	Ba$_3$(AsO4)$_2$	8.62	8.84	5.67	4.46
Birnessite	MnO$_2$	-9.66	-9.08	-10.53	-11.71
Brucite	Mg(OH)$_2$	-3.92	-3.65	-3.82	-9.54
Ca$_3$(AsO4)$_2$:4w	Ca$_3$(AsO4)$_2$:4H$_2$O	-10.91	-10.45	-11.8	-12.36
Calcite	CaCO$_3$	0.43	0.57	0.97	0.81
CO$_2$(g)	CO$_2$	-2.97	-3.09	-2.59	-1.84
Cu(OH)$_2$	Cu(OH)$_2$	-1.8	-1.82	-2.04	-2.3
Cu$_3$(AsO4)$_2$:6w	Cu$_3$(AsO4)$_2$:6H$_2$O	-13.41	-13.94	-15.48	-14.08
CupricFerrite	CuFe$_2$O$_4$	13.45	12.51	12.98	12.38
CuSO$_4$	CuSO$_4$	-15.61	-15.94	-15.68	-14.19
Diaspore	AlOOH	1.07	0.77	0.79	1.41
Diopside	CaMgSi$_2$O$_6$	-1.38	-0.86	-1.03	-2.6
Dolomite	CaMg(CO$_3$)$_2$	0.85	1.13	1.86	1.79

Epsomite	$MgSO_4{:}7H_2O$	-4.37	-4.37	-4.11	-3.02
Fe(OH)$_3$(a)	$Fe(OH)_3$	1.36	0.92	1.24	1.07
Gibbsite	$Al(OH)_3$	-0.16	-0.46	-0.44	0.18
Goethite	FeOOH	7.25	6.81	7.13	6.96
Gypsum	$CaSO4{:}2H_2O$	-1.78	-1.78	-1.45	-0.62
Halite	NaCl	-6.7	-6.74	-6.95	-5.82
Hematite	Fe_2O_3	16.5	15.63	16.27	15.93
Magnesite	$MgCO_3$	-0.17	-0.03	0.31	0.4
Magnetite	Fe_3O_4	15.72	14.27	15.57	15.71
Manganite	MnOOH	-3.71	-3.26	-4.38	-4.9
O$_2$(g)	O_2	-33.95	-33.43	-34.75	-37.35
Quartz	SiO_2	0.24	0.24	0.29	0.29
Rhodochrosite	$MnCO_3$	-0.67	-0.47	-0.76	0.12
Talc	$Mg_3Si_4O_{10}(OH)_2$	2.41	3.18	2.89	0.92

Major ion composition of water samples

Plots of various major elements versus TDS values were drawn to determine the contributing elements to groundwater mineralization and the major hydrogeochemical processes. Figure 4-4 shows that Ca, Mg and SO$_4$ are the key contributors to groundwater mineralization resulting from dissolution of evaporite minerals and cation exchange.
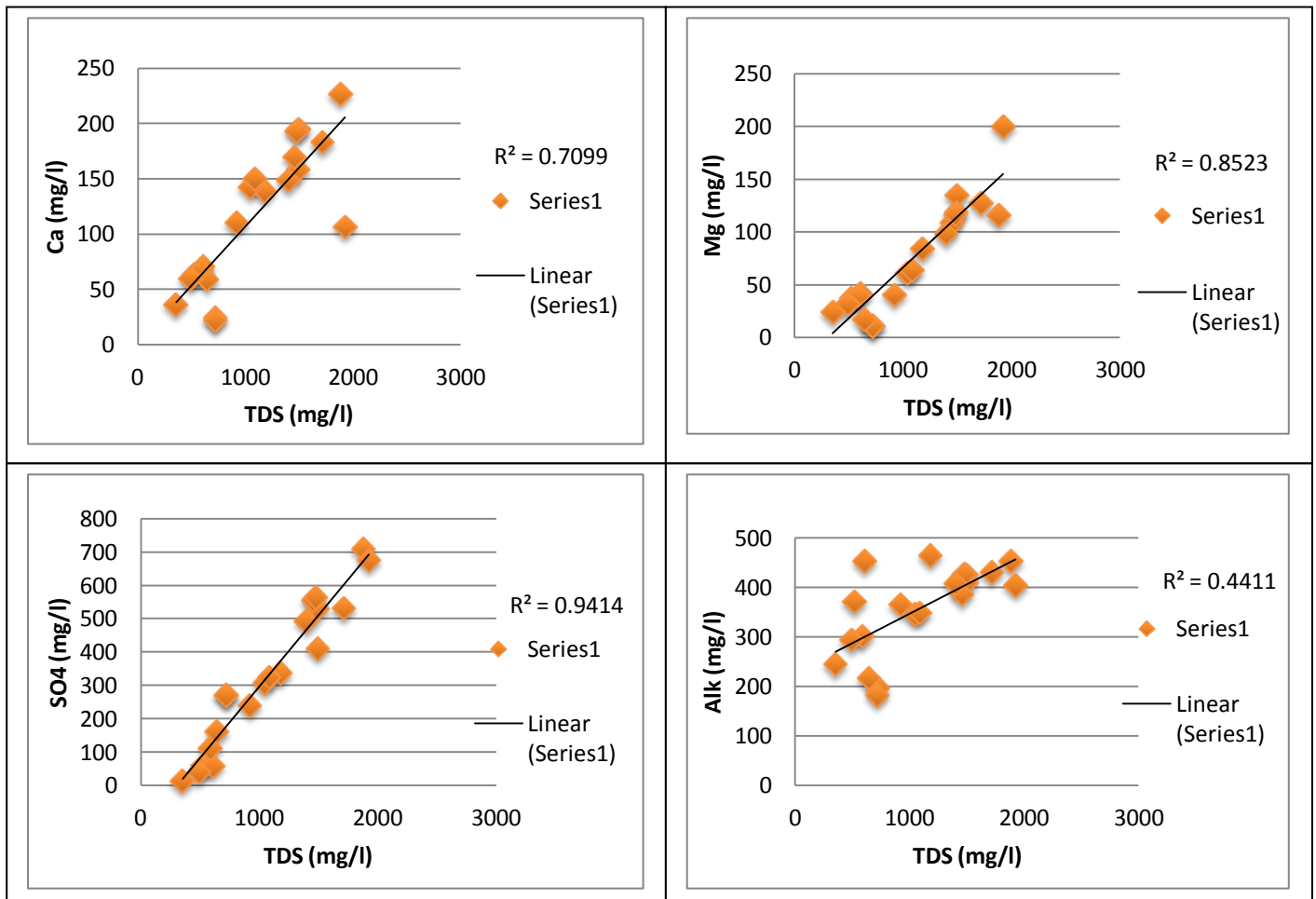
Figure 4-4: Major elements and Alkalinity vs TDS
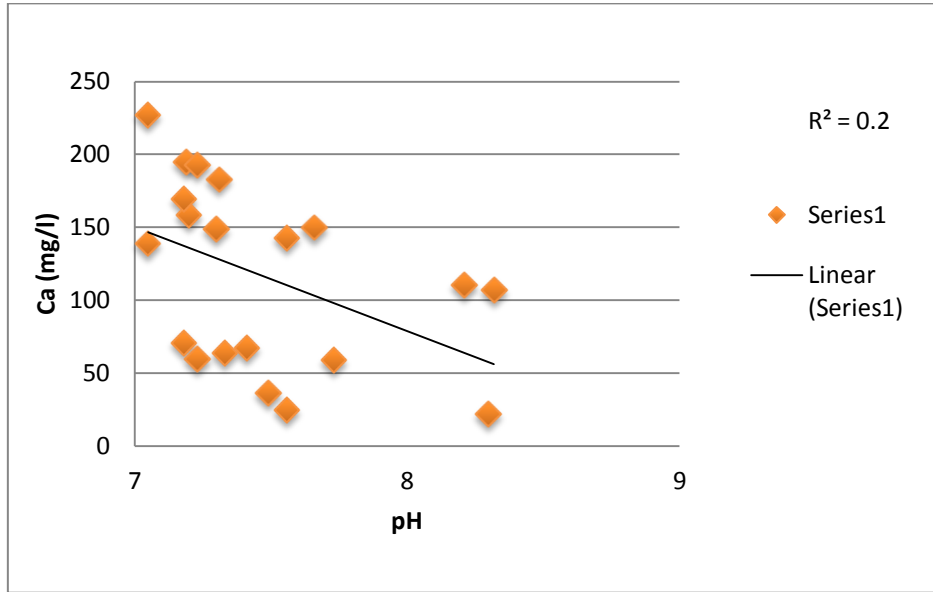
Figure 4-5: Calcium versus pH

Element cross plots and spearman's correlation

Calcium has a fair negative correlation with pH (Figure 4-5), implying that elevated pH might be due to dissolution of carbonates promoted by replacement of Na by Ca on exchange sites. This is typical for cation exchange and the global equation for the process is:

$CaCO_3$ + CO_2 + H_2O + Na_2-X = 2Na+ + $2HCO_3^-$ + Ca-X (Claesson and Fagerberg, 2003)
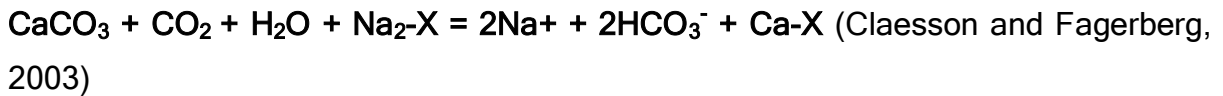
The positive correlations shown in Figure 4-6 between Mg vs SO4, Ca vs SO4 and Ca vs alkalinity are all due to dissolution of sulphate and carbonate containing minerals (Table 4-4).
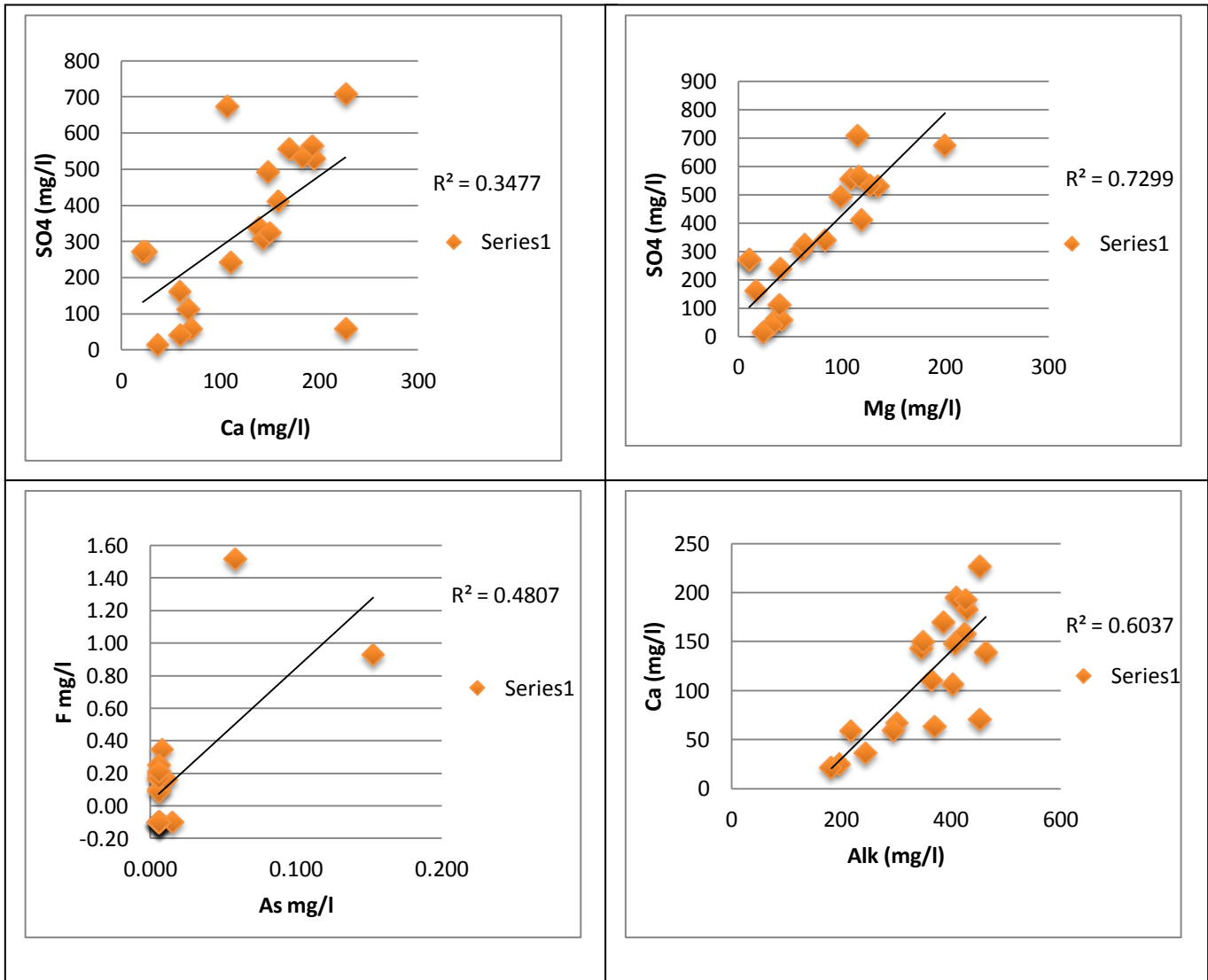
Figure 4-6: Correlation between other chemical parameters

Spearman's correlation coefficients were calculated to observe potential link between the measured parameters (Table 4-6). Arsenic concentrations are also plotted against selected physicochemical parameters (Appendix Figure D 1, Figure D 2, Figure D 3 and Figure D 4). The arsenic concentrations did not show any good correlation with most of these parameters which confirms that the arsenic and these other parameters are not of same origin.

Table 4-6: Spearman's correlation coefficients

	pH	EC	Ca	Mg	Na	K	MAlk	F	Cl	NO2(N)	Br	NO3(N)	PO4	SO4	As	Si
pH	1.000															
EC	-0.303	1.000														
Ca	-0.625	0.689	1.000													
Mg	-0.409	0.814	0.863	1.000												
Na	0.194	0.622	0.054	0.181	1.000											
K	0.064	0.630	0.265	0.414	0.705	1.000										
Malk	-0.592	0.727	0.860	0.861	0.137	0.260	1.000									
F	0.721	-0.442	-0.582	-0.560	-0.087	-0.084	-0.559	1.000								
Cl	-0.237	0.939	0.752	0.852	0.568	0.579	0.689	-0.552	1.000							
NO2(N)	0.565	-0.445	-0.436	-0.372	-0.241	-0.286	-0.391	0.797	-0.466	1.000						
Br	0.302	-0.497	-0.336	-0.326	-0.295	-0.281	-0.392	0.571	-0.419	0.845	1.000					
NO3(N)	-0.557	0.536	0.832	0.676	-0.018	0.176	0.535	-0.535	0.663	-0.301	-0.133	1.000				
PO4	0.624	-0.241	-0.458	-0.166	-0.094	-0.120	-0.320	0.628	-0.277	0.858	0.684	-0.392	1.000			
SO4	-0.336	0.851	0.779	0.798	0.543	0.681	0.734	-0.537	0.896	-0.511	-0.392	0.555	-0.348	1.000		
As	0.562	-0.016	-0.195	-0.184	0.367	0.229	-0.155	0.663	-0.119	0.526	0.367	-0.198	0.457	-0.090	1.000	
Si	-0.594	0.158	0.636	0.430	-0.352	0.041	0.619	-0.177	0.151	-0.045	0.081	0.472	-0.257	0.342	-0.079	1.000

Hardness in water samples

Water hardness is principally the amount of calcium (Ca) and magnesium (Mg) and to a lesser extent, iron in water. It is being calculated by summing the concentration of Ca and Mg and expressed as meq/l, mg $CaCO_3$, or hardness degree.

Water hardness in most groundwater is naturally occurring from weathering of limestone, sedimentary rock and calcium bearing minerals. Hardness can also occur locally in groundwater from chemical and mining industry effluent or excessive application of lime to the soil in agricultural areas (Water Stewardship Information Series hardness in groundwater, 2007).

The DWAF domestic use guidelines divide hardness into the following categories;

Table 4-7: Hardness range and description

From: DWAF Domestic use guidelines	
Hardness range	Description of hardness
0 - 50	Soft
50 - 100	Moderately soft
100 - 150	Slightly hard
150 - 200	Moderately hard
200 - 250	Hard
>300	Very hard

By referring to Table 4-7 hardness for the water samples were categorised as follows:

Table 4-8: Ca and Mg hardness of water samples

Site name	Ca hardness	Mg hardness	Total hardness	Comments
Mine Shaft	62	43	105	Slightly hard
Jagersfontein Borehole 1	276	166	442	Very hard
17 Weil Street	487	554	1041	Very hard
11 Fauresmith Street	567	474	1041	Very hard
Palmerston Street	457	524	981	Very hard
Itumeleng	396	488	884	Very hard
Charlesville (surface water)	267	819	1086	Very hard
10 Voortrekker Street	357	251	608	Very hard
6 Ried Street	147	71	219	Hard
20 Ooskloof Street	169	162	331	Very hard
9 Ooskloof Street	371	405	776	Very hard
11 Ooskloof Street	347	345	692	Very hard
35 Harrington Street	483	479	961	Very hard
6 Wek Street	423	445	869	Very hard
TPB 1	149	130	279	Hard
TPB 2	91	98	189	Moderately hard
NG Kerk	54	44	99	Moderately soft

From Table 4-8, it can be concluded that the groundwater from the study area is generally hard. According to Murphy, 2007, hard water is often derived from the drainage of calcareous (calcite-rich) sediments, because calcite ($CaCO_3$) dissolves, releasing the calcium and also drainage from operating and abandoned mine sites can contribute calcium, magnesium, iron, manganese, and other ions if minerals containing these constituents are present and are exposed to air and water. In this light, it can be concluded that hardness of these water samples may be as result of the dissolution of geological constituents in the study area which is made up of sedimentary rocks rich in calcite minerals and from abandoned mine which is made of a Kimberlite pipe rich with magnesium containing minerals.

4.2 Indices of Base Exchange (IBE)

Control of the dissolution of undesirable constituents in waters is impossible during the subsurface run off but it is essential to know the various changes undergone by water during the travel (Pojasek, 1977; Johnson, 1979 cited in Nagaraju *et al.*, 2005). The ion exchange between the groundwater and its host environment during residence or travel can be understood by studying the chloro-alkaline indices. To know the direction of exchange during the path of groundwater through the aquifer, Schoeller (1965, 1977) suggested 2 chloroalkaline indices CAI 1 and CAI 2 to indicate the exchange of ions between groundwater and its host environment. This is positive when there is an exchange of Na and K from the water with Mg and Ca of the rocks and it's called a direct exchange and is negative when there is an exchange of Mg and Ca of the waters with Na and K of the rocks, called indirect exchange (Nagaraju *et al.*, 2005). The indices as defined by Aghazadeh and Mogaddam (2010) are

$$CAI\ 1 = \frac{[Cl - (Na + K)]}{Cl}$$

Equation 4-1

$$CAI\ 2 = \frac{[Cl - (Na + K)]}{(SO_4 + HCO_3 + CO_{3+}NO_{3)}}$$

Equation 4-2

All concentrations are in mg/l.

CAI 1 and CAI 2 are calculated for the water samples (appendix Table C 7).

Presented Figure 4-9 in are the samples and the exchange type occurring in the water samples.

Table 4-9: Exchange types of water samples

Samples	CAI 1 value range	CAI 2 value range	Exchange type
17 Wstr, 11Fstr, Pstr, Itumeleng, Cv, 6 Wstr, 35 Hstr and 10 Vstr.	0.06 - 0.57	0.01 - 0.5	Direct exchange. Exchange of Na/K

			from water with Mg/Ca of rocks.
Mineshaft, JBH1, NG Kerk, 9 Ostr, 11 Ostr, 20 Ostr, 6 Rstr, TPB 1 and TPB 2.	-4.01 - -0.31	-0.31 - -0.02	Indirect exchange. Exchange of Mg/Ca from water with Na/K of rocks.

The geology of the Jagersfontein area which is dominated by sedimentary rocks (section 1.3.4) comprises of evaporite minerals (for example calcite, magnetite and gypsum) which make up the chemistry of the rock in the aquifer system. Most of these minerals amongst others, as shown in Table 4-4 and Table 4-5 are undersaturated (negative saturation indice meaning dissolution), hence contribute to the availability for these elements (Mg, Na, Ca, K) for exchange. The composition of Kimberlite as discussed in section 1.3.5 is composed of minerals (appendix Table A 2) which are abundant in magnesium, hence making it a potential source of magnesium available for exchange.

4.3 Arsenic concentrations in groundwater

Water samples were collected from the mine and also from individual boreholes in the Jagersfontein town. These samples show diverse arsenic concentrations over the study area with Mineshaft, JRaw, JFinal, JCaltex, Mw, JBH1 and NG Kerk samples showing elevated arsenic concentrations surpassing the SANS 241: 2006 guideline value for arsenic in groundwater (<0.01 mg/l). The rest of the individual boreholes in the town show arsenic concentrations less than 0.006 mg/l (Figure 4-7). JRaw is a sample collected by Bloemwater from the mine shaft while JFinal is water sample from the mine shaft that has been treated in a package plant. Presented in Figure 4-7 is the time series graph of the samples. This graph shows the changes in arsenic concentration over the time period from February 2011 to June 2012. JFinal which is treated mine water still shows high arsenic concentration. This implies the treatment method being used in the package plant (see Chapter 5 for process description) needs to be upgraded for it is not very effective. Just one sampling analysis result was obtained for NG Kerk, Mw and JCaltex samples which show high arsenic concentrations (Figure 4-8). For this reason these samples will be given a benefit of

doubt and it is recommended that the water service provider in the Jagersfontein town should consider testing the water being supplied to the public to keep in check the arsenic concentrations in the water. Emphasis is placed on Mw sample as it was collected from a public tap in the Jagersfontein town and also not forgetting the fact that JFinal sample still shows high arsenic concentration.
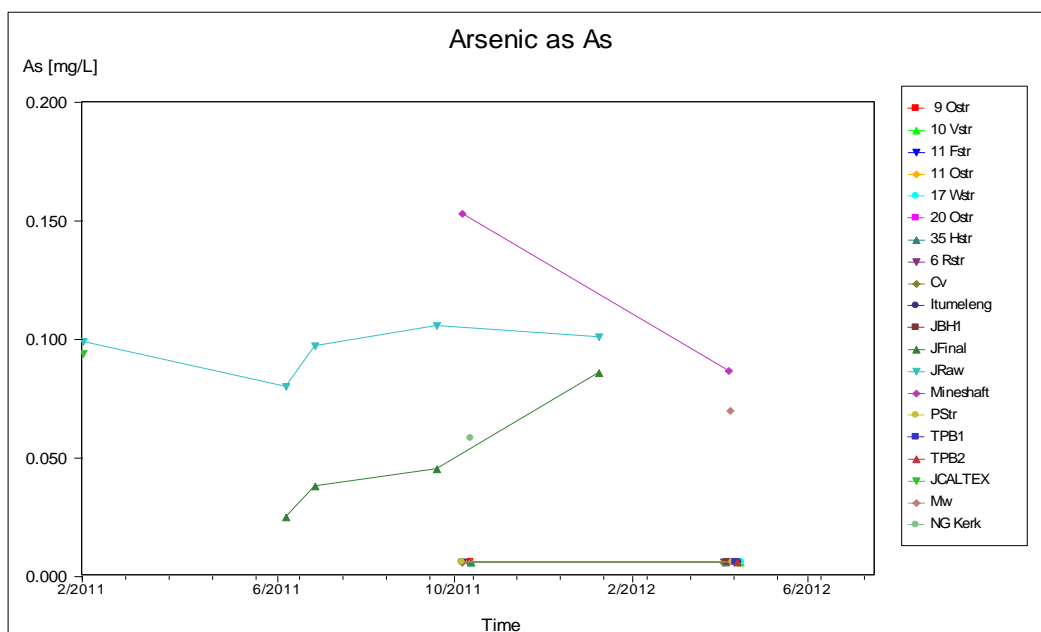
Figure 4-7: Time series graph of Arsenic
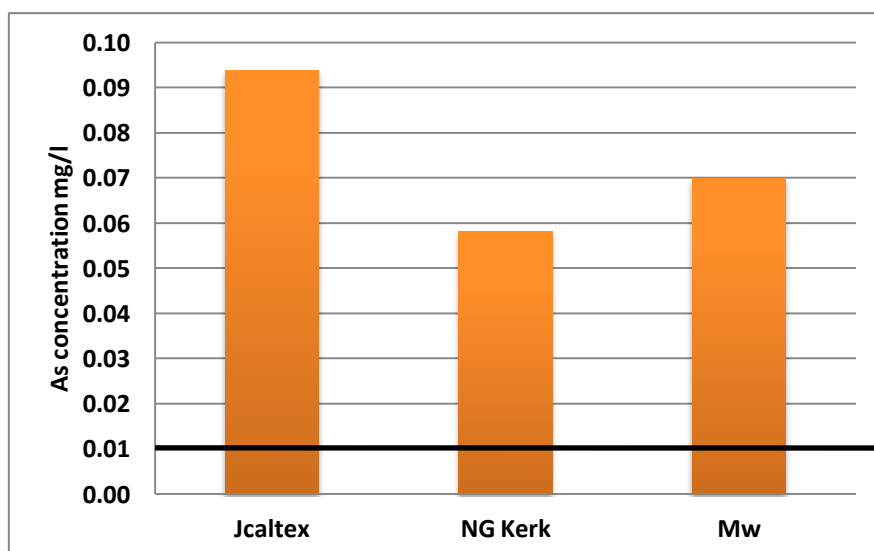
Figure 4-8: Arsenic concentrations of one-off samples
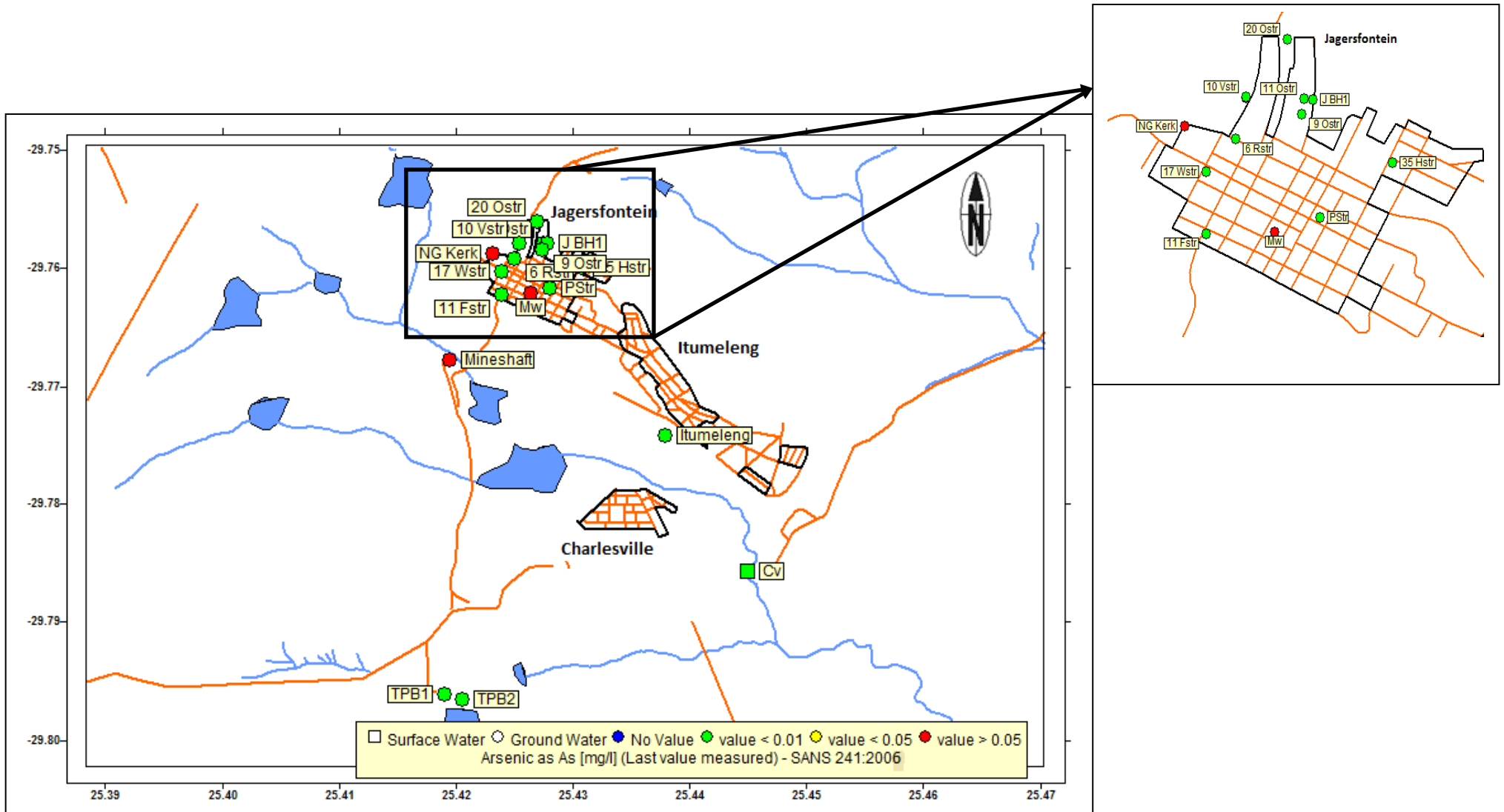
Figure 4-9: Spatial distribution of arsenic in the Jagersfontein area

4.3.1 Improvement of water quality

Due to the inefficiency of the package plant in treating arsenic contaminated mine water; a bigger treatment plant was put in place which went operational in July 2012. As a way of upgrading the water quality, water from the Kalkfontein dam is being treated in this plant and mixed with treated water from the mine shaft before being supplied to the community. Description of how these processes take place is discussed in Chapter 5.

As a result of this new development, few more samples were collected to do a general chemistry analysis of the water and also to determine how effectively arsenic concentration in the final treated water have been reduced. Samples were collected from the mine before and after treatment (RM and TM respectively), the dam before and after treatment (RD and TD respectively) and the other from the point when both have been mixed already (MW) and another, from a public tap in the community (CW).

Figure 4-10 illustrates the arsenic concentrations of these samples. Arsenic concentration is still high in both the raw mine water (RM) and in the treated mine water (TM). MW and CW which are both mixture of treated dam water and treated mine water show arsenic concentration below 0.01 mg/l. Hence the dilution of treated mine water with treated dam water reduced the arsenic concentration to an accepted level.

Figure 4-11 illustrates the piper, expanded durov and stiff diagrams of the samples. The samples from the dam (RD and TD) show a water character of Magnesium Bicarbonate while mixed water (MW), community water (CW), raw and treated mine water (RM and TM) show a character of Sodium/Potassium Sulphate. Nevertheless MW and CW show low sodium and potassium concentrations as portrayed by their stiff diagrams (Figure 4-11).
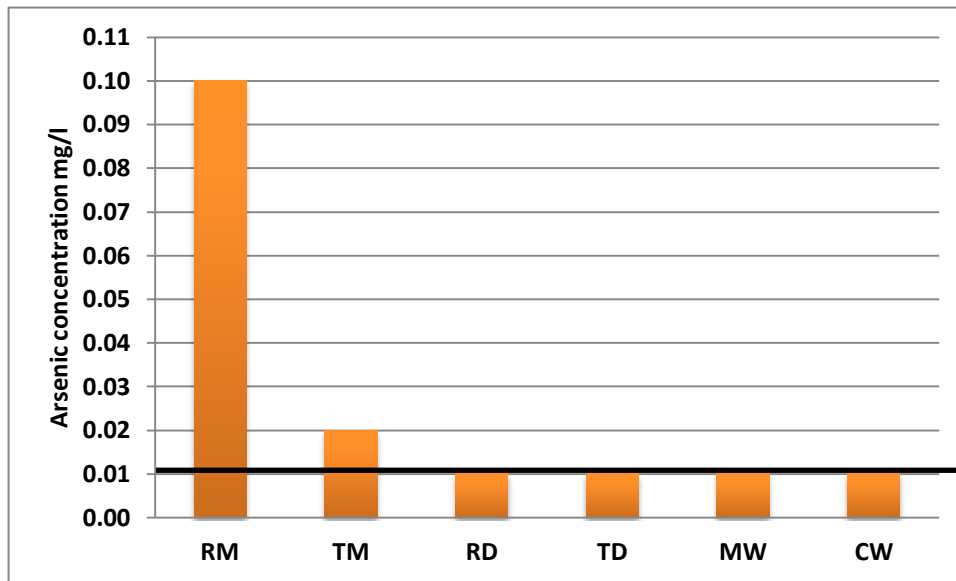
Figure 4-10: Arsenic concentrations of Dam and mine shaft water samples

With the results presented in Figure 4-8 and Figure 4-10 it is concluded that the package plant is inefficient in treating arsenic. Before July 2012, treatment of the arsenic contaminated mine water was done only in the package plant and then supplied to the community; that is why samples JFinal, JCaltex (collected from tap at Caltex garage) and Mw (collected from public tap in main town) still show high arsenic concentrations. Figure 4-10 presents the samples collected in November 2012, after a bigger treatment plant had already been under operation. As illustrated, there is still high arsenic in the treated mine water (TM) but after dilution with treated dam water the arsenic concentration is reduced.

In order to determine the dominant arsenic specie present in the water samples in the Jagersfontein area, concentrations of arsenic species were calculated in PHREEQC using the wateq4f database and was realised that arsenic (V) (native and dissolved) is generally the dominant arsenic specie in Jagersfontein water as illustrated in Figure 4-12. Arsenic (V) species are more often than not the major form of arsenic in oxic groundwater. These species are in an anionic form at natural pH of water, sorbs easily on rock or aquifer material, less mobile and easier to remove from water than arsenic (III).
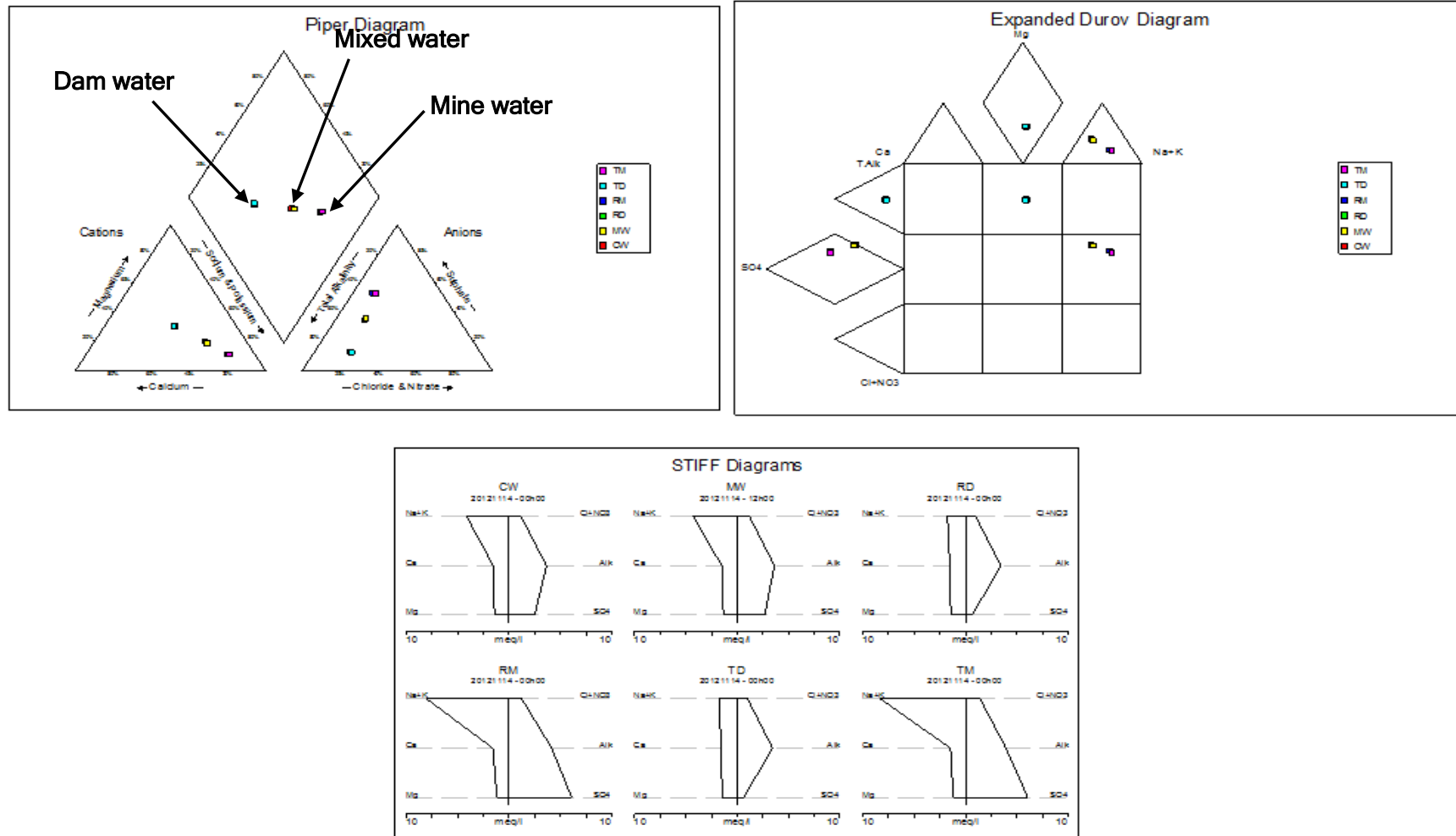
Figure 4-11: Piper, expanded durov and stiff diagram
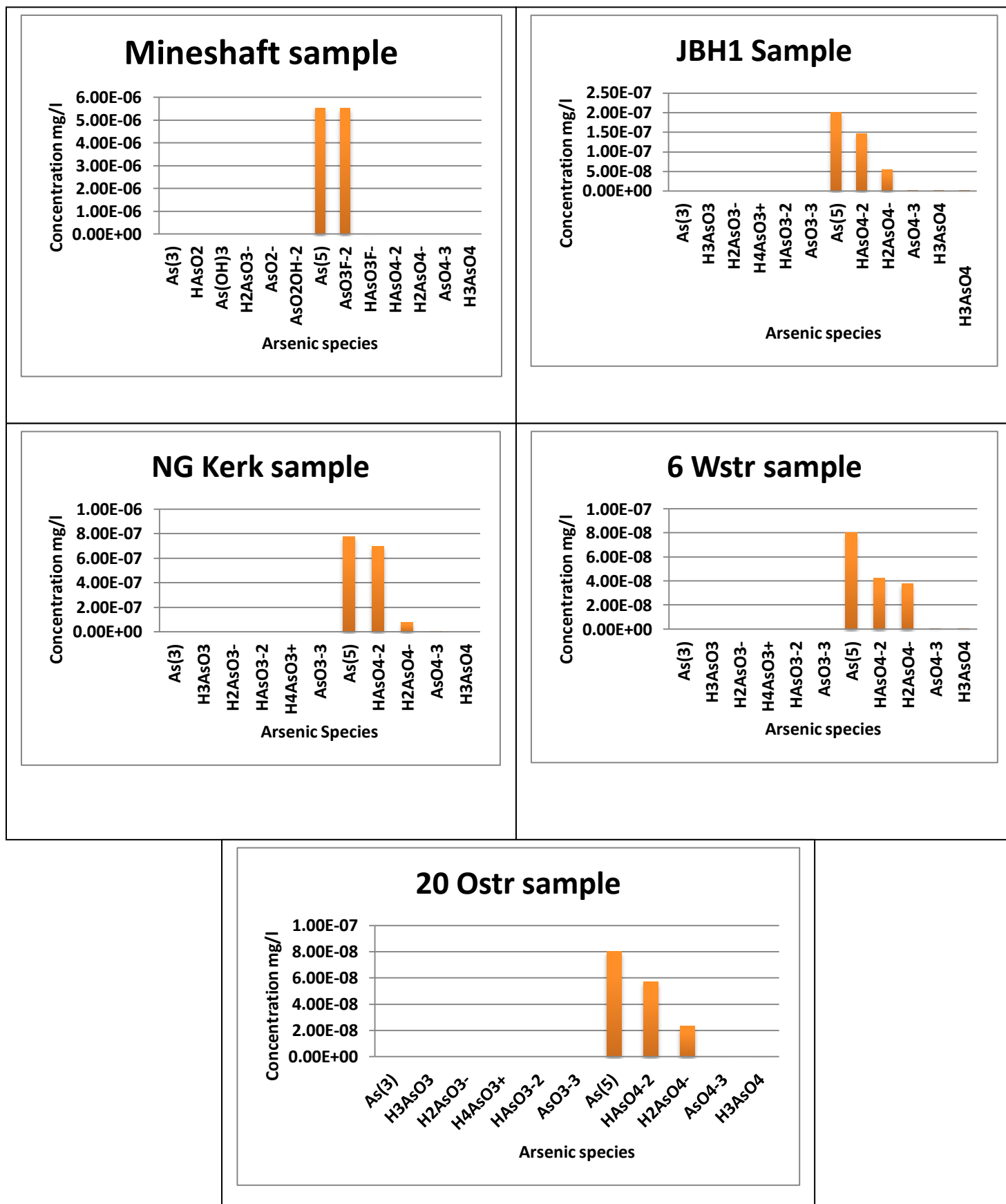
Figure 4-12: Dominant arsenic species of some selected samples

Carcinogenic Risk Assessment

The geology of some countries consist of rocks with high natural levels of arsenic (e.g. Bangladesh), and this can lead to unusually high levels of arsenic in soil or water. Others have hazardous waste sites containing large quantities of arsenic. If the material is not properly disposed of, it can get into surrounding water, air, or soil. People living in an area like this, could take in above-average amounts of arsenic from the soil or from food grown in the area or from the water. Others involved in sawing or sanding arsenic-treated wood, could inhale some of the sawdust. Similarly, if arsenic-treated wood is burned, arsenic could be inhaled in the smoke (Cedar Grove Environmental, Inc). Therefore the pathways in which people can be exposed to arsenic are ingestion (drinking of groundwater), inhalation (breathing of contaminant in air) and dermal sorption (sorption through skin in baths and showers).

A population exposed to arsenic stand a risk of getting cancer, since arsenic is a human carcinogen. In Jagersfontein, the arsenic concentration in the community water (CW) is less than the SANS 241: 2006 limit of arsenic concentration in groundwater which is 0.01 mg/l. It is understood that the community uses this water for different purposes which could include cooking, drinking, bathing and laundry. Carcinogenic assessment can be calculated, it takes into account route/pathways of exposure. Before calculating the risks associated with carcinogenic assessment, the total dose and lifetime average dose have to be defined. The equations used to define risks associated with human exposure to contaminated groundwater are generally based on those specified in the USEPA "Risk Assessment Guidance for Superfund" (USEPA, 1989).

For each pathway, the total dose that will reach a human has to be calculated. The total dose is defined as:

$$\text{Dose} = C \times IR \times ED$$

<div align="right">Equation 4-3</div>

Where

Dose =Total dose

C = Maximum concentration of contaminant. In this case 0.001 mg/l

IR = Average intake rate

ED = Exposure duration

Carcinogenic risk assessments are determined over a human's lifetime. Therefore the lifetime average daily dose (LADD) is calculated as:

$$LADD = \frac{Total\ dose}{BW\ x\ lifetime}$$

<div align="right">Equation 4-4</div>

The carcinogenic risk calculation is based on a Poisson model:

$$Risk = 1 - e^{-LADD\ x\ CPF} \approx LADD\ x\ CPF$$

<div align="right">Equation 4-5</div>

CPF is the cancer potency factor which is 1.5 $(mg/kg.d)^{-1}$ for arsenic (http://www.oehha.org/pdf/corrections.pdf).

For the sake of these calculations, the following assumptions are made

- ➢ It is assumed that an adult weighs 70 kg.
- ➢ It is assumed that a person drinks 2 L of water a day.
- ➢ It is assumed that the average lifetime of human is 70 years.

In the case of Jagersfontein, using the arsenic concentration in Municipal water sample, carcinogenic risk can be calculated as follows:

$$Dose = \frac{0.001mg}{l} \times \frac{2l}{day} \times 25550 days$$

51.1 mg

$$LADD = \frac{51.1 mg/day}{70kg\ \times 25550 days}$$

2.86 x 10-5 mg/kg.d

$$Risk = \frac{2.86 * 10^{-5} mg}{kg}.d \times 1.5(\frac{mg}{kg}.d)^{-1}$$

Risk= 4.29 x 10-5 = 0.0000429

Risk of 0.0000429 which is a low carcinogenic risk implies that, 429 cases of cancer per population of 10,000000 are expected when the population is exposed to 0.001 mg/l of arsenic.

4.5 Isotopic characterization

Hydrogen and Oxygen like other elements exist in nature as atoms of different mass numbers, called isotopes. ^1H (proteum), ^2H or D (Deuterium) and ^{18}O, ^{17}O, ^{16}O are naturally occurring isotopes of Hydrogen and Oxygen respectively. With respect to radioactivity, isotopes can be classified as stable isotopes (non-radioactive) and radioactive. The stable isotopes commonly used in the field of hydrogeology include ^1H, ^2H or D, ^{18}O, and ^{16}O. These isotopes do not engage in nuclear transformation, meaning that in a closed system, their abundance would remain constant with time. On the other hand, radioactive isotopes which include tritium (^3H) or radiocarbon (^{14}C) will decay over time and can therefore be used for groundwater dating (Appelo and Postma, 2005). Radioactive isotopes unlike stable isotopes would have their abundance altered even if they are in a closed system.

It is not convenient to measure absolute isotopic ratios, hence δ(delta) notation is used instead and stable isotope abundances are reported as a ratio to some abundant isotope of the same element or as positive or negative deviations of these isotope ratio (R) away from a standard (Weaver *et al.*, 1999).

The normal reference standard is the V-SMOW (Vienna Standard Mean Ocean Water) (Drever, 1997).

$$\delta x = \frac{Rx - RSMOW}{RSMOW} * 1000$$

R_x = isotope ratio of sample

R_{SMOW} = isotope ratio of standard

δ = Relative abundance.

4.5.1 $\delta^{18}O$ and δD

Isotopes of the same chemical element have almost identical physical and chemical properties. Because of their differing mass numbers, isotopes tend to behave differently when exposed to different chemical, biological, and physical environments. In that regard, the changes in ^{18}O and ^{2}H concentrations along groundwater flow paths is an effective tool to determine the extent of groundwater recharge, estimations of mixing proportions of different sources or component flows and the relationships between ground and surface water (Gat, 1996). Also physical processes such as diffusion, evaporation, condensation and melting produce isotopic differentiation. All these variations in the isotopic composition, produced by chemical or physical processes, in compounds or phases, present in the same system, are called isotopic fractionation (Mook and Geyh, 2000). Vapour-liquid fractionation during evaporation and condensation is the most important process causing variation of isotopic composition. Fractionation is a partial separation of isotopes of the same element during physical (e.g. evaporation) or chemical (e.g. precipitation) processes. When water vapour condenses to form rain, fractionation takes place in the reverse direction with liquid being isotopically heavier than the vapour (Figure 4-13). If fractionation during condensation is about -10 $^{o}/_{oo}$, then the first rain to fall from water vapour over the ocean would have a $\delta^{18}O$ value of about -3 $^{o}/_{oo}$ (Drever, 1997).
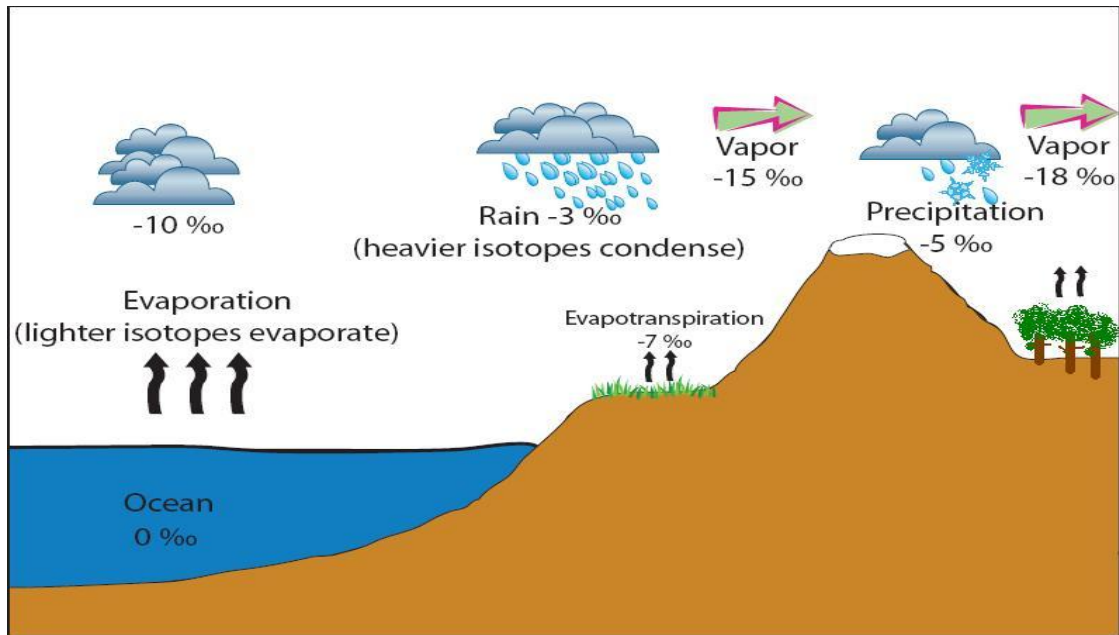
Figure 4-13: A schematic diagram of isotope fractionation process via evaporation, condensation, and evapotranspiration (Bruckner, 2012)

The $\delta^{18}O$ and δD values in precipitation generally plot close to a straight line called the meteoric water line with equation

$$\delta D = 8\,\delta^{18}O + 10$$

Where 8 is a constant determined by the physical properties of the isotopes and 10 is the intercept also called d-excess. It is generally applicable to the worlds composite set of samples (Dansgaard, 1964, cited in Weaver *et al.*, 1999).

Water composition falling on the meteoric water line is assumed to have originated from the atmosphere and to be unaffected by other isotopic processes. Evaporation from open water and exchange with rock minerals are two of more commonly observed processes causing deviations from meteoric water line (Domenico and Schwartz 1990, cited in Weaver *et al.*, 1999).

(Appendix Table C 5) shows the isotopic composition of water samples. The values range between -5.09 ‰ to -0.64 ‰ for $\delta^{18}O$ and -28.37 ‰ to -4.22 ‰ for δ^2H (October samples), while for the April samples, values range between -4.90 ‰ to -2.14 ‰ for $\delta^{18}O$ and -27.42 ‰ to 11.78 ‰ for δ^2H. $\delta^{18}O$ and δ^2H are in a certain sense ideal geochemical tracers of groundwater because their concentrations are not

subject to changes by interaction with aquifer material. Once underground and removed from zone of evaporation the isotopes ratio are conservative and only affected by mixing (Weaver *et al.*, 1999). The October water samples plot very close to the GMWL (Figure 4-16) implying the groundwater is meteoric and is derived from the atmosphere. Since these samples were collected long after the last rain, it is concluded that the groundwater was recharged at least during the last rainy season. Clustering of the samples around the GMWL hints they might be of the same age. However one water sample (Charlesville) plots away from the GMWL (October samples), it is heavier (less negative) in both $\delta^{18}O$ and δ^2H implying it has lost its lighter isotopes most probably by evaporation because being a surface water body it is open to the atmosphere and most liable to evaporation.

In comparison with the isotopic plot of April samples, there is a very minute difference in the isotopic compositions but for Charlesville sample. It is an effect of rainfall since samples were collected a day after it rained. This is the same reason as why there is a drastic drop in the Chlorine concentration as illustrated in Figure 4-15 (sample indicated by black arrow). Figure 4-14 shows a plot of $\delta^{18}O$ versus δD for both sampling runs.
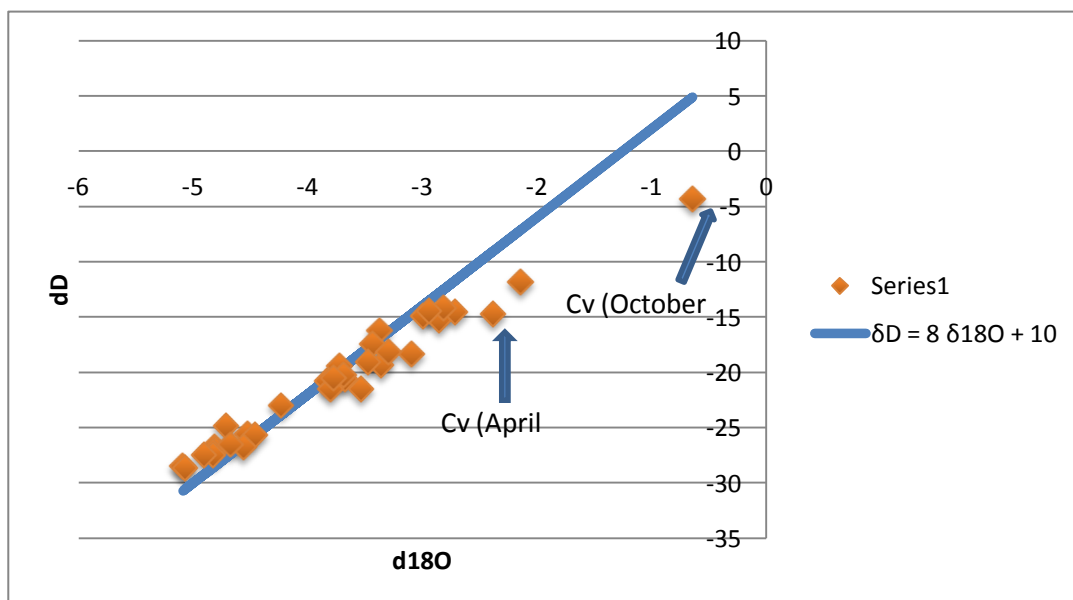
Figure 4-14: $\delta^{18}O$ versus δD plot of water samples combined

The significance of evaporation and dissolution processes is observed in the Cl^- versus $\delta^{18}O$ diagram (Figure 4-15). It is noticed that all of the samples with high chloride concentration are not correlated with the $\delta^{18}O$ values. However one of the samples (indicated by black arrow) shows good correlation between Cl^- and $\delta^{18}O$, this can be attributed to evaporation process.
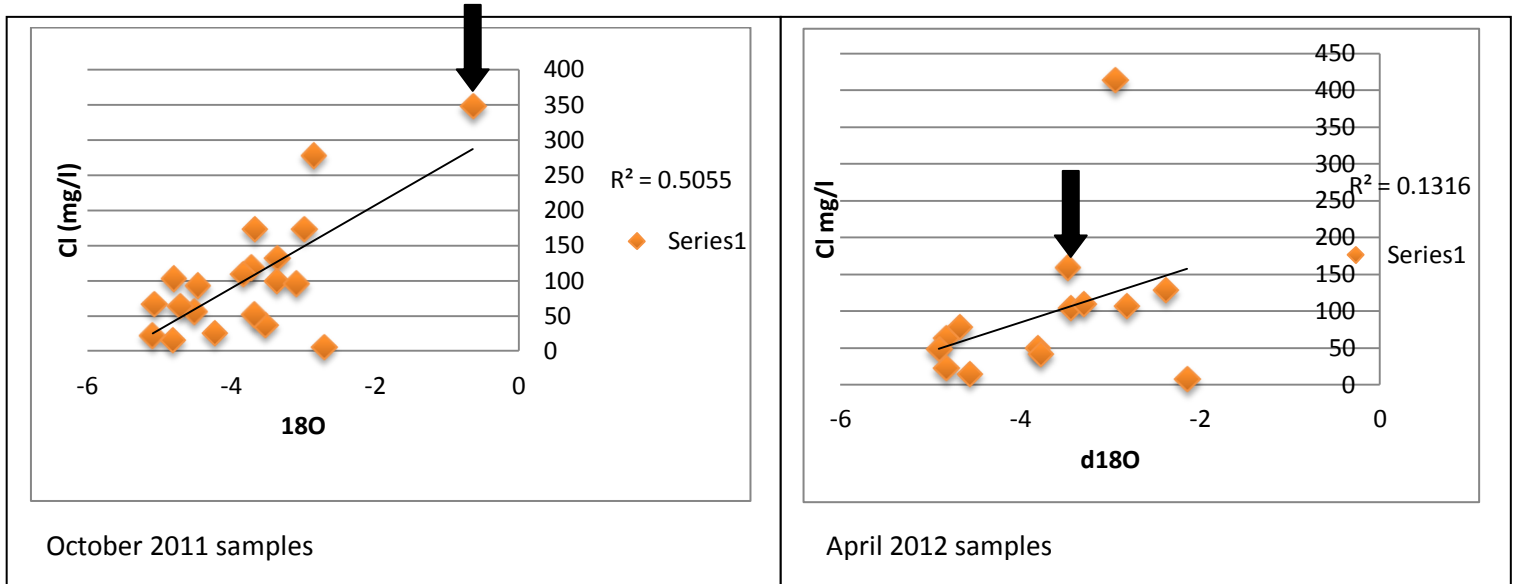
Figure 4-15: Cl vs $\partial^{18}O$ relationship
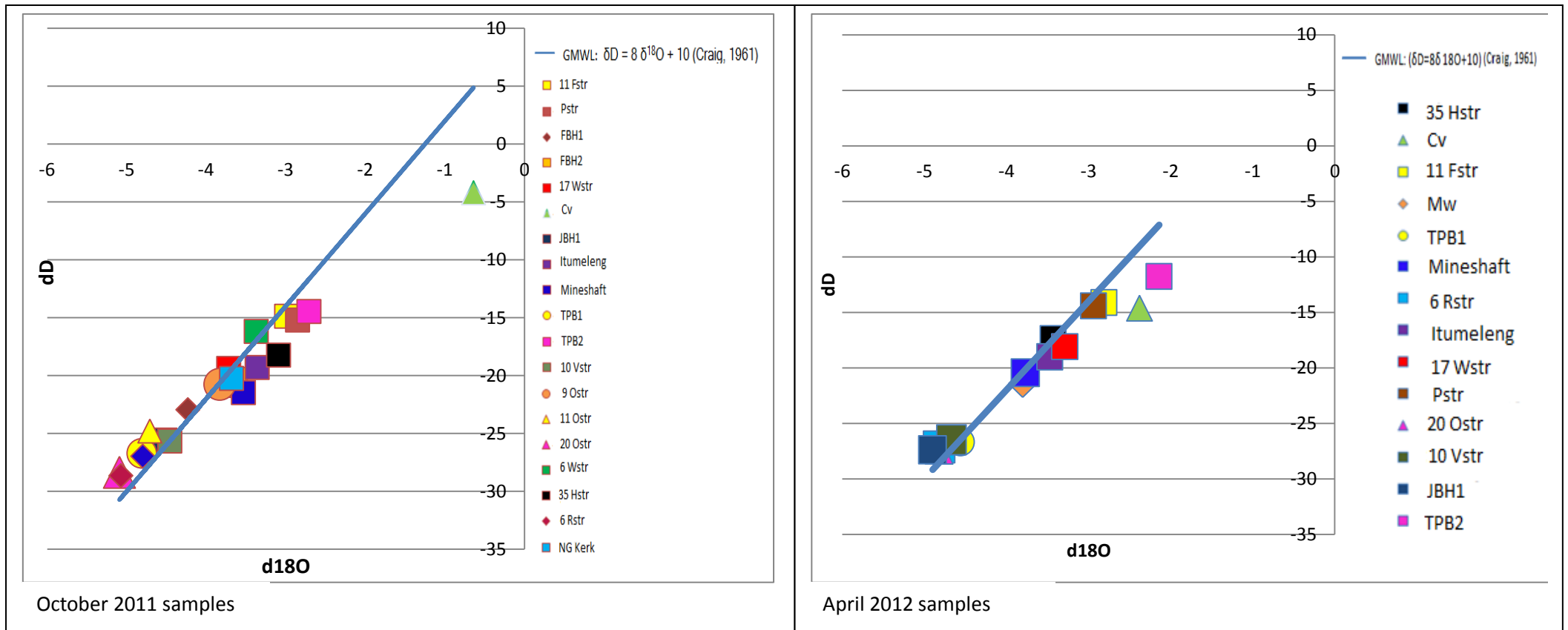
Figure 4-16: $\delta^{18}O$ Vs δD plot of water samples

4.5.2 Tritium analysis

Tritium is a radioactive isotope of hydrogen with a half life of 12.3 years. It is produced naturally in the atmosphere by interaction of cosmic rays with nitrogen and oxygen in the atmosphere (Drever, 1997). The concentration of tritium in water is expressed by ratio of T-atoms and H-atoms. A ratio $T/H = 10^{-18}$ is defined as 1 tritium unit (1 T.U). Natural production of tritium introduces about 5 T.U to precipitation and surface waters. In the saturated zone, this water is isolated from the atmosphere and the drop in tritium concentration due to radioactive decay should provide a useful tool for groundwater dating (Weaver *et al.*, 1999).

The age of recent groundwater recharge can be known by using the great amount of tritium that made way to the hydrological cycle in the 1960s. Water recharged during the late 1950s and 1960s will show high levels of tritium (approximately > 30 T.U); modern recharge will exhibit moderate levels of tritium and detection levels close to approximately 1 T.U, are likely to be sub modern or paleo-groundwater that have mixed with shallow modern groundwater (Clark and Fritz, 1997).

Table 4-10: Classification of groundwater age based on Tritium levels

Tritium levels	Categorisation
<0.8 TU	Pre-modern water (prior to 1950s)
0.8 - 4 TU	Mixture of pre-modern and modern
5 -15 TU	Modern (<5 to 10 years)
15 - 30 TU	Some bomb tritium
>30 TU	Recharge in the 1960s to 1970s

The recorded environmental tritium content of the 13 groundwater samples and one surface water sample used for the analysis varied from 0 T.U to 4.3 T.U with an average of 1.9 T.U. Comparing the results obtained during this analysis with the standard ^3H values put forward by Clark and Fritz (1997), it is obvious almost all the samples contain a mixture of pre-modern and modern water.

According to Ravikumar and Somashekar (2010), natural tritium in precipitation varies between approximately 1 T.U and 10 T.U. 71 % of the samples have values

more than 1 T.U (Figure 4-17) suggesting that the water samples involve mixture of pre-modern and modern water that has undergone radioactive decay and the origin of the water is meteoric (groundwater was recharged by precipitation). 29 % of samples have values <0.8 T.U indicating old (pre-modern) water.

Table 4-11: Tritium results

Laboratory number	Sample identification	Tritium (T.U)
IGS 139	Mineshaft	2.6 ± 0.4
IGS 140	Jagersfontein Borehole 1 (JBH1)	0.2 ± 0.3
IGS 141	20 Ooskloof street (20 Ostr)	0.6 ± 0.3
IGS 142	Palmerston street (Pstr)	3.3 ± 0.9
IGS 142	11 Fauresmith street (11 Fstr)	2.4 ± 0.4
IGS 144	10 Voortrekker street (10 Vstr)	0.2 ±0.3
IGS 145	35 Harrington street (35 Hstr)	1.9 ± 0.3
IGS 146	17 Weil street (17 Wstr)	2.8 ± 0.4
IGS 147	Itumeleng	2.6 ± 0.4
IGS 148	6 Ried street (6 Rstr)	1.3 ± 0.4
IGS 149	Municipal water (Mw)	1.6 ± 0.3
IGS 150	TPB1	0.0 ± 0.3
IGS 151	TPB2	4.3 ± 0.4
IGS 152	Charlesville (Cv)	2.1 ± 0.3
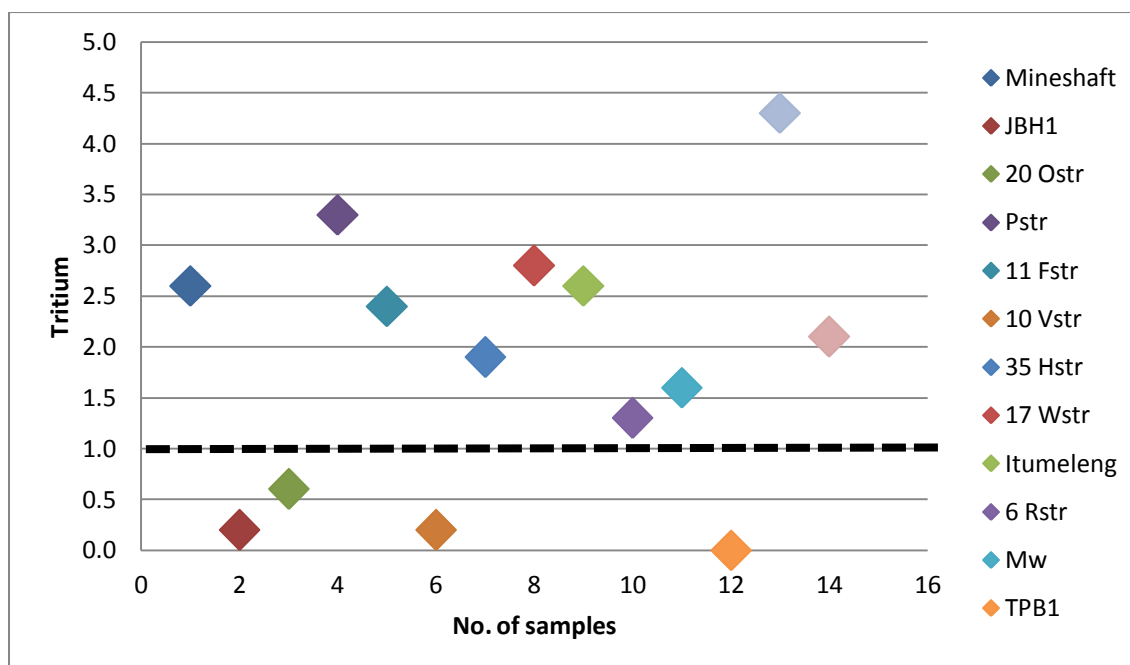
Figure 4-17: Plot of Tritium versus number of samples

Tritium and Arsenic relationship

There is no understandable trend in the plot of tritium against arsenic. Almost all of the samples have the same concentration for arsenic (<0.006 mg/l). However, taking into consideration the two samples (mineshaft and Mw) that have higher arsenic concentration (0.087 mg/l and 0.070 mg/l respectively), the sample with higher arsenic concentration also shows higher tritium level. Nevertheless, two sample values can not be useful enough in concluding that, there is a correlation between these two parameters.
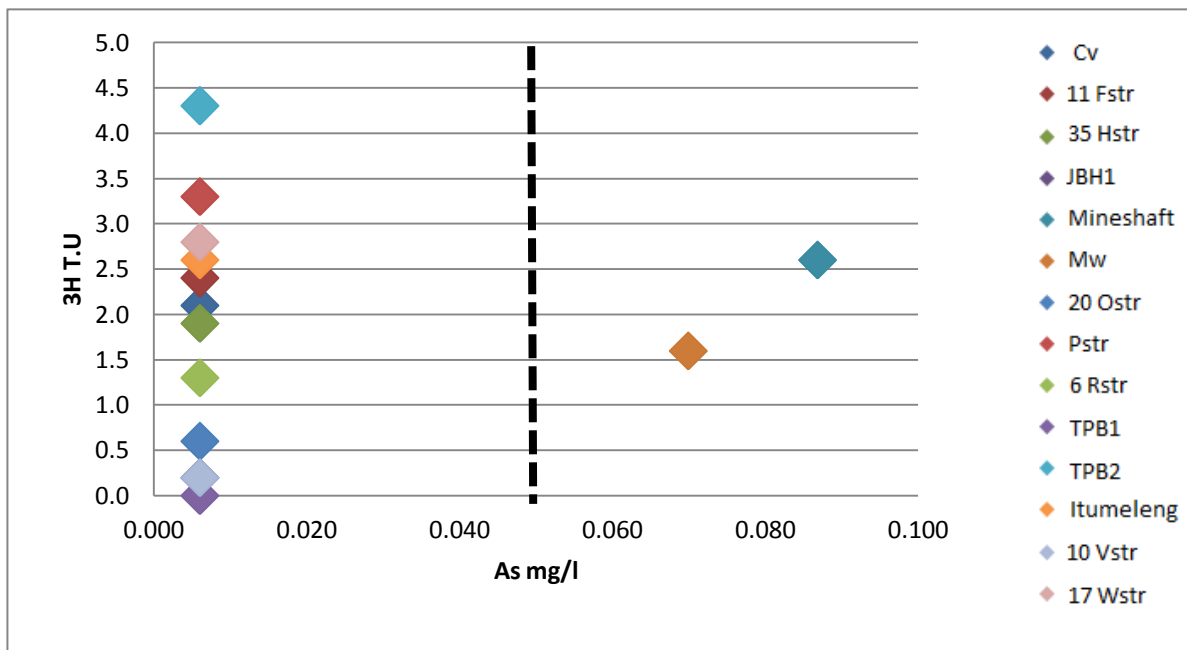
Figure 4-18: Plot of Tritium versus Arsenic

Tritium and Nitrate relationship

Isotopes can suggest the source of high nitrate concentrations to an important groundwater supply and can demonstrate the irrigation return flow and pollution hazard in any region (Ravikumar and Somashekar, 2010). The plot of tritium against nitrate concentrations (Figure 4-19) for the groundwater samples shows no clear trend though it underlines the fact that most of the samples are of low nitrate content (below SANS 241: 2005 <20 mg/l). Most of the samples with low nitrate concentration are also the ones with low ^{3}H values indicating that most of the samples are not contaminated with nitrate. However, one of the samples (Itumeleng)

show high nitrate content. This sample happens to be taken from a not well constructed supposed borehole where sewerage water runs nearby.
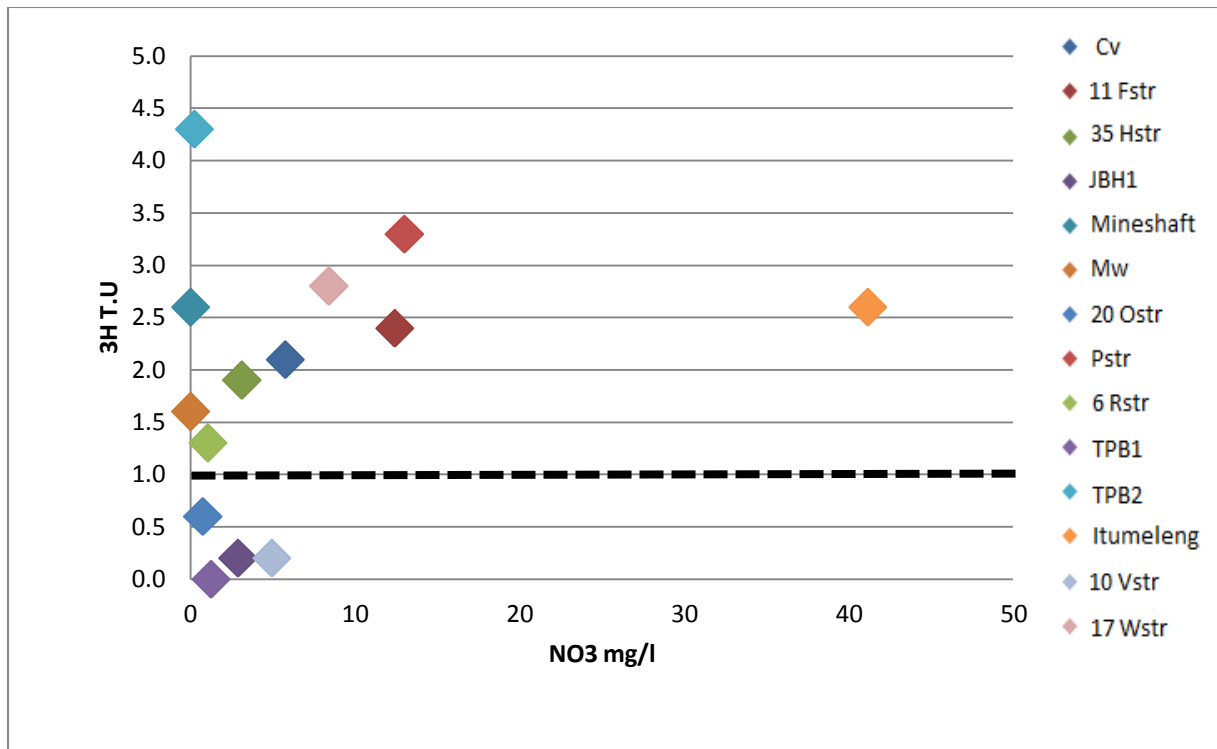
Figure 4-19: Plot of Tritium versus Nitrate

Tritium and Fluoride relationship

The plot of tritium against fluoride concentrations for the groundwater samples highlights the fact that majority of the samples have a relatively low fluoride concentration (SANS 241: 2005, <1.5 mg/l). This point towards the fact that these samples come from a shallow aquifer containing recently infiltrated rainwater with short residence time. Nevertheless, two other samples (mineshaft and Mw) show high fluoride concentrations (>1.5 mg/l), suggesting samples come from deep aquifers, with long residence time of water (Figure 4-20) and perhaps much contribution from geogenic sources/weathering. These same samples also show high arsenic concentrations (Figure 4-18). Note should be taken that these two samples are of same source. Mw sample is mineshaft water that has undergone some sort of treatment before it was analyzed.
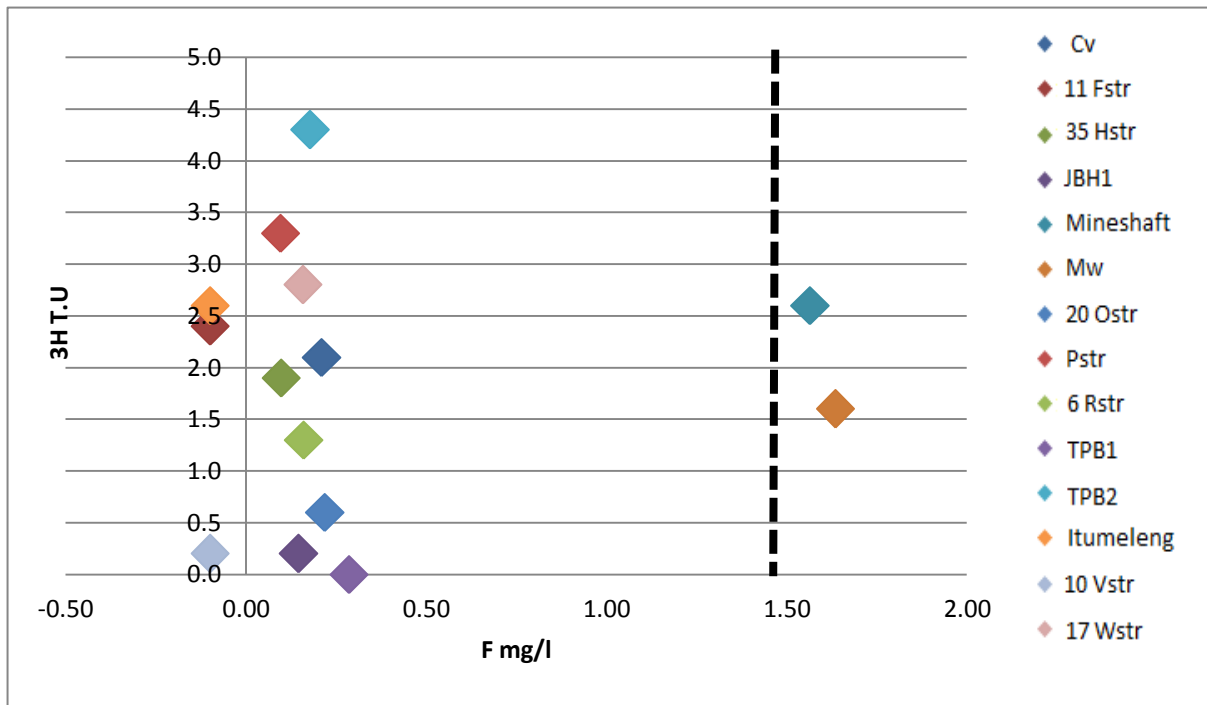
Figure 4-20: Plot of Tritium versus Fluoride

Tritium and pH relationship

The plot of pH and tritium indicates that all of the samples fall under the normal range of pH. This can be attributed to recharge with modern rainfall neutralized with minerals present in soils and rocks (Figure 4-21) and have a short residence time.
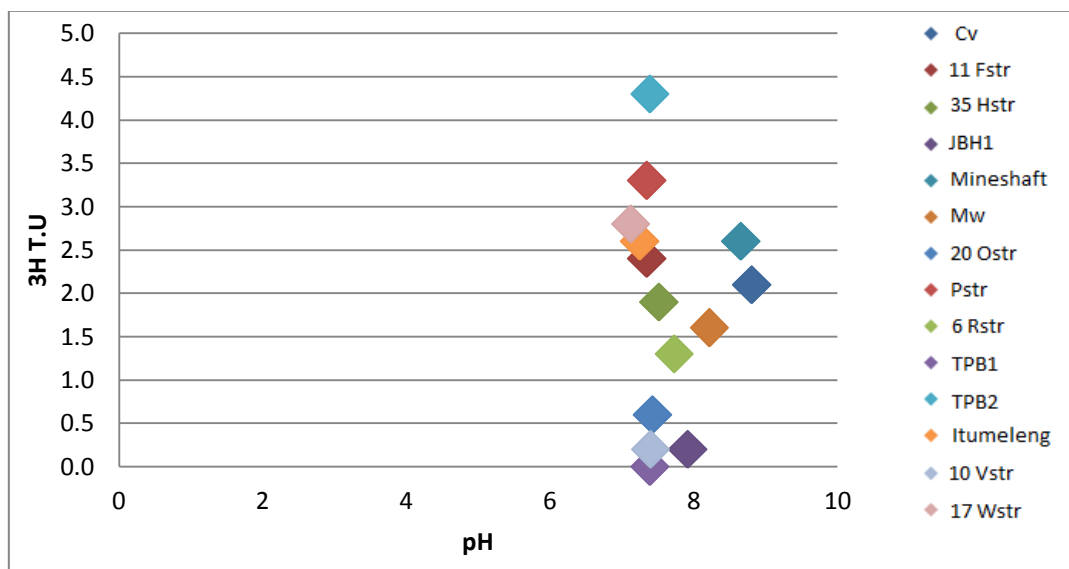
Figure 4-21: Plot of Tritium versus pH

5 Remediation options

5.1 Introduction

Arsenic toxicity has no known effective medicine for treatment (Ahmed, 2001). Hence, provision of arsenic free water is urgently needed to mitigate arsenic toxicity and protection of health and well being of people exposed to arsenic contaminated water. Treatment of arsenic contaminated water for the removal of arsenic to an acceptable level is one of the options for safe water supply. Switching to a new source of water is often considered more feasible than arsenic removal but it requires a major technological shift in water supply.

There are several methods available for removal of arsenic from water in large conventional treatment plants. The most commonly used processes of arsenic removal from water have been described by Cheng et al., 1994, Hering et al., 1996 and 1997, Kartinen and Martin, 1995, Shen, 1973 and Joshi and Chaudhuri, 1996. A detailed review of arsenic removal technologies has been presented by Sorg and Logsdon, 1978. Jekel (1994) has documented several advances in arsenic removal technologies (Ahmed *et al.*, 2005). In this chapter, it is intended to review some of these technologies of arsenic removal and also a description of the arsenic remediation processes being carried out in Jagersfontein

5.2 Current arsenic treatment processes in Jagersfontein

Presently in Jagersfontein, treatment of arsenic contaminated water is done in a package plant (Figure 5-1). In this plant just two processes are carried out; rapid mixing with chemicals such as ferric chloride (to enhance precipitation) and filtration. Water from the mine shaft is pumped into the mixing reservoir. Along this pipeline, Chlorine (Cl_2) is being added to the water which serves as an oxidant. In the reservoir Ferric Chloride ($FeCl_3$) is added to the water and rapid mixing is employed to facilitate precipitation. From the mixing reservoir, the water is pumped into the pressure filters which are made up of vertical layers of sand, gravel and stones. The filtered water is collected in another reservoir (balancing reservoir) from where it is being pumped to the storage reservoir.

Figure 5-1: Package plant

As discussed in Chapter 4 treated mine water still shows high arsenic concentration. As a way of reducing the arsenic concentration, water from the Kalkfontein dam is treated in a bigger treatment plant (Figure 5-3) and mixed with treated mine water.

Water from the Kalkfontein dam is collected in a catchment from where it is pumped into a pre-mixing chamber. In this chamber the chemicals; Sudfloc 3456 (a polymer blend that functions in coagulation and flocculation) and Sodium Hypochlorite (NaClO) are added to the water. Water flows into the rapid mixture chamber where water and chemicals are mixed vigorously. This enhances coagulation. From the rapid mixture chamber, water flows into the flocculation chamber where larger flocs are form and easily settles. Through a water dividing chamber, water flows into a

clarification chamber where it rests and settleable particles or flocs settle out. As water flows through a second water dividing chamber into the filters (made of sand and nozzles), sludge is being pumped out for disposal (Figure 5-2). Filtered water is collected in a sump and finally pumped into the storage reservoir. From this reservoir water is being supplied to the community.

Figure 5-2: Picture showing location of plants and sludge disposal site

Figure 5-3: Treatment plant

Note should be taken that the storage reservoir in which the treated mine water is stored is the same as that in which the treated dam water is also stored. Therefore the water supplied to the community is a mixture of treated mineshaft water and treated Kalkfontein dam water. Figure 5-4 presents the process flow in the package plant and the treatment plant. The chemical constituents of these two water sources before and after treatment have been discussed in Chapter 4. As it was noticed arsenic concentration in the treated mine water is still high and by virtue of diluting/mixing with treated dam water which is low in arsenic, the arsenic concentration is reduced.

Dilution is the attenuation of metals, anions or pH in water by mixing. It is a known method for reducing concentration of contaminants in water. However it is generally not acceptable. Dilution of contaminated water is commonly allowed to improve water chemistry prior to treatment or reuse in mining or manufacturing processes. Although dilution alone may not be an acceptable approach, it can achieve regulatory acceptance when combined with other treatment methods (American Geological institute, 1998). In the case of Jagersfontein, a certain volume of treated dam water is mixed with a certain volume of treated mine water hence arsenic concentration is reduced. The mass balance equations that follow assist in obtaining these volumes.

$$C_F V_F = C_1 V_1 + C_2 V_2$$

Equation 5-1

$$V_F = V_1 + V_2$$

Equation 5-2

Where

C_F = Final Concentration.

V_F = Final Volume (estimated volume of storage reservoir)

C_1 = Concentration of treated mine water (TM)

V_1 = Volume of treated mine water

C_2 = Concentration of uncontaminated water in this case treated dam water (TD)

V_1 = Volume of uncontaminated water (TD)

Results of chemical analysis of the water samples showed concentrations of arsenic to be

C_1 = 0.02 mg/l

C_2 = 0.001 mg/l

For the sake of this calculation, it is assumed:

C_F = 0.01 mg/l

V_F = 902 l

Fitting values in the Equation 5-2

902 l = V_1 + V_2

$$V_1 = 902 - V_2$$

Equation 5-3

Fitting values in Equation 5-3 and Equation 5-1,

0.01 mg/l x 902 l = 0.02 mg/l(902 l – V_2) + 0.001 mg/l x V_2

9.02 mg = 18.04 mg – 0.02 (mg/l)V_2 + 0.001 (mg/l)V_2

-9.02 mg = -0.019 (mg/l)V_2

V_2 = 474.7 l

From Equation 5-3,

V_1 = 902 l – 474.7 l

V_1 = 427.3 l

From the calculations and values obtained, it is concluded that to reduce the arsenic concentration of the mine water to an acceptable concentration of 0.01 mg/l, 474.7 l of uncontaminated water (TD) should be mixed with 427.3 l of treated mine water (TM). As a result, mine water becomes potable.
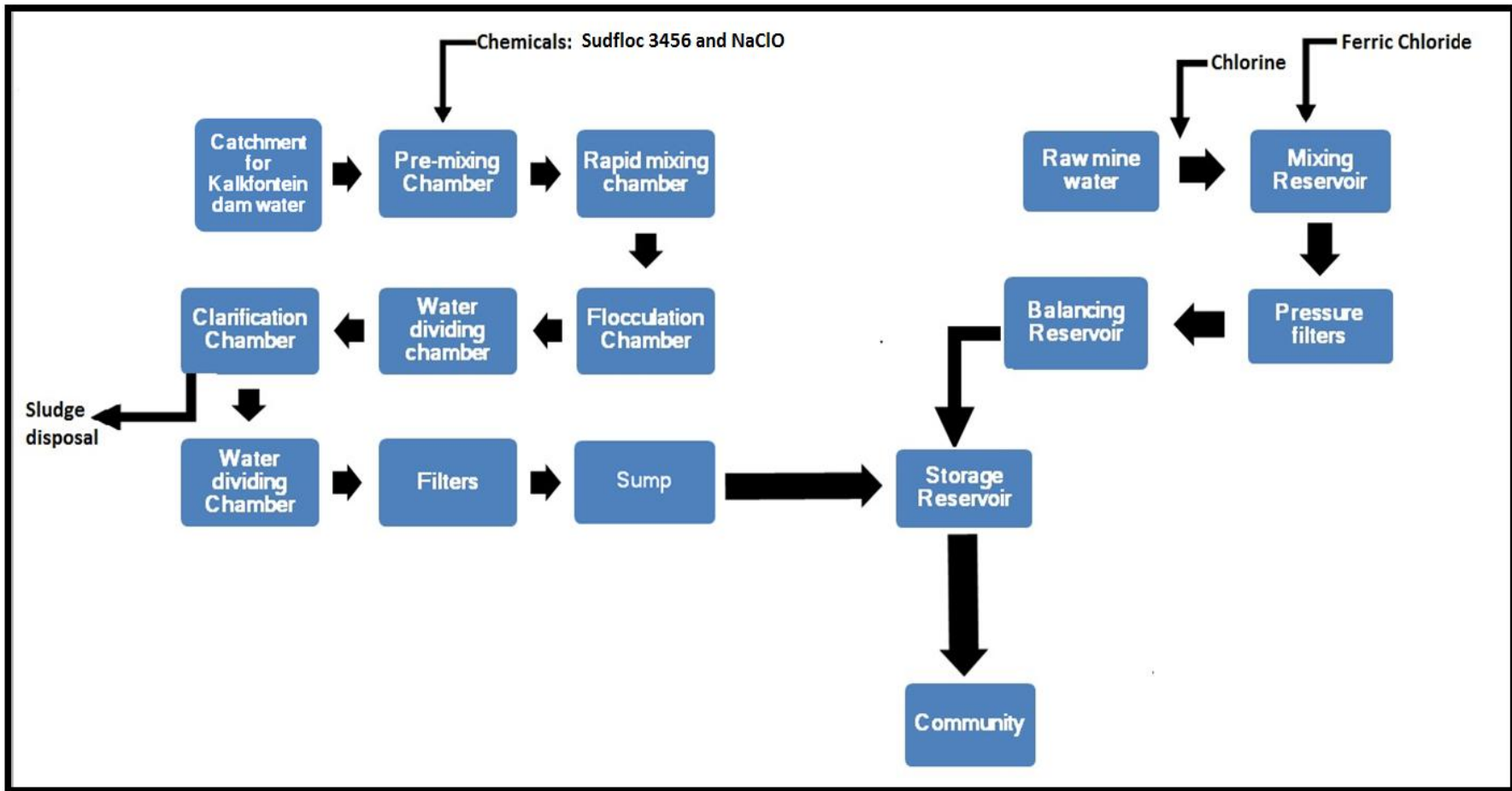
Figure 5-4: Process flow in package plant and treatment plant

5.3 Other arsenic removal technologies

The basic principles of arsenic removal from water are based on physical-chemical processes such as oxidation, coprecipitation and adsorption on coagulated flocs, adsorption onto sorptive media, ion exchange, and membrane filtration. Most treatment options need the oxidation of As(III) to As(V) for efficient removal of arsenic.

Oxygen, ozone, free chlorine, hypochlorite (HClO), permanganate ($KMnO_4$) and hydrogen peroxide can be used to oxidise arsenite to arsenate. Atmospheric oxygen, hypochlorite and permanganate are commonly used for oxidation in developing countries (Ahmed, 2001). The possible chemical equations of aresnite oxidation are as follows:

$$H_3AsO_3 + \tfrac{1}{2}O_2 \longrightarrow H_2AsO_4^- + H^+$$

$$H_3AsO_3 + HClO \longrightarrow HAsO_4^{2-} + Cl^- + 3H^+ \ zz$$

$$3H_3AsO_3 + 2KMnO_4 \longrightarrow 3HAsO_4^{2-} + 2MnO_2^+ + 2K^+ + 4H^+ + H_2O$$
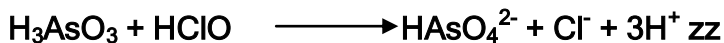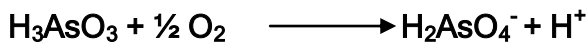
Atmospheric oxidation of arsenic is very slow and can take weeks for a complete oxidation process (Pierce and Moore, 1982 cited in Ahmed, 2001) but chemicals like chlorine and permanganate can rapidly oxidize arsenite to arsenate under wide range of conditions.

5.3.1 Coagulation and filtration

The process of coagulation and filtration, involves precipitation (the formation of insoluble compounds), coprecipitation (the incorporation of soluble arsenic species into a growing metal hydroxide phase) and adsorption (the electrostatic binding of soluble arsenic to external surfaces of the insoluble metal hydroxide) mechanisms for the removal of arsenic from solution.

These mechanisms including coagulation with metal salts and lime followed by filtration are well documented method for the removal of arsenic.

This method is linked with additional health and aesthetic advantages because alongside arsenic, it also removes dissolved solids such as fluoride, phosphate, manganese, iron and microorganisms. It reduces turbidity, colour and odour and hence improves the water quality appreciably.

Precipitation/coprecipitation has been the most frequently used method to treat arsenic contaminated water, including groundwater, surface water, leachate, mine drainage, drinking water, and wastewater (USEPA, 2002).

Like most treatment options, oxidation of As(III) to As(V) is required as a pre-treatment for efficient removal. Preformed Iron and aluminium hydroxides remove arsenic through adsorption, while in situ formation leads to coprecipitation. In alum coagulation the removal is most effective in the pH range 7.2-7.5, and in iron coagulation efficient removal is achieved in a wider pH range, usually between 6.0 and 8.5 (Ahmed, 2005 and Rahaman, 2000). The effects of cations and anions are very important in arsenic removal by coagulation. Anions compete with arsenic for sorptive sites and lower the arsenic removal rates (Ahmed, 2005).

Technology Description

Through the process of coagulation, reagents or coagulants are added to the contaminated water and rapidly mixed. This facilitates the formation of larger particles (flocs) (precipitation). Polymers are added next alongside gentle mixing which aids the flocs to agglomerate into larger settleable flocs (coprecipitation). Many micro-particles and negatively charged ions as well as arsenic are attached onto the flocs (adsorption) during the coagulation-flocculation process.

The precipitated/coprecipitated solid is then removed from the liquid phase by clarification or filtration. Figure 5-5 illustrates the model of a precipitation/coprecipitation system. Arsenic precipitation/coprecipitation can use combinations of the chemicals listed in Table 5-1;

Table 5-1: Some examples of coagulants and oxidants

Chemicals		Chemical formula
Ferric salts	Ferric Chloride	$FeCl_3 \cdot 6H_2O$ coagulant
	Ferric sulphate	$Fe_2(SO_4)_3 \cdot 9H_2O$ coagulant
	Ferric hydroxide	$Fe(OH)_3$
Alum (Aluminium sulphate)		$Al_2(SO_4)_3 \cdot 14H_2O$ coagulant
Lime stone (Calcium hydroxide)		$Ca(OH)_2$ coagulant
Potassium permanganate		$KMnO_4$ oxidant
Hypochlorite		$HClO$ oxidant
Manganese sulphate		$MnSO_4$

The possible chemical equations of alum and iron coagulation are as follows:

Alum dissolution:

$$Al_2(SO_4)_3.14H_2O \longrightarrow 2Al^{3+} + 3SO_4^{2-} + 14H_2O$$
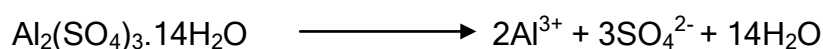
Aluminium precipitation (acidic):

$$2Al^{3+} + 6H_2O \longrightarrow 2Al(OH)_3 + 6H^+$$

Co-precipitation:

$$Al(OH)_3 + 3H_2AsO_4 \longrightarrow (Al(H_2AsO_4)_3) + 3OH^-$$

$$Fe_2(SO_4)_3 + 3H_2AsO_4^- \longrightarrow Fe(H_2AsO_4^-)_3 + 3SO_4^{2-}$$
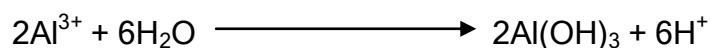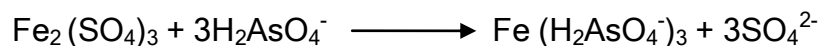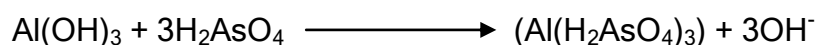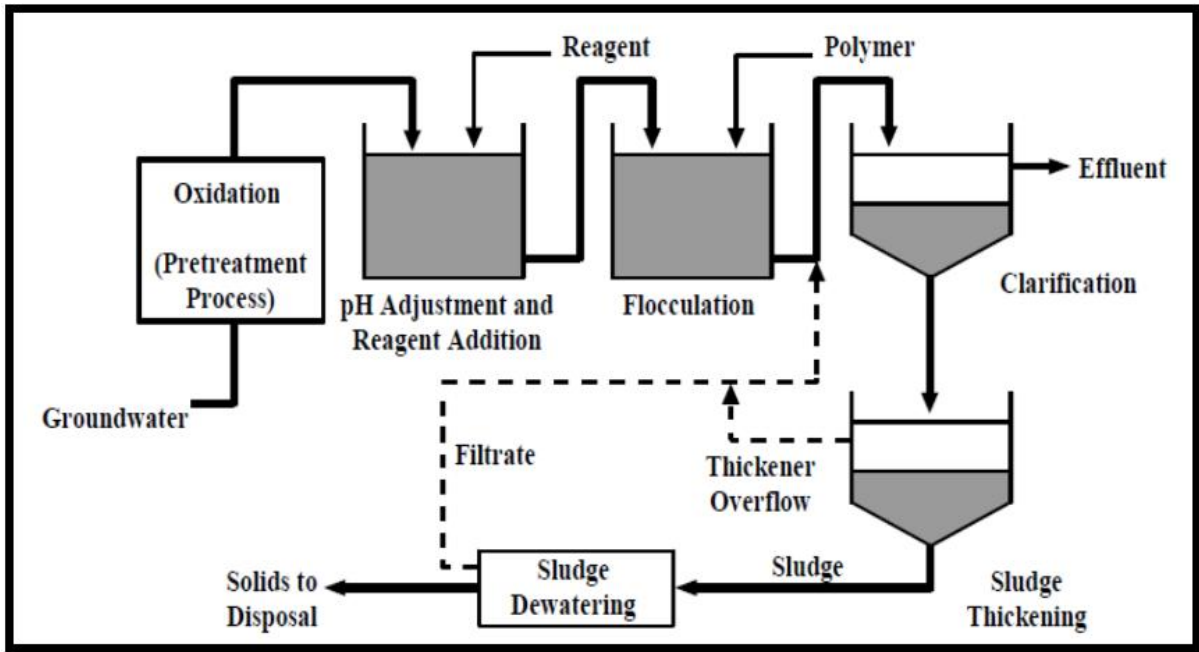
Figure 5-5: Model of a precipitation/Coprecipitation system (USEPA, 2002).

The technologies developed based on the coagulation-sedimentation-filtration process in Asia include:

• Bucket treatment unit

• Stevens Institute technology

• Fill and draw treatment unit

• Tubewell-attached arsenic treatment unit

These methods and descriptions are all adopted from an overview of arsenic removal technologies in Bangladesh and India (Ahmed, 2001) and arsenic mitigation technologies in South and East Asia (Ahmed, 2005).

Bucket treatment unit (BTU)

The bucket treatment unit, developed by the Department of Public Health and Engineering (DPHE)-Danida Project and improved by the Bangladesh University of Engineering and Technology (BUET), is based on coagulation, coprecipitation, and adsorption processes. It consists of two 20 l buckets, usually placed one above the other. Arsenic contaminated water is poured into the upper bucket, coagulants and oxidants (Table 5-1) are added. A wooden stick is used to rapidly stir the mixture to

ensure coagulation. Gentle stirring for about 90 seconds enhances flocculation. The mixed water is allowed to settle for 1 to 2 hours. The supernatant water flows by a flexible plastic pipe into the lower bucket in which a sand filter is installed and water is collected through it.

The modified bucket treatment unit shown in Figure 5-6, has been found to efficiently remove iron, manganese, phosphate, and silica together with arsenic (Ahmed, 2005).
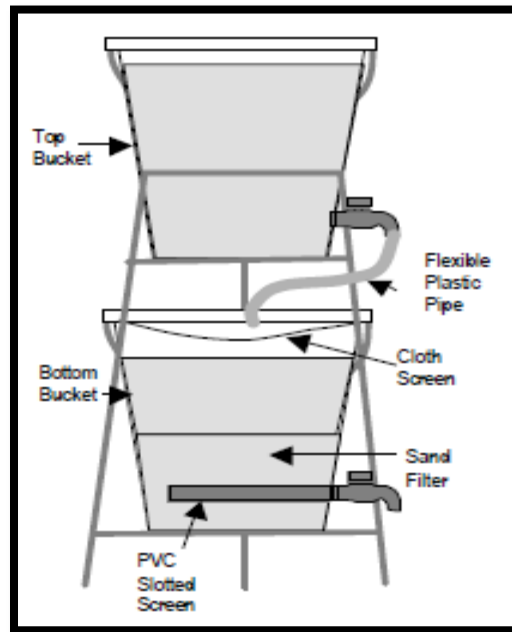
Figure 5-6: Bucket treatment unit (Ahmed, 2001).

The BTU is a promising technology for arsenic removal at household level at low cost. It can be built by locally available materials and is effective in removing arsenic if operated properly (Ahmed, 2001).

Stevens Institute technology

This technology also uses two buckets, one to mix chemicals (reported to be iron sulphate and calcium hypochlorite) supplied in packets and the other to separate flocs by the processes of sedimentation and filtration. The second bucket has a second inner bucket with slits on the sides (demonstrated in Figure 5-7) to help sedimentation and keeping the filter sand bed in place. The chemicals form visible

large flocs on mixing by stirring with stick. The sand bed used for filtration is quickly clogged by flocs and requires washing at least twice a week (Ahmed, 2001).

:
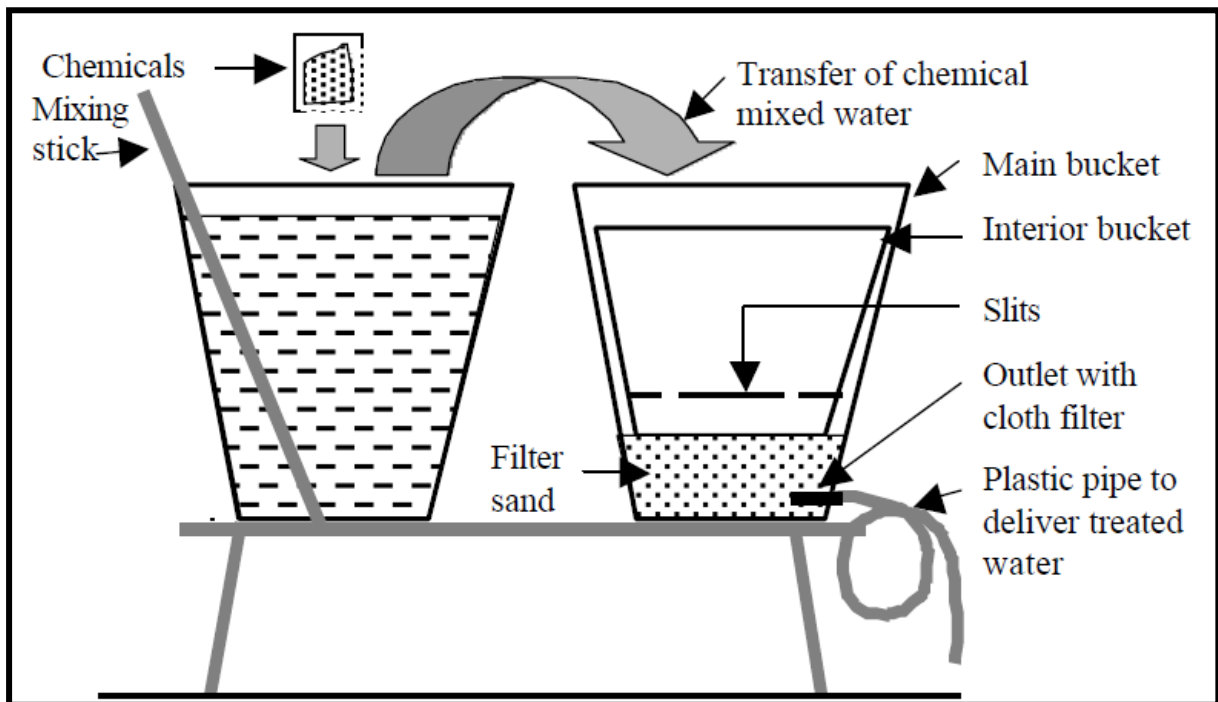
Figure 5-7: Stevens institute technology setup (Ahmed, 2001)

Fill and draw treatment unit

It is a community type treatment unit designed and installed under Department of Public Health and Engineering (DPHE)-Danida Arsenic Mitigation Pilot Project. It is a 600 l capacity (effective) tank with slightly tapered bottom for collection and withdrawal of settled sludge. The tank is fitted with a manually operated mixer with flat-blade impellers. The tank is filled with arsenic contaminated water and required quantity of oxidant and coagulant are added to the water. The water is then mixed for 30 seconds by rotating the mixing device at the rate of 60 revolutions per minute (rpm) and left overnight for sedimentation. The water takes some time to become completely still which helps flocculation. The floc formation is caused by the hydraulic gradient of the rotating water in the tank. The settled water is then drawn through a pipe fitted at a level, few inches above the bottom of the tank and passed through a sand bed and finally collected through a tap for drinking purpose (Figure 5-8). The

mixing and flocculation processes in this unit are better controlled to effect higher removal of arsenic. The experimental units installed by Department of Public Health and Engineering (DPHE)-Danida project are serving clusters of families and educational institutions.
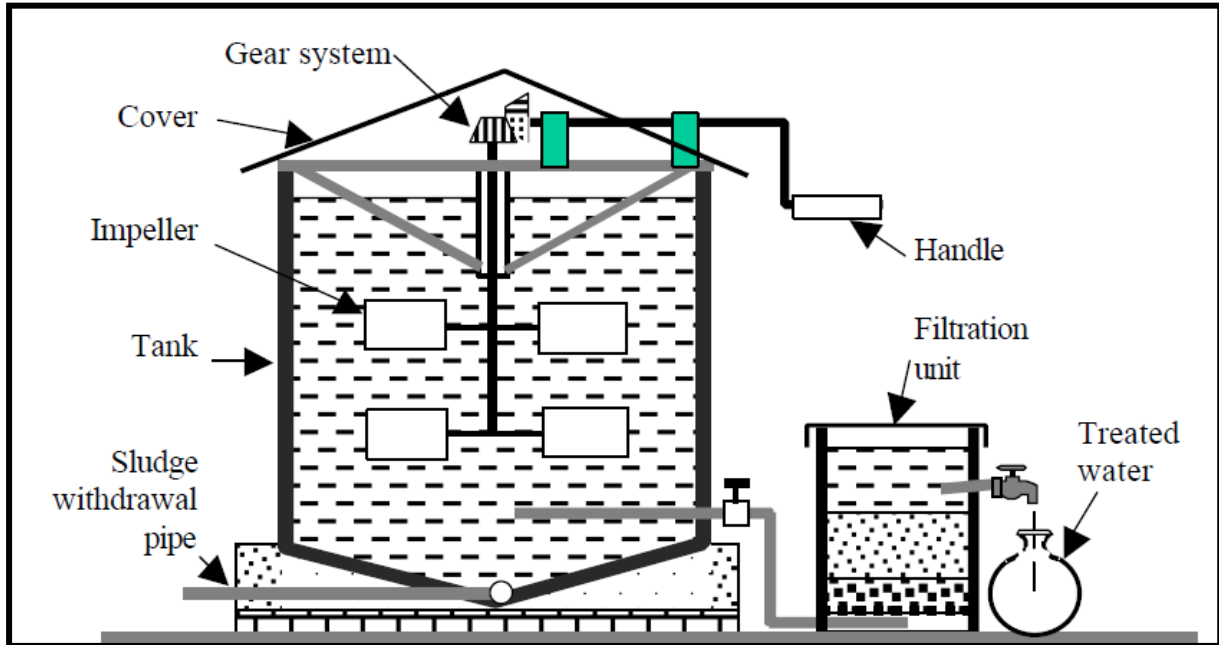
Figure 5-8: DPHE-Danida Fill and Draw arsenic removal unit (Ahmed, 2001)

Tubewell-attached arsenic treatment unit

The principles of arsenic removal by alum coagulation, sedimentation and filtration have been employed in a compact unit for water treatment in the village level in West Bengal, India. The arsenic removal plant attached to hand tubewell as illustrated in Figure 5-9, has been found effective in removing 90 percent arsenic from tubewell water having initial arsenic concentration of 300 mg/L. The treatment process involves addition of sodium hypochlorite, and aluminium alum in diluted form, mixing, flocculation, sedimentation and up flow filtration in a compact unit (Ahmed, 2001).
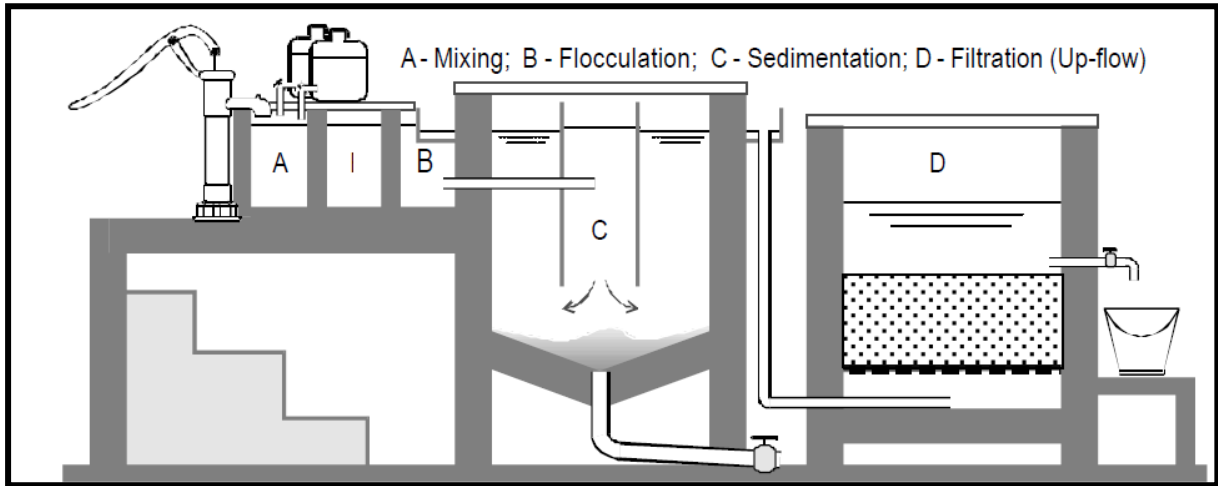
Figure 5-9: **Arsenic removal plants attached to tubewell (designed and constructed in India) (Ahmed, 2001)**

Factors affecting the performance of precipitation/coprecipitation technique.

• **Valence state of arsenic** - The presence of the more soluble trivalent state of arsenic may lessen the removal efficacy. Oxidation to As(V) could improve arsenic removal through precipitation/coprecipitation.

• **pH** - In general, arsenic removal will be maximized at the pH at which the precipitated species is least soluble. The optimal pH range for precipitation/coprecipitation depends upon the waste treated and the specific treatment process.

• **Presence of other compounds** - The presence of other metals or contaminants may impact the effectiveness of precipitation/coprecipitation.

For example, sulfate could decrease arsenic removal in processes using ferric chloride as a coagulant, while the presence of calcium or iron may increase the removal of arsenic in these processes (USEPA, 2002).

5.3.2 Sorptive filtration

Quite a number of sorptive media have been reported to remove arsenic from water. These are activated alumina, activated carbon, iron and manganese-coated sand, kaolinite clay, hydrated ferric oxide, activated bauxite, titanium oxide, cerium oxide, silicium oxide, and many natural and synthetic media. The efficiency of sorptive

media depends on the use of an oxidizing agent as an aid to sorption of arsenic (Ahmed, 2001).

Depending on the precise sorption affinity of the medium to the given component, different contaminants and components of water saturate the media at different stages of the operation. Saturation means that the sorptive sites of the medium have all been filled and contaminants can no longer be adsorbed onto the media.

Technology Description

In adsorption, solutes (contaminants) concentrate at the surface of a sorbent, thereby reducing their concentration in the bulk liquid phase. The adsorption media is usually packed into a column and as contaminated water is passed through it, contaminants are adsorbed (Figure 5-10). The sorbent regularly used for the removal of arsenic from drinking water is Activated alumina (AA). It has also been used for groundwater. The reported adsorption capacity of AA ranges from 0.003 to 0.112 grams of arsenic per gram of AA. It is available in different mesh sizes and its particle size affects contaminant removal efficiency. Up to 23 400 bed volumes of wastewater can be treated before AA requires regeneration or disposal and replacement with new media (USEPA, 2002).

Bed volume (volume per hours of liquid to be treated / volume of resin) = 210 000 $(As)^{-0.57}$ (Ahmed, 2001).

Columns must be regenerated and replaced with new ones when adsorption sites become filled. Regeneration takes place in four steps:

• Backwashing
• Regeneration
• Neutralization
• Rinsing

The regeneration process desorbs the arsenic. Sodium hydroxide solution is usually used for the regeneration of AA and is neutralized with sulfuric acid solution. Aluminium hydroxide precipitate might be formed in the washed-out regeneration

and neutralization fluids due to the fact that alumina may be able to dissolve in the strong base and strong acid solutions used for regeneration and neutralization respectively and hence leads to the production of sludge. This sludge typically contains a high concentration of arsenic.

Other types of sorbent used in adsorption to treat arsenic includes; activated carbon (AC), copper-zinc granules, greensand filtration ($KMnO_4$ coated glauconite), proprietary media and surfactant-modified zeolite (USEPA, 2002), metallic iron, cerium oxide, ion exchange media (Ahmed, 2001), granulated ferric oxide and hydroxide, Iron-coated sand or brick dust (Ahmed, 2001 and USEPA, 2002).
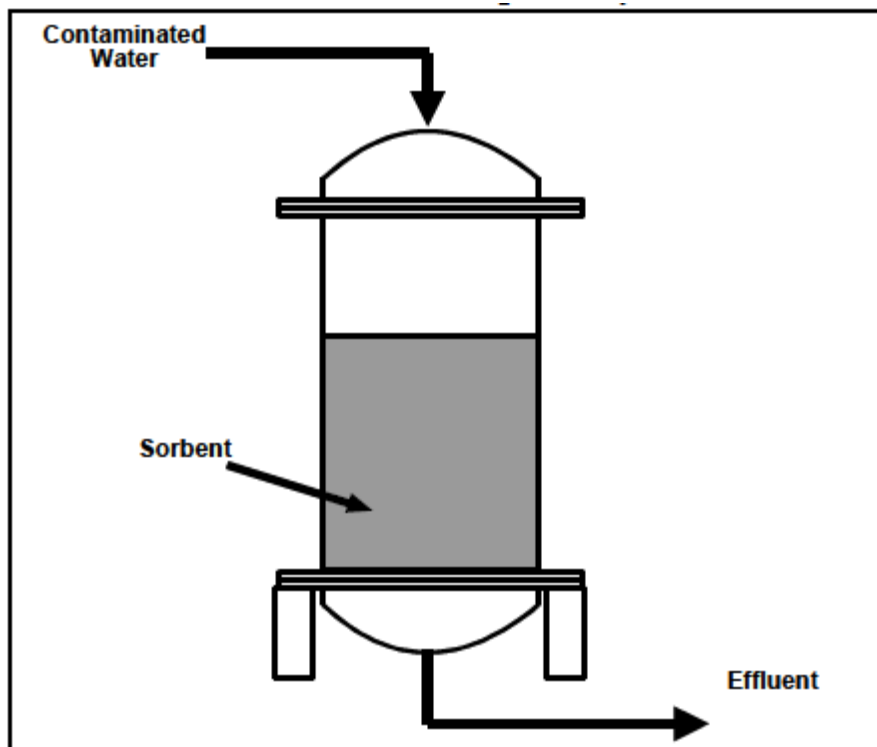
Figure 5-10: Model of a sorption system (USEPA, 2002)

The activated alumina-based sorptive media used in Bangladesh and India includes:
• BUET activated alumina
• Alcan enhanced activated alumina
• Apyron arsenic treatment unit (Ahmed, 2001).

Activated carbon (AC) is an organic sorbent commonly used to eliminate organic and metal contaminants from drinking water, groundwater, and wastewater. Regeneration of AC media used for arsenic removal from water might not be viable because thermal techniques are employed to desorb and volatilize contaminants during the regeneration process. The arsenic might not volatilize at the temperatures typically used in AC regeneration. In addition, off-gas containing arsenic from the regeneration process may be difficult or expensive to manage. The reported adsorption capacity of AC is 0.020 grams of As(V) per gram of AC. As(III) is not effectively removed by AC. AC impregnated with metals such as copper and ferrous iron has a higher reported adsorption capacity for arsenic. The reported adsorption capacity for As(III) is 0.048 grams per gram of copper impregnated carbon and for As(V) is 0.2 grams per gram of ferrous iron-impregnated carbon.

Iron-based adsorption media include granular ferric hydroxide, ferric hydroxide-coated newspaper pulp, ferric oxide, iron oxide-coated sand, sulfur-modified iron, and iron filings mixed with sand. These media have been used primarily to remove arsenic from drinking water. Processes that use these media typically remove arsenic using adsorption in combination with oxidation, precipitation/coprecipitation, ion exchange, or filtration. For example, iron oxide-coated sand uses adsorption and ion exchange with surface hydroxides to selectively remove arsenic from water. The media requires periodic regeneration or disposal and replacement with new media. The regeneration process is similar to that used for AA, and consists of rinsing the media with a regenerating solution containing excess sodium hydroxide, flushing with water, and neutralizing with a strong acid, such as sulfuric acid.

Factors affecting sorption performance

• **Fouling** - The presence of suspended solids, organics, solids, silica, or mica, can cause fouling of sorption media.

• **Arsenic oxidation state** - Sorption is more effective in removing As(V) than As(III).

• **Flow rate** - Increasing the rate of flow through the sorption unit can decrease the sorption of contaminants.

• **Wastewater pH** - The optimal pH to maximize sorption of arsenic by activated alumina is acidic (pH 6). Therefore, pre-treatment and post-treatment of the water could be required.

5.3.2.1 Ion exchange treatment

Ion exchange process is quite similar to that of activated alumina but differs in the medium used. Resins made from synthetic organic materials, inorganic materials, or natural polymeric materials that contain ionic functional groups to which exchangeable ions are attached are used as adsorption medium in the ion exchange process. Four types of ion exchange media have been used: strong acid, weak acid, strong base, weak base.

Strong and weak acid resins exchange cations while strong and weak base resins exchange anions. Because dissolved arsenic is usually in an anionic form, and weak base resins tend to be effective over a smaller pH range, strong base resins are typically used for arsenic treatment.

Arsenic exchange:

$$2R\text{-}Cl + HAsO_4^{2-} = R_2HAsO_4 + 2Cl^- \text{ (Ahmed, 2001)}$$

Where R = ion exchange resin

Resins are also classified by the ion that is exchanged with the one in solution. For example, resins that exchange a chloride ion are referred to as chloride-form resins. They can also be classified by the type of ion in solution that the resin preferentially exchanges. For example, resins that preferentially exchange sulfate ions are referred to as sulfate-selective. Both sulfate-selective and nitrate selective resins have been used for arsenic removal. Just like in the case of Activated alumina, the resin is packed into a column, and as contaminated water is passed through the column, contaminants are exchanged for other ions such as chloride or hydroxide in the resin (Figure 5-11). To prevent pollution and reduction of the resins' efficiency, treatment such as filtration and oil-water separation to remove organics, suspended solids, and contaminants are part of the ion exchange process. Ion exchange resins must be

periodically regenerated to remove the adsorbed contaminants and reload the exchanged ions. Regeneration of a resin occurs in three steps:

• Backwashing

• Regeneration with a solution of ions

• Final rinsing to remove the regenerating solution

The regeneration process results in a backwash solution, a waste regenerating solution, and waste rinse water. The number of ion exchange bed volumes that can be treated before regeneration is needed can range from 300 to 60 000. The regenerating solution may be used up to 25 times before treatment or disposal is required.

Regeneration

$$R_2HAsO_4 + 2Na+ + 2Cl^- = 2R\text{-}Cl + HAsO_4^{2-} + 2Na^+ \text{ (Ahmed, 2001)}$$
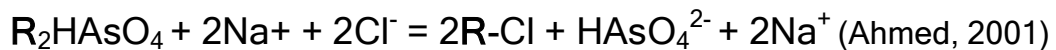
Where R = ion exchange resin

Ion exchange can be operated using multiple beds in series to reduce the need for bed regeneration; beds first in the series will require regeneration first, and fresh beds can be added at the end of the series. Multiple beds can also allow for continuous operation because some of the beds can be regenerated while others continue to treat water. Ion exchange beds are typically operated as a fixed bed, in which the water to be treated is passed over an immobile ion exchange resin. One variation on this approach is to operate the bed in a nonfixed, countercurrent fashion in which water is applied in one direction, usually downward, while spent ion exchange resin is removed from the top of the bed. Regenerated resin is added to the bottom of the bed. This method may reduce the frequency of resin regeneration (USEPA, 2002).
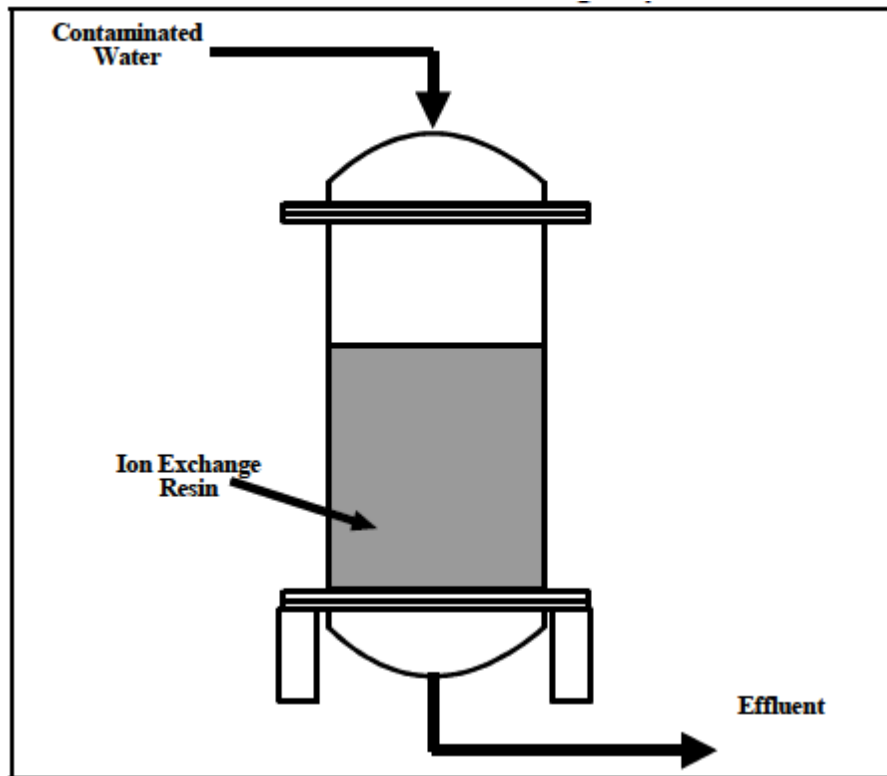
Figure 5-11: Model of an Ion exchange system (USEPA, 2002)

Factors affecting ion exchange performance

• **Valence state** - As(III) is generally not removed by ion exchange.

• **Presence of competing ions** - Competition for the exchange ion can reduce the effectiveness of ion exchange if ions in the resin are replaced by ions other than arsenic, resulting in a need for more frequent bed regeneration.

• **Fouling** - The presence of organics, suspended solids, calcium, or iron, can cause fouling of ion exchange resins.

• **Presence of trivalent iron** - The presence of Fe (III) could cause arsenic to form complexes with the iron that are not removed by ion exchange.

• **pH** - For chloride-form, strong-base resins, a pH in the range of 6.5 to 9 is optimal. Outside of this range, arsenic removal effectiveness decreases quickly (USEPA, 2002).

5.3.3 Membrane filtration

In membrane filtration, the use of synthetic membranes is employed. These membranes can remove many contaminants from water including salts, viruses, bacteria, and various metal ions. Two major types of membranes exist; low-pressure membranes, used in microfiltration and ultrafiltration; and high-pressure membranes, used in nanofiltration and reverse osmosis. The latter have pore sizes appropriate to the removal of arsenic (Ahmed, 2001).

Technology Description

Membrane filtration separates contaminants from water by passing it through a semi-permeable barrier or membrane. The membrane allows some constituents to pass through, while blocking others (Figure 5-12). There exist four types of membrane processes which are employed for the removal of arsenic. They are; Nanofiltration (NF), Reverse osmosis (RO), Microfiltration (MF) and Ultrafiltration (UF).

Nanofiltration and Reverse osmosis require fairly high pressure and Microfiltration and Ultrafiltration require lower pressure. The low pressure processes primarily remove contaminants through physical sieving, and the high pressure processes through chemical diffusion across the permeable membrane (USEPA, 2002).
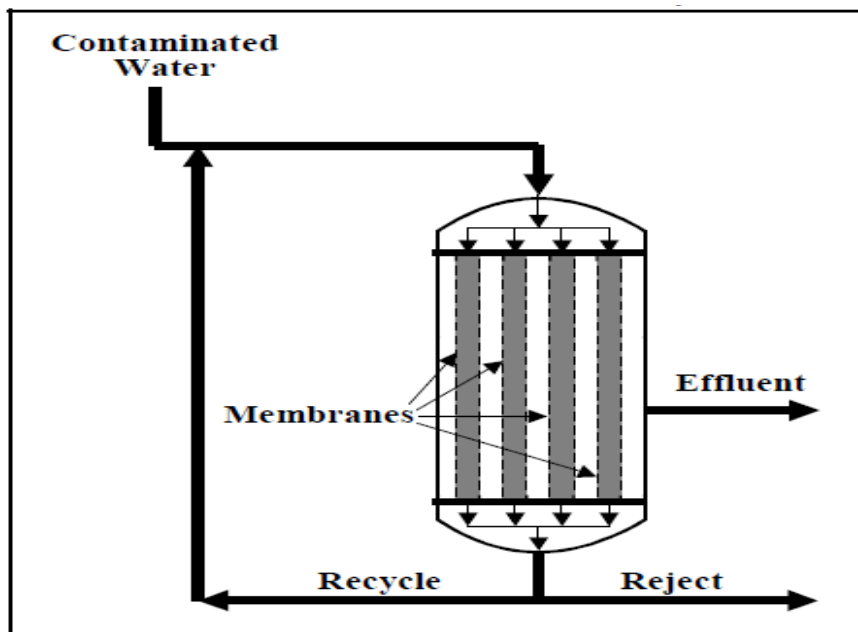
Figure 5-12: Model of a membrane filtration system (USEPA, 2002)

Arsenic species dissolved in water tend to have relatively low molecular weights hence NF and RO membrane processes are liable to effectively treat dissolved arsenic. MF has been used with precipitation/coprecipitation to remove solids containing arsenic. Two treatment residuals are generated from the influent waste stream during the MF process: a treated effluent (permeate) and a rejected waste stream of concentrated contaminants (reject). RO is a high pressure process that principally removes smaller ions typically associated with total dissolved solids. The molecular weight cut off for RO membranes ranges from 1 to 20 000, which is a significantly lower cut off than for NF membranes. The molecular weight cut off for NF membranes ranges from approximately 150 to 20 000. NF is a high pressure process that primarily removes larger divalent ions associated with hardness (for example, calcium (Ca), and magnesium (Mg) but not monovalent salts (for example, sodium [Na] and chlorine [Cl]). NF is slightly less efficient than RO in removing dissolved arsenic from water.

MF is a low-pressure process that primarily removes particles with a molecular weight above 50 000 or a particle size greater than 0.050 micrometers. The pore size of MF membranes is too large to effectively remove dissolved arsenic species, but MF can remove particulates containing arsenic and solids produced by precipitation/coprecipitation (USEPA, 2002).

Factors affecting membrane filtration performance

• Fouling - The presence of suspended solids, high molecular weight particles, dissolved solids, organic compounds, and colloids in the feed stream may cause membrane fouling.
• Oxidation state of arsenic - As(V) is normally bigger than As(III), it can be effectively captured by the membrane. Thus prior oxidation of the influent stream to convert As(III) to As(V) will increase arsenic removal.
• pH - pH may affect the adsorption of arsenic on the membrane by creating an electrostatic charge on the membrane surface.

- Temperature - Low temperatures of influent stream decreases membrane flux. Increasing system pressure or increasing the membrane surface area may compensate for low influent stream temperature.

Table 5-2: Comparison of main Arsenic removal technologies (Ahmed, 2005)

Technologies	Advantages	Disadvantages
Oxidation: air oxidation, chemical oxidation	• Relatively simple, low cost, but slow process (air). • Relatively simple and rapid process (chemical) • Oxidizes other impurities and kills microbes	• Processes remove only some of the arsenic • Used as pretreatment for other processes.
Coagulation, Sedimentation and filtration	• Relatively low capital cost • Relatively simple in operation • Common chemicals available	• Not ideal for anion- rich water treatment • Produces toxic sludges • Low removal of Arsenic (III) • Pre-oxidation is required • Efficiencies maybe inadequate to meet strict standards
Sorption techniques: activated alumina, iron coated sand, ion exchange resin, other sorbents	• Relatively well known and commercially available • Well defined technique • Many possibilities and scope for development	• Not ideal for anion-rich water treatment • Produces arsenic-rich liquid and solid wastes • Replacement/regeneration is required • High-tech operation and maintenance • Relatively high cost
Membrane filtration: nanofiltration, reverse osmosis.	• Well-defined and high removal efficiency	• High capital and running costs • High-tech operation and

	• No toxic solid wastes produced • Capable of removal of other contaminants	maintenance • Arsenic-rich rejected water is produced	

Table 5-3: Comparing removal efficiencies of technologies (modified from Feenstra *et al.*, 2007)

Technology		Removal efficiency	
		As (III)	As (V)
Oxidation: air oxidation, chemical oxidation		-	-
Coagulation, Sedimentation and filtration	Using iron salts	++	+++
	Using alum	-	+++
Sorption techniques	Activated alumina	+/++	+++
	Ion exchange resin	-	+++
Membrane filtration	Nanofiltration	-/++	++
	Reverse osmosis	-/++	++

+++   Constantly > 90%
++   Usually 60-90%
+   Generally 30-60%
-       < 30%

5.4 Suitable treatment technique for Jagersfontein

When a particular source of water needs to be treated, there are certain main aspects that must be taken into account before a treatment option is chosen. These aspects include:

❖ The quality of the water source (raw water quality) and its variability;
❖ The quality of the treated water to be produced;
❖ The volume of water to be treated (capacity of the plant);
❖ The cost limitations;

❖ The level of sophistication that is acceptable taking into account plant locality and level of expertise available to control and operate the plan;

❖ The support services available to assist with plant optimisation, trouble shooting and maintenance and repair problems.

The more polluted a water source is, the more sophisticated the treatment process required to produce high quality water will be and hence will involve high cost. Quality of raw water (mine shaft sample) has been discussed in Chapter Four. Other chemical constituents of this water sample fall under the standards of good quality water. Therefore treatment required will be to remove principally arsenic and hence it will be less sophisticated and less costly. Table 5-4, Table 5-5, Table 5-6 and Table 5-7 present estimated costs for treating arsenic contaminated water using coagulation and filtration technique, adsorption technique (ion exchange and activated alumina) and membrane filtration techniques (Reverse Osmosis) respectively. Note should be taken that these values are estimates just to serve as an idea of what costs are involved in incorporating either of these techniques to treat arsenic contaminated water. It has been adopted from USEPA manuals.

Table 5-4: Cost estimate for coagulation and filtration treatment system (Chen *et al.*, 2009)

Technology Flow rate: 250 gpm = 16 l/s	Capital cost		Operational and maintenance cost		
	Cost of equipment	$168,142	R1,411,804	Chemical usage	$0.016/1000 gal	R0.13/3785 l
Coagulation and filtration	Site engineering	$53,435	R449,185	Electricity consumption	$209.50/month $0.006/1000 gal	R1759/month R0.05/3745 l
	System installation, shakedown and startup	$83,870	R704,214	Labour	$0.16/1000 gal	R1.34/3785 l
	Total cost	$305,447	R2,565,203	Total cost	$0.18/1000 gal	R1.52/3785 l

Ion exchange process can be operated manually or automatically hence the costs will depend on the manner of operation as illustrated in Table 5-5. Capital cost of water treatment by Ion exchange involves cost for treatment vessels, ion exchange resin, processing pipe, valves and accessories, instruments and controls and salt and brine storage. Operational costs include cost of treatment chemicals, operating labour, utility, Replacement ion exchange resin and replacement parts and miscellaneous material.

Table 5-5: Cost estimate for Ion exchange treatment system (Rubel, 2003)

Flow rate:620 gpm = 39 l/s		Manual Operation		Automatic operation	
Capital cost	Process equipment	$303,000	R2,544,140	$407,000	R3,417,376
	Process equipment installation	$69,000	R579,359	$104,000	R873,236
	Miscellaneous installed items	$158,000	R1,326,647	$158,000	R1,326,647
	subtotal	$530,000	R4,450,146	$669,000	R5,617,259
	Contingency: 10% of subtotal	$53,000	R445,762	$67,000	R563,510
	TOTAL	**$583,000**	**R4,895,908**	**$736,000**	**R6,180,769**
Operational cost		$0.30/1000gal	R2.5/3785L	$0.28/1000gal	R2.4/3785L

In the case of water treatment by adsorptive media (activated alumina), there exist four different types of adsorptive media that could be used in the water treatment plants. The capital cost and operational cost (Table 5-6) will therefore depend on the media being incorporated. Capital cost involves cost for treatment vessels and media, processing pipes valves and accessories, instruments and controls, chemical storage tanks. Operational cost involves treatment chemicals, operating labour, replacement treatment media and replacement part and miscellaneous material.

Table 5-6: Cost estimate for the various types of adsorptive media treatment system (Rubel, 2003)

Flow rate: 570 gpm = 36 l/s		Manual operation with media replacement without pH adjustment		Manual operation with media replacement with pH adjustment		Manual operation with media regeneration with pH adjustment		Automatic operation with media regeneration with pH adjustment	
Capital cost	Process equipment	$143,000	R1,202,716	$197,000	R1,655,888	$221,000	R1,858,743	$287,000	R2,413,842
	Process equipment installation	$51,000	R428,222	$73,000	R613,974	$76,000	R638,134	$105,000	R883,113
	Miscellaneous installed items	$54,000	R453,411	$77,000	R647,616	$205,000	R1,721,283	$205,000	R1,724,173
	Sub total	$248,000	R2,084,349	$347,000	R2,917,478	$502,000	R4,218,160	$597,000	R5,021,128
	Contingency: 10% of subtotal	$25,000	R210,265	$35,000	R293,878	$50,000	R419,825	$60,000	R503,790
	TOTAL	**$273,000**	**R2,294,614**	**$382,000**	**R3,211,356**	**$553,000**	**R4,637,985**	**$657,000**	**R5,524,918**
Operational and maintenance cost		$2.52/1000 gal	R21/3785.4 l	$0.73/1000 gal	R6.13/3785 l	$0.47/1000 gal	R4/3785 l	$0.19/1000 gal	R2/3785 l

Table 5-7 presents costs involved in treating water by reverse osmosis method. The costs are based on the capacity of the plant. Reverse Osmosis maybe be cost effective if removal of other contaminants is needed and water quantity is not a concern (USEPA: Office of water, 2000).

Table 5-7: Cost estimate for reverse osmosis treatment system (USEPA: Office of water, 2000)

Cost component	Plant Capacity				Capital cost category
	1.0 mgd	44 l/s	10 mgd	438 l/s	
Manufactured Equipment	$474,210	R3,988,390	$3,458,480	R29,087,892	Process
Labour	$70,420	R591,282	$346,850	R2,912,326	Construction
Electrical	$65,740	R551,986	$486,270	R4,082,966	Process
Housing	$64,260	R539,559	$462,650	R3,884,641	Process
Contingencies	$101,190	R849,642	$713,140	R5,997,935	Construction
Total	$775,820	R6,520,859	$5,467,390	R45,965,760	

For the case of Jagersfontein, coagulation and filtration technology ($FeCl_3$ as coagulant) will be the best option as per its advantages stated in and also its efficiency in removing arsenic (V) (Table 5-3) which happens to be the dominant specie in the mine water. It is also the cheapest technique as it has been demonstrated and it is less sophisticated.

6 Conclusion and recommendations

This chapter will review and summarise the main methods used in carrying out the research which was aimed at characterising the groundwater of Jagersfontein town, assessing the concentration of the arsenic and degree of contamination and propose possible and feasible remediation techniques. It will also review the implications of the results obtained during the study.

Groundwater in Jagersfontein town has been known for its arsenic contamination. The now decommissioned diamond mine located some few metres from the main town is the principal suspect of the source of arsenic. In this study, the primary objective was to assess arsenic contamination in the Jagersfontein area in order to know the degree and extend of the contamination. This was realized by carrying out a hydrocensus from where, boreholes were located and water samples collected. Three water samples (500 ml each) were collected from each borehole from which one was sent to the IGS lab for general chemistry analysis with specific element arsenic (As), the second was sent to School of Bioresources Engineering and Environmental Hydrology, University of KwaZulu-Natal for isotopes (oxygen-18 and Deuterium) analysis and the third to iThemba Labs in Gauteng for Tritium analyses. Additional data was obtained from Bloemwater because they have been involved in monitoring the water quality in the mine before and after treatment for a couple of years. Hence their data was important to show the changes that have been happening in the water quality over this period of time.

From the different chemical plots (WISH plots) used in presenting the data, the dominant cation is Magnesium (Mg) while the dominant anion is sulphate (SO_4). The water samples show three different water types; Sodium/Potassium-Sulphate, Magnessium-Sulphate and Magnessium-Bicarbonate. With respect to the general chemical composition of water samples and the stiff diagrams, it is concluded that the water samples are from different sources. However, water samples such as Mine shaft, NG Kerk and Mw are from the same source as their stiff diagram geometry is similar. So too is the case with water samples TPB1 and TPB2. Sample collected from the mineshaft showed highest arsenic concentration while all other individual

boreholes in the main town of Jagersfontein showed low arsenic concentration (<0.006mg/l), hence concluding that arsenic contamination comes from the mine. Mine water that has been treated in package plant (JFinal) still shows high arsenic concentration. Water from Kalkfontein dam is being treated in a bigger treatment plant (went operational in July 2012) and there after mixed with treated mine water. This reduces the arsenic concentration of water to an acceptable level before it is finally supplied to the community. Community water (CW) sample which happens to be water available for the consumption of the inhabitants of Jagersfontein, showed arsenic concentration of 0.001 mg/l. This value is below the limit which is 0.01 mg/l. Calculating the carcinogenic risk using this concentration (0.001 mg/l), a value of 4.29×10^{-5} was obtained. This means 429 cases of cancer per population of 10,000000 are expected when the population is exposed to 0.001 mg/l of arsenic. Hence the community stand a low carcinogenic risk. Isotopic results show water is meteoric since they plot along the GMWL and clustering around it implies they are of the same age. The recorded environmental tritium content of the 13 groundwater samples and one surface water sample used for the analysis varied from 0 T.U to 4.3 T.U with an average of 1.9 T.U. 71 % of the samples have values more than 1 T.U, suggesting that the water samples involve mixture of pre-modern and modern water that has undergone radioactive decay and the origin of the water is meteoric (groundwater was recharged by precipitation). 29 % of samples have values <0.8 T.U indicating old (pre-modern) water. Cross plots and spearman's correlation calculations show arsenic does not correlate with most of the other chemical parameters implying its source is not geogenic. Saturated indices of some selected minerals, calculated in Phreeqc generally indicate dissolution (negative saturation indices). In view of the concentrations of arsenic species calculated in Phreeqc, arsenic (V) was identified as the dominant specie of arsenic in the groundwater. This specie is anionic at natural pH of water, sorbs easily hence less mobile and thus can be removed easily from water.

There are many techniques that have been used to remove arsenic in groundwater in many different countries. Techniques such as; Oxidation (which is principally used as a pre-treatment for efficient removal of arsenic in other treatment techniques),

Coagulation, Sedimentation and filtration, Sorptive filtration and Membrane filtration have been used in the Asian countries and in the USA at large scale and household levels. There are a couple of techniques developed based on the Coagulation, Sedimentation and filtration process in Asia. These techniques include Bucket treatment unit, Stevens Institute technology, Fill and draw treatment unit and Tubewell-attached arsenic treatment unit. These techniques are easy to operate and involve a low cost of construction and serves households and the community at large. By comparing these techniques, Coagulation, Sedimentation and filtration technique is the best option to be used in treating groundwater in Jagersfontein. This technique is less sophisticated, efficiently removes arsenic (V) which is the dominant arsenic specie in Jagersfontein water and it involves low cost. However what is currently done in Jagersfontein to reduce the concentration of arsenic in water is dilution/mixing. Mine water treated in a package is mixed with treated water from Kalkfontein dam. Water (not arsenic contaminated) from Kalkfontein dam is treated in a bigger treatment plant which went operational in July 2012.

Considering the results obtain and other findings gotten during field work the following recommendations are put forward;

- The package plant should be upgraded and complete technology employed in order to remove arsenic more efficiently.
- Continuous monitoring of boreholes to have knowledge of how arsenic concentration in water varies and what influences it.
- Measuring water levels which will aid in determining groundwater flow directions hence identify beforehand boreholes that stand a risk of arsenic contamination.
- Perform pump test of boreholes in the main town of Jagersfontein in order to determine the sustainable yield of each borehole. By so doing, every owner of a borehole in the community will have adequate supply of groundwater.
- If Itumeleng (appendix Figure C 8) borehole is to be used as production borehole in the future, sewage water running by it should be taken care of. For this borehole showed highest concentration of nitrate.

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Appendix A

Temperature and rainfall data of Jagersfontein

Kimberlite minerals

Table A 1: **Temperature and rainfall data of Jagersfontein**

Month	Midday temperatures	Night time temperatures	Rainfall
January	30	15	42
February	29	14	50
March	26	12	54
April	23	8	29
May	19	3	10
June	16	0	1
July	16	0	1
August	19	2	2
September	22	5	6
October	25	9	23
November	27	11	30
December	29	13	30

Table A 2: some minerals present in Kimberlites

Minerals		Chemical formula
Olivine		$(Mg, Fe)_2SiO_4$
Phlogopite (magnesium mica)		$KMg_3AlSi_3O_{10}(F, OH)_2$
Serpentine		$(Mg, Fe)_3Si_2O_5(OH)_4$
Clionopyroxene (commonly Diopside)		$CaMgSi_2O_6$
Monticellite (grey silicate mineral)		$CaMgSiO_4$
Apatite (Phosphate mineral)		$Ca_5(PO_4)_3(F, Cl, OH)$
Spinel		$MgAl_2O_4$
Perovskite		$CaTiO_3$
Ilmenite		$FeTiO_3$
Picroilmenite (Mg rich ilmenite)		$MgTiO_3$
Chromium spinels	Chromite	$FeCr_2O_4$
	Magnesiochromite	$MgCr_2O_4$
Pyrope (magnesian garnet)		$Mg_3Al_2(SiO_4)_3$
Enstatite		$MgSiO_3$

Appendix B

Countries with arsenic contamination problem

Arsenic bearing minerals

Table B 1: some countries with Arsenic contamination problem

Ghazni Cordoba, Salta, La Pampa, Santa Fe, Tucuman, Santiago del Estero, san Luis, and parts of Buenos	Afghanistan	Natural
Aires	Argentina	Natural
Victoria gold-mining region	Australia	Anthropogenic
50 of 64 districts	Bangladesh	Natural
Minas Gerais in southeastern Brazil	Brazil	Anthropogenic
Srednogorie	Bulgaria	Anthropogenic
Halifax county of Nova Scoti; mainland coast of southern British Columbia, and Toronto, Ontario	Canada	Natural and anthropogenic
Antofagasta, Aracamenan settlements near Calama, and Chquicamata copper mine	Chile	Natural and anthropogenic
Cairo	Egypt	Natural
Obuasi area in the Ashanti region and Bolgatanga area of the Upper East region	Ghana	Natural
Lavrion	Greece	Natural
Southern part of the Great Hungarian Plain	Hungary	Natural
West Bengal, Bihar, Uttar Pradesh, Jharkhand, and Northeastern states	India	Natural and anthropogenic
Sendai, Tkasuki,	Japan	Natural and anthropogenic

Kuamoto, Nakajo, Toroku, and Matsuo		
Kurdistan province	Iran	Natural
Lagunera region, State of Hidago, Torreon city, Silesia, and San Luis de Potosi	Mexico	Natural and anthropogenic
Ayeyarwady division	Myanmar	Natural
Terai region and Rupandehi district	Nepal	Natural
Rawalpindi, Attock, Gujrat, Jhelum, Sargodha, and Chakwal	Pakistan	Natural
Northwestern parts of Transylvania	Romania	Natural
Northern Sweden	Sweden	Anthropogenic
Ticino, Grisons, and Valais cantons	Switzerland	Natural
South-West coast of Taiwan	Taiwan China	Natural
Ronpibool district	Thailand	Anthropogenic
Utah, Oregon, California, Navada, New Hamshire, Alaska, and Minnesota	USA	Natural and anthropogenic
South-West England, and Central Scotland	United Kingdom	Anthropogenic

Table B 2: Arsenic bearing minerals

Class		Minerals					
Arsenates	**Names**	Annabergite	Scorodite	Olivenite	Adamite	Cornubite	Austinite
	Chemical formula	$Ni_3(AsO_4)_2 \cdot 8H_2O$	$Fe(AsO_4).2H_2O$	$Cu_2(AsO_4)OH$	$Zn_2(AsO_4)(OH)$	$Cu_5(AsO_4)2(OH)_4$	$CaZn(AsO_4)(OH)$
Sulphides	**Names**	Arsenopyrite	Realgar	Orpiment			
	Chemical formula	$AsFeS$	AsS	As_2S_3			
Sulfosalts	**Names**	Enargite	Prousite	Samsonite			
	Chemical formula	Cu_3AsS_4	Ag_2AsS_3	$Ag_4MnSb_2S_6$			
Arsenides	**Names**	Algodonite	Domeykite	Löllingite	Nickeline	Safflorite	Skutterudite
	Chemical formula	Cu_6As	Cu_3As	$FeAs_2$	$NiAs$	$(Co,Fe)As_2$	$(Co,Ni)As_3$
Arsenites	**Names**	Reinerite	Cafarsite				
	Chemical formula	$Zn_3(AsO_3)_2$	$Ca_8(Ti,Fe2+,Fe3+,Mn)_{67}(AsO_3)12 \cdot 4H_2O$				
Silicates	**Names**	Nelenite	Holdenite	Schallerite			
	Chemical formula	$(Mn,Fe)_{16}Si_{12}O_{30}(OH)_{14}[As_3O_6(OH)_3]$	$Mn_6Zn_3(OH)_8(AsO_4)_2(SiO_4)$	$Mn_{16}Si_{12}O_{30}(OH)_{14}[As_3O_6(OH)_3]$			
Oxides	**Names**	Arsenolite					
	Chemical formula	AsO_3					

Appendix C

Historical data and current work data

Picture of boreholes sampled

Expanded Durov Diagram

Expanded Durov diagram shows more details of the environment where the water samples came from. It also shows clearly the major cations and anions present in the samples. Figure C 1 shows the layout of the fields in an Expanded Durov diagram.
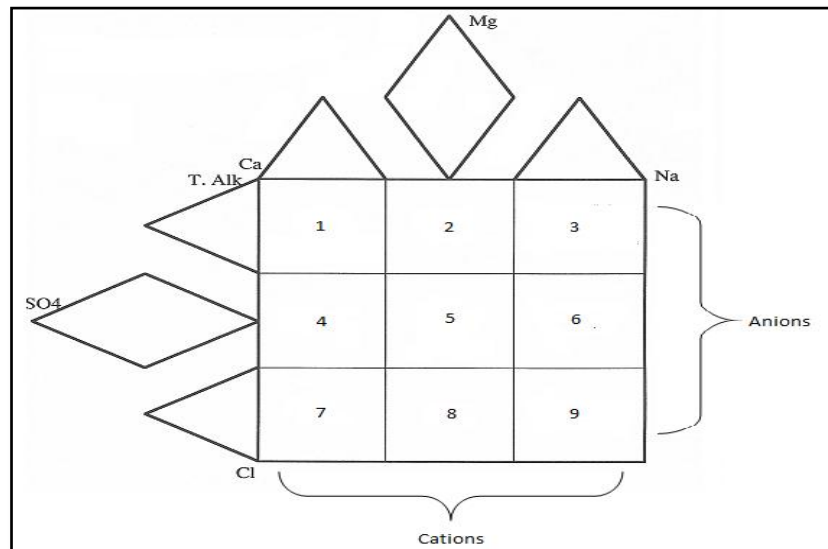
Figure C 1: Layout of fields of the Expanded Durov diagram

This diagram only goes to help give an idea or describe the water quality signature of each sample but can't be used as a clear-cut guideline. It is summarized as follows:

Field 1: Fresh, very clean recently recharged groundwater with HCO_3 and CO_3 dominated ions.

Field 2: represents fresh, clean, relatively young groundwater that has started to undergo Mg ion exchange, often found in dolomitic terrain.

Field 3: This field indicates fresh, clean, relatively young groundwater that has undergone Na ion exchange (sometimes in Na - enriched granites or felsic rocks) or because of contamination effects from a source rich in Na.

Field 4: Fresh, recently recharged groundwater with HCO_3 and CO_3 dominated ions that has been in contact with a source of SO_4 contamination or that has moved through SO_4 enriched bedrock.

Field 5: Groundwater that is usually a mix of different types - either clean water from fields 1 and 2 that has undergone SO_4 and NaCl mixing / contamination or old stagnant NaCl dominated water that has mixed with clean water.

Field 6: Groundwater from field 5 that has been in contact with a source rich in Na or old stagnant NaCl dominated water that resides in Na rich host rock / material.

Field 7: Water rarely plots in this field that indicates NO_3 or Cl enrichment or dissolution.

Field 8: Groundwater that is usually a mix of different types - either clean water from fields 1 and 2 that has undergone SO_4, but especially Cl mixing / contamination or old stagnant NaCl dominated water that has mixed with water richer in Mg.

Field 9: Old or stagnant water that has reached the end of the geohydrological cycle (deserts, salty pans etc) or water that has moved a long time and / or distance through the aquifer or on surface and has undergone significant ion exchange because of the long distance or residence time in the aquifer (source: Report on Geohydrological Investigation as part of the EMPR for the proposed Verkeerdepan Coal Mining Projects, April 2008).

Sodium Adsorption Ratio (SAR) diagram

In terms of suitability of the groundwater for agricultural use (irrigation) the SAR diagram (Sodium Adsorption Ratio) is a handy tool to assess the suitability of the water. Sodium enrichment with respect to Ca and Mg in groundwater will present a risk of sodium accumulation in soils (especially when clayey) and cause deterioration in soil structure and increase erodability because of dispersion reactions in the soil.

Table C 1: Irrigation water type based on EC values (from IGS laboratory).

EC mS/m	
0-25	C_1: Low salt content: No danger for brakishness on well drained soils.
26-75	C_2: Medium salt content. Provision must be made for leaching of salts and plants sensitive to brakishness must be avoided.
76-225	C3: High salt content. Can only be used on soils with a good drainage. Leaching is needed periodically and plants sensitive to brakish water

	must be avoided.
>225	C4: Very high salt content. Not fit for irrigation under normal conditions. Can be used in an emergency on sandy soils.

Table C 2: Irrigation water type based on SAR values (from IGS Laboratory).

SAR Range	
0 - 10	S_1: Low Sodium: Can be used for irrigation - contains a low brakish danger.
10 - 18	S2: Medium Sodium: Mainly to be used on sandy soils with a very good drainage.
18 - 26	S3: High Sodium: Not to be used on soils with limited drainage.
26 - 34	S_4: Very high sodium: Not fit for irrigation because of the high sodium content.

The SAR types of all samples fall within the range suitable for irrigation. By referring to Table C 1 and Table C 2 DWA's water samples are shown to be C2/C3S1 SAR type which is generally suitable for soils with good drainage. Bloemwater's water samples are shown to be of the C3S2 SAR type which is mainly to be used on sandy soil with good drainage and plants sensitive to brackishness must be avoided.
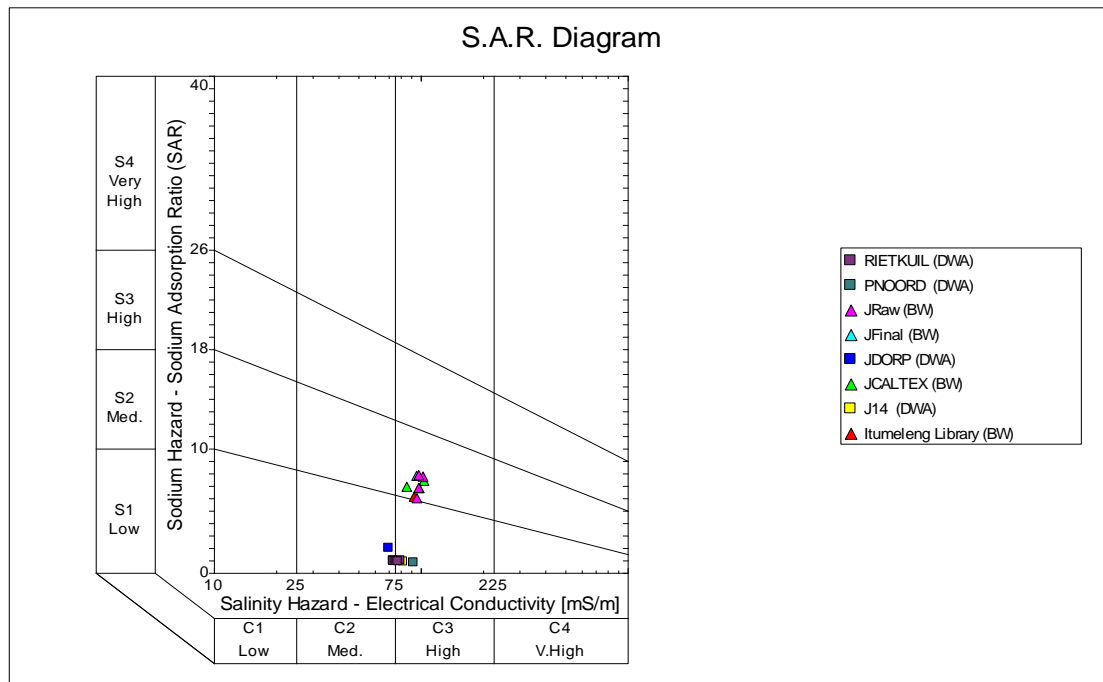
Figure C 2: SAR diagram of historical data

Sodium Adsorption Ratio (SAR) diagram

Table C 1 and Table C 2 resent the standards used by the IGS laboratory to propose the fitness of water for irrigation. These standards were used in this study to determine the suitability of the groundwater for irrigational purposes. Table C 3 and Table C 4 present the classification of the water samples with respect to the dates of sampling.

Table C 3: SAR classification of water samples (October 2011)

SAR type	Water samples	
C_3S_2	NG Kerk, Mine shaft	Mainly to be used on sandy soil with good drainage and plants sensitive to brackishness must be avoided.
C_3S_1	9 Ostr, Pstr, 17 Wstr, 10 Vstr, 6 Wstr, Itumeleng, 35 Hstr, FB1A, 6 Rstr, J BH 1 and 11 Ostr.	Can be used for irrigation provided soil has good drainage capacity and plants sensitive to brackish water are avoided.

C_2S_1	TPB1, TPB2, 20 Ostr, and FB 1	Can be used for irrigation provided provision for soil leaching of salts is made and plants sensitive to brackishness are avoided
C_4S_1	Cv, 11 Fstr	Not fit for irrigation but can be used on sandy soil

Table C 4 illustrates some water samples changed in SAR type. For instance, Cv and 11 Fstr samples changed from C4S1 to C3S1, 20 Ostr changed from C2S1 to C3S1 and Pstr sample changed from C_3S_1 to C_4S_1.
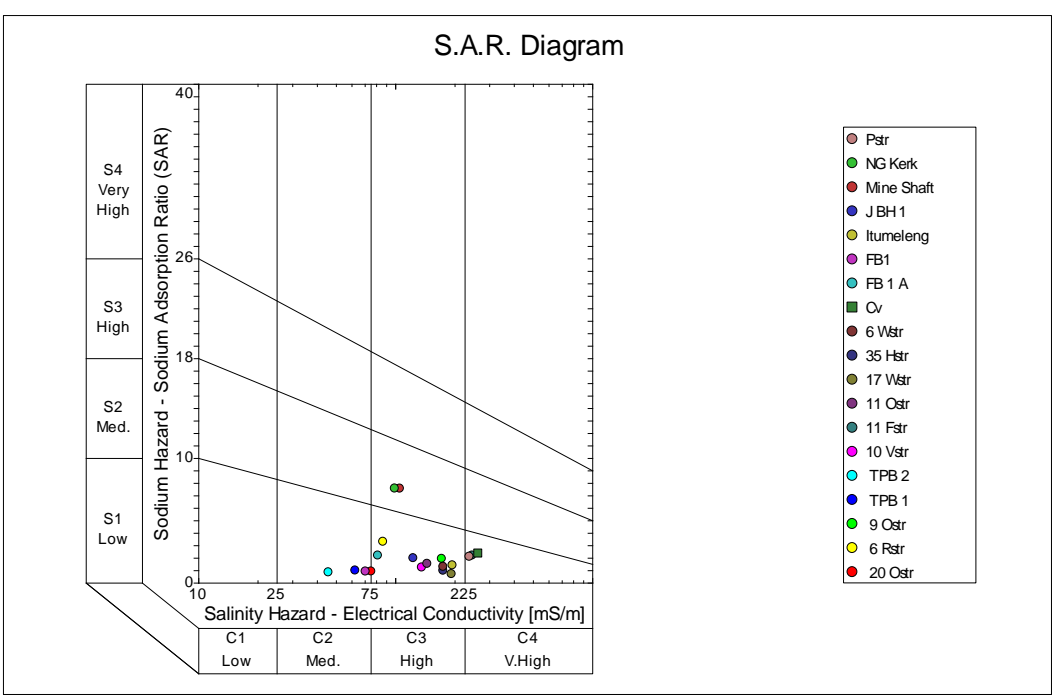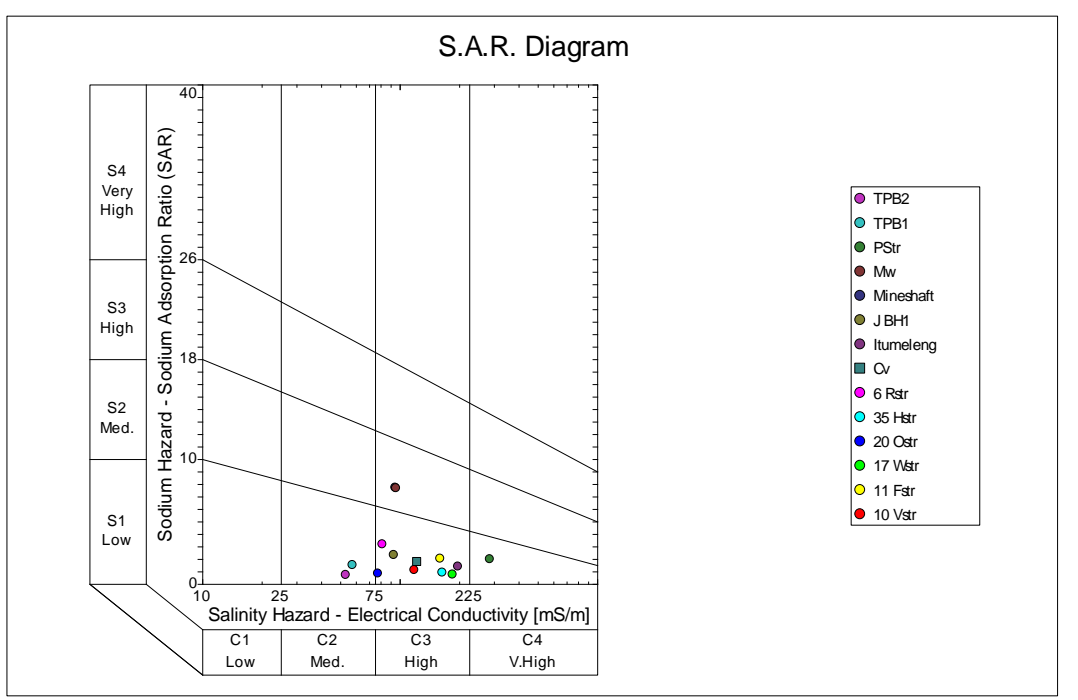
Figure C 3: SAR diagram of water samples

Table C 4: SAR classification of water samples (April 2012)

SAR type	Water samples	
C_3S_2	Mine shaft, Mw	Mainly to be used on sandy soil with good drainage and plants sensitive to brackishness must be avoided.
C_3S_1	Cv, 20 Ostr, 17 Wstr, 10 Vstr, Itumeleng, 35 Hstr, 6 Rstr, J BH 1 and 11 Fstr.	Can be used for irrigation provided soil has good drainage capacity and plants sensitive to brackish water are avoided.
C_2S_1	TPB1, TPB2	Can be used for irrigation provided provision for soil leaching of salts is made and plants sensitive to brackishness are avoided
C_4S_1	Pstr	Not fit for irrigation but can be used on sandy soil

Most of the water samples' SAR is within the recommended range for irrigation. TPB1 and TPB2 water samples have a higher aptness for irrigation more than the other samples.

Table C 5: δ^2H and δ^{18}O analysis results for October samples

Sample Name	δ^2H Reportable Value (permil)	δ^{18}O Reportable Value (permil)	Analysis Date
11 Fauresmith st	-14.85	-2.99	02-11-2011
Palmerston	-15.21	-2.85	02-11-2011
Fauresmith Borehole 1	-22.96	-4.23	02-11-2011
Fauresmith Borehole 1A	-20.59	-3.67	02-11-2011
17 Weil	-19.39	-3.72	02-11-2011
Charlesville	-4.22	-0.64	02-11-2011
Jagersfontein Borehole 1	-25.55	-4.52	02-11-2011
Itumeleng	-19.28	-3.36	02-11-2011
Mine Shaft	-21.46	-3.53	02-11-2011
TPB1	-26.71	-4.81	02-11-2011
TPB2	-14.47	-2.71	02-11-2011
10 Voortrekker st	-25.63	-4.46	02-11-2011
10 Voortrekker st Treated	-26.94	-4.80	02-11-2011
9 Ooskloof	-20.74	-3.83	02-11-2011
11 Ooskloof	-24.80	-4.71	02-11-2011
20 Ooskloof	-28.37	-5.09	02-11-2011
Fauresmith st	-16.18	-3.37	02-11-2011
35 Harrington st	-18.24	-3.09	02-11-2011
6 Ried st	-28.64	-5.07	07-11-2011
NG Kerk	-20.22	-3.68	07-11-2011

Table C 6: LGR DT-100 Standard checks on IGS: 081111 run 7 November 2011 (Std Dev n=30)

SBEEH STANDARD	Calibrated δ^2H ($^o/_{oo}$)	Current run δ^2H ($^o/_{oo}$)	Std Dev Current run δ^2H ($^o/_{oo}$)	Calibrated δ^{18}O($^o/_{oo}$)	Current run δ^{18}O ($^o/_{oo}$)	Std Dev Current run δ^{18}O ($^o/_{oo}$)
IO	6.33	6.50	0.40	0.68	0.68	0.19
IO/SW	-32.21	-32.56	0.53	-4.88	-4.81	0.20
SW	-71.56	-71.42	0.54	-10.02	-10.05	0.26
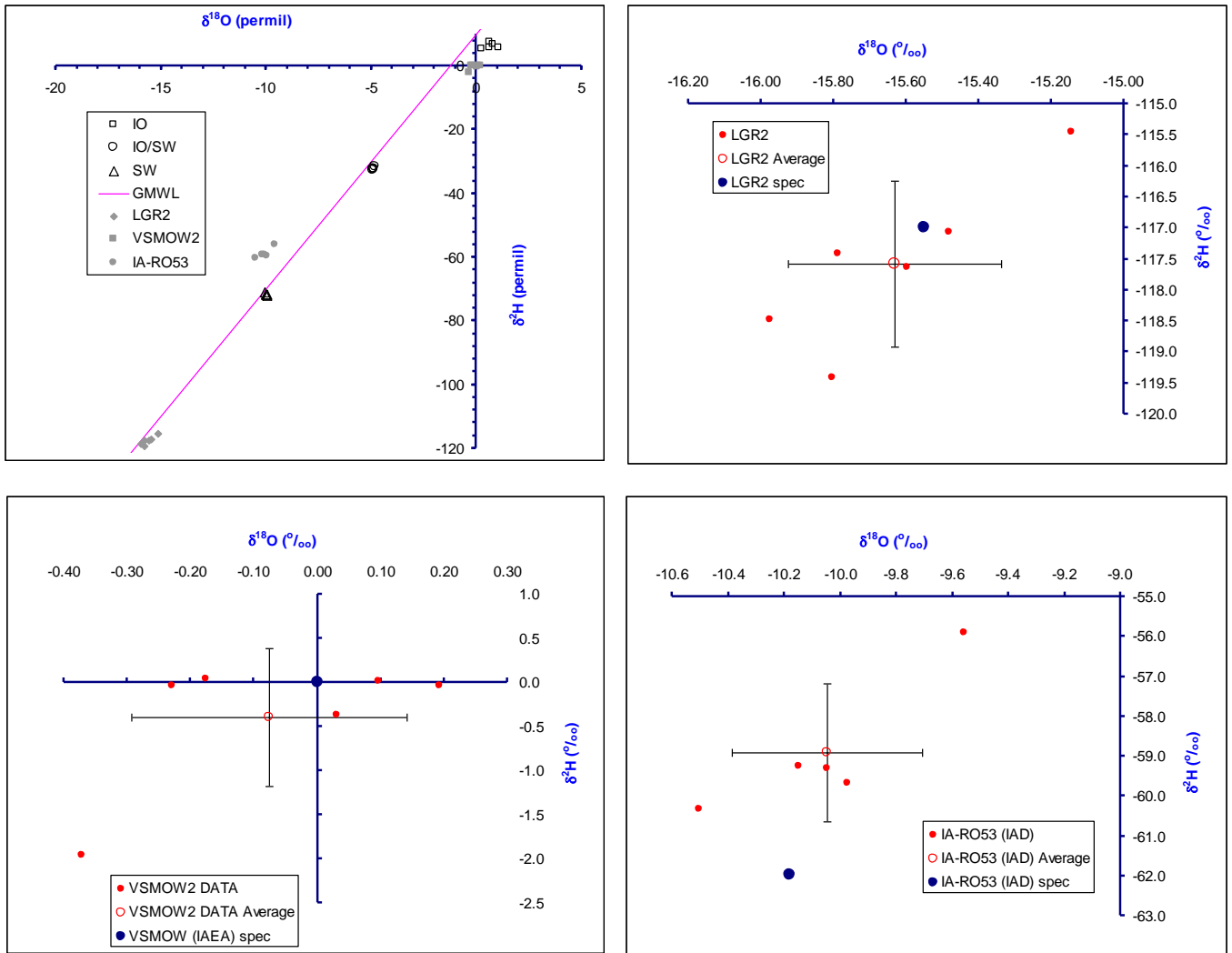
Figure C 4: Calibration of SBEEH standards (top left) against known standards

Table C 7: Chloroalkaline indices for water samples

Samples	CAI 1	CAI 2
Mine shaft	-4.01	-0.31
JBH1	-0.72	-0.07
17 Wstr	0.57	0.07
11 Fstr	0.06	0.01
Pstr	0.46	0.13
Itumeleng	0.28	0.04
Cv	0.47	0.15
6 Wstr	0.12	0.01
35 Hstr	0.28	0.03
NG Kerk	-2.42	-0.28
9 Ostr	-0.13	-0.02
11 Ostr	-0.43	-0.03
20 Ostr	-0.72	-0.04
6 Rstr	-0.69	-0.12
TPB 1	-1.49	-0.07
TPB 2	-3.68	-0.08
10 Vstr	0.25	0.04

Table C 8: Historical Chemistry Data

SiteName	Ycoord	Xcoord	DateTimeMeas	pH	EC mS/m	Ca mg/L	Mg mg/L	Na mg/L	K mg/L	MAlk mg/L	F mg/L
JRaw (BW)	-29.767807	25.419410	2011/03/23 00:00	8.4	102.00	27.84	13.53	200.27	6.19	189.00	1.49
JRaw (BW)	-29.767807	25.419410	2011/04/20 00:00	8.3	97.30	25.41	11.32	190.58	5.94	165.00	1.44
JCALTEX (BW)	-29.760995	25.423400	2011/02/01 00:00	8.0	85.10	22.23	9.58	156.01	6.73	166.00	1.62
JCALTEX (BW)	-29.760995	25.423400	2011/03/23 00:00	8.4	103.00	31.92	14.38	201.58	6.35	189.00	1.47

Table continues

SiteName	Ycoord	Xcoord	DateTimeMeas	Cl mg/L	NO3-N mg/L	PO4 mg/L	SO4 mg/L	Fe mg/L	Al mg/L	As mg/L	Si mg/L
Itumeleng Library (BW)	-29.774768	25.445312	2011/02/01 00:00	43.02	0.07	-0.10	228.00	0.19	0.16	0.09	-1.00
JFinal (BW)	-29.760627	25.425736	2010/11/19 00:00	51.00	-0.05	-0.10	248.00	0.01	0.02	-1.00	-1.00
JFinal (BW)	-29.760627	25.425736	2011/04/20 00:00	41.19	-0.05	-0.10	336.26	0.01	-1.00	-1.00	-1.00
JRaw (BW)	-29.767807	25.419410	2010/11/19 00:00	50.00	-0.05	-0.10	255.00	0.01	0.01	-1.00	-1.00
JRaw (BW)	-29.767807	25.419410	2011/02/01 00:00	43.00	-0.05	-0.10	239.00	0.27	0.21	0.10	-1.00
JRaw (BW)	-29.767807	25.419410	2011/03/23 00:00	42.84	0.11	-0.10	264.00	0.05	-1.00	-1.00	-1.00
JRaw (BW)	-29.767807	25.419410	2011/04/20 00:00	40.93	0.05	-0.10	335.02	0.05	-1.00	-1.00	-1.00
JCALTEX (BW)	-29.760995	25.423400	2011/02/01 00:00	43.26	0.14	-0.10	236.00	0.17	0.19	0.09	-1.00
JCALTEX (BW)	-29.760995	25.423400	2011/03/23 00:00	45.09	0.14	0.10	266.00	0.05	-1.00	-1.00	-1.00

Table C 9: Data for October Sampling

SiteName	DateTimeMeas	pH	EC mS/m	Ca mg/L	Mg mg/L	Na mg/L	K mg/L	PAlk mg/L	MAlk mg/L	F mg/L	Cl mg/L
Mine Shaft	2011/10/20 12:00	7.56	106	24.7	10.6	177.2	6.1	3.08	197	0.93	36.6
JBH 1	2011/10/20 12:00	8.21	124	110.3	40.5	93.7	1.5	0.00	365	-0.10	55.5
17 Wstr	2011/10/20 12:00	7.19	194	194.9	135.1	49.4	1.8	0.00	410	0.10	118.2
11 Fstr	2011/10/20 12:00	7.05	247	226.8	115.7	159.7	3.2	0.00	453	0.16	173.2
Pstr	2011/10/20 12:00	7.31	239	182.9	127.7	148.0	2.1	0.00	430	0.09	277.8
Itumeleng	2011/10/20 12:00	7.20	196	158.3	119.0	93.2	2.3	0.00	426	-0.10	132.3
Cv	2011/10/20 12:00	8.32	265	106.7	199.9	175.2	7.9	0.00	404	-0.10	348.0
6 Wstr	2011/10/26 12:00	7.18	176	169.4	108.6	84.7	3.013	0.00	386	-0.1	99.39
35 hstr	2011/10/26 12:00	7.23	176	193.1	116.7	66.8	1.736	0.00	427	-0.1	95.26
NG Kerk	2011/10/26 12:00	8.30	99.9	21.7	10.8	171.8	6.136	0.00	182	1.519	52.11
9 Ostr	2011/10/26 12:00	7.30	173	148.5	98.9	120.9	1.891	0.00	408	-0.1	108.97
11 Ostr	2011/10/26 12:00	7.05	146	138.9	84.2	89.9	1.532	0.00	464	-0.1	63.96
20 Ostr	2011/10/26 12:00	7.41	75.9	67.5	39.5	36.5	1.155	0.00	302	0.1981	21.92
6 Rstr	2011/10/26 12:00	7.73	87.1	58.9	17.4	110.7	1.010	0.00	218	0.1727	66.05
TPB 1	2011/10/26 12:00	7.23	62.9	59.6	31.7	36.6	1.610	0.00	295	0.2532	15.38
TPB 2	2011/10/26 12:00	7.49	46	36.3	23.9	25.4	1.410	0.00	245	0.2118	5.73
10 Vstr	2011/10/26 12:00	7.56	137	142.8	61.3	67.8	1.511	0.00	346	-0.1	92.46

Table continues

SiteName	DateTimeMeas	NO2-N mg/L	Br mg/L	NO3-N mg/L	PO4 mg/L	SO4 mg/L	As mg/L	Si mg/L
Mine Shaft	2011/10/20 12:00	-0.10	-0.4	-0.50	-1	272	0.153	10.800
JBH 1	2011/10/20 12:00	-0.10	-0.4	2.99	-1	241	0.015	14.200
17 Wstr	2011/10/20 12:00	-0.10	-0.4	12.87	-1.0	530	0.006	24.10
11 Fstr	2011/10/20 12:00	-0.10	-0.4	9.86	-1.0	709	0.006	26.20
Pstr	2011/10/20 12:00	-0.10	-0.4	3.84	-1	533	0.006	14.700
Itumeleng	2011/10/20 12:00	-0.10	-0.4	34.26	-1	411	0.006	21.8
Cv	2011/10/20 12:00	-0.10	-0.4	1.46	1.6	675	0.006	5.70
6 Wstr	2011/10/26 12:00	-0.1	0.95	10.65	-1	556	0.006	26.1
35 hstr	2011/10/26 12:00	-0.1	-0.40	3.19	-1	565	0.006	23.4
NG Kerk	2011/10/26 12:00	-0.01	-0.04	-0.05	-0.1	271	0.058	10.7
9 Ostr	2011/10/26 12:00	-0.1	-0.40	4.60	-1	493	0.006	21.8
11 Ostr	2011/10/26 12:00	-0.1	-0.40	0.54	-1	338	0.006	22.1
20 Ostr	2011/10/26 12:00	-0.01	0.11	0.86	-0.1	113	0.006	16.6
6 Rstr	2011/10/26 12:00	-0.01	0.23	2.20	-0.1	161	0.006	7.7
TPB 1	2011/10/26 12:00	-0.01	0.09	2.29	-0.1	41	0.006	15.2
TPB 2	2011/10/26 12:00	-0.01	0.06	0.21	-0.1	14	0.006	19.7
10 Vstr	2011/10/26 12:00	-0.1	-0.4	5.89	-1	307	0.006	14.0

Table C 10: Data for April sampling

SiteName	DateTimeMeas	pH	EC mS/m	Ca mg/l	Mg mg/l	Na mg/l	K mg/l	PALK mg/l	MALK mg/l	F mg/l	Cl mg/l	NO2(N) mg/l	Br mg/l	NO3(N) mg/l
Cv	2012/04/17 12:00	8.81	123	54.12	95.62	91.28	6.06	6.46	199	0.21	128.3	-0.1	-0.4	5.8
11 Fstr	2012/04/18 12:00	7.35	161	151.07	79.76	121.96	2.38	0	354	-0.10	107.0	-0.1	-0.4	12.4
35 Hstr	2012/04/19 12:00	7.52	165	187.05	115.56	62.34	1.38	0	463	0.10	104.3	-0.1	-0.4	3.1
J BH1	2012/04/20 12:00	7.92	93.7	77.78	28.72	93.19	1.32	0	298	0.15	48.0	0.0	0.2	2.9
Mineshaft	2012/04/21 12:00	8.66	95.3	22.62	9.77	173.70	5.86	5.56	201	1.57	41.5	0.0	0.2	0.0
Mw	2012/04/22 12:00	8.22	96.2	22.34	9.73	171.91	5.83	1.58	194	1.64	49.2	0.0	0.0	0.0
20 Ostr	2012/04/23 12:00	7.43	77.9	79.07	44.75	36.23	0.87	0	314	0.22	22.3	0.0	0.2	0.8
PStr	2012/04/24 12:00	7.35	287	267.39	183.07	169.27	2.36	0	414	0.10	413.3	-0.1	0.9	13.0
6 Rstr	2012/04/25 12:00	7.73	82.0	54.76	14.31	101.22	1.12	0	206	0.16	63.3	0.0	0.3	1.1
TPB1	2012/04/26 12:00	7.39	57.9	49.95	21.66	49.92	0.99	0	276	0.29	14.6	0.0	0.1	1.3
TPB2	2012/04/27 12:00	7.39	53.5	49.97	31.89	25.49	1.13	0	281	0.18	7.9	0.0	0.0	0.2
Itumeleng	2012/04/28 12:00	7.25	198	178.86	134.68	99.14	1.96	0	420	-0.10	158.8	-0.1	-0.4	41.2
10 Vstr	2012/04/29 12:00	7.40	119	135.86	58.53	60.24	1.33	0	355	-0.10	77.6	-0.1	-0.4	5.0
17 Wstr	2012/04/30 12:00	7.12	186	206.49	142.17	55.44	1.67	0	261	0.16	109.1	-0.1	-0.4	8.4

Table continues

SiteName	DateTimeMeas	PO4 mg/l	SO4 mg/l	Al mg/l	As mg/l	Ba mg/l	Cu mg/l	Fe mg/l	Mn mg/l	Mo mg/l	Zn mg/l	Si mg/l
Cv	2012/04/17 12:00	1.0	322.1	0.009	0.006	0.029	0.010	0.016	0.014	0.024	0.012	2.077
11 Fstr	2012/04/18 12:00	-1.0	432.2	0.004	0.006	0.006	0.007	0.010	0.007	0.013	0.014	27.914
35 Hstr	2012/04/19 12:00	-1.0	474.2	0.004	0.006	0.005	0.006	0.013	0.024	0.000	0.142	20.332
J BH1	2012/04/20 12:00	-0.1	168.7	0.004	0.006	0.010	0.008	0.025	0.011	0.014	0.040	12.389
Mineshaft	2012/04/21 12:00	-0.1	248.0	0.008	0.087	0.010	0.009	0.013	0.018	0.137	0.015	11.269
Mw	2012/04/22 12:00	-0.1	249.0	0.012	0.070	0.012	0.011	0.034	0.013	0.159	0.033	11.226
20 Ostr	2012/04/23 12:00	-0.1	117.7	0.004	0.006	0.015	0.007	0.013	0.010	0.004	0.033	16.766
PStr	2012/04/24 12:00	-1.0	798.0	0.004	0.006	0.019	0.012	0.027	0.249	0.020	3.552	12.078
6 Rstr	2012/04/25 12:00	-0.1	152.0	0.004	0.006	0.012	0.013	0.013	0.013	0.010	0.044	7.609
TPB1	2012/04/26 12:00	-0.1	33.0	0.004	0.006	0.005	0.047	0.011	0.023	0.006	0.194	13.591
TPB2	2012/04/27 12:00	-0.1	24.7	0.006	0.006	0.004	0.010	0.014	0.012	0.002	0.018	20.019
Itumeleng	2012/04/28 12:00	-1.0	447.0	0.004	0.006	0.019	0.010	0.011	0.011	0.021	0.015	22.545
10 Vstr	2012/04/29 12:00	-1.0	244.8	0.004	0.006	0.005	0.007	0.009	0.010	0.005	0.011	14.503
17 Wstr	2012/04/30 12:00	-1.0	653.0	0.004	0.006	0.006	0.009	0.011	0.009	0.026	0.031	25.504

Table C 11: Data for November samples

Site name	pH	EC	Ca	Mg	Na	K	PAlk	MAlk	F	Cl	NO2(N)	Br	NO3(N)	PO4
CW	8.15	70.9	30.67	17.06	91.26	5.83	0	183	0.76	41.4	<0.01	0.1589	0.0847	<0.1
MW	7.62	73.3	30.24	16.31	95.15	6.07	0	181	0.83	41.7	<0.01	0.1171	0.0811	<0.1
RM	8.25	110.7	31.43	14.26	180.36	6.66	0	208	1.30	44.5	<0.1	0.2749	<0.5	<1
RD	8.46	47.8	30.56	17.39	37.58	5.27	0	172	0.30	34.3	<0.01	0.2272	0.0352	<0.1
TD	8.22	48.6	31.54	17.82	37.69	5.24	0	172	0.28	35.6	<0.01	0.2143	0.1226	<0.1
TM	8.19	113.0	29.38	14.47	186.84	6.67	0	197	1.62	50.1	<0.1	<0.4	<0.5	<1

Table continues

Site name	SO4	Si	CA Hard.	Mg Hard.	Tot. Hard.	TDS (sum)	Al	As	Cr	Cu	Fe	Mn	Mo	Pb	Zn
CW	121	4.33	77	70	147	491	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	0.070	<0.010	<0.010
MW	129	4.71	76	67	142	501	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	0.080	<0.010	<0.010
RM	293	11.3	79	58	137	777	<0.010	0.100	<0.010	0.020	<0.010	<0.010	0.190	<0.010	<0.010
RD	31	0.25	76	71	148	329	<0.010	<0.010	<0.010	0.010	<0.010	<0.010	<0.02	<0.010	<0.010
TD	31	0.21	79	73	152	331	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.02	<0.010	<0.010
TM	291	10.9	73	59	133	773	<0.010	0.020	<0.010	<0.010	<0.010	<0.010	0.190	<0.010	<0.010
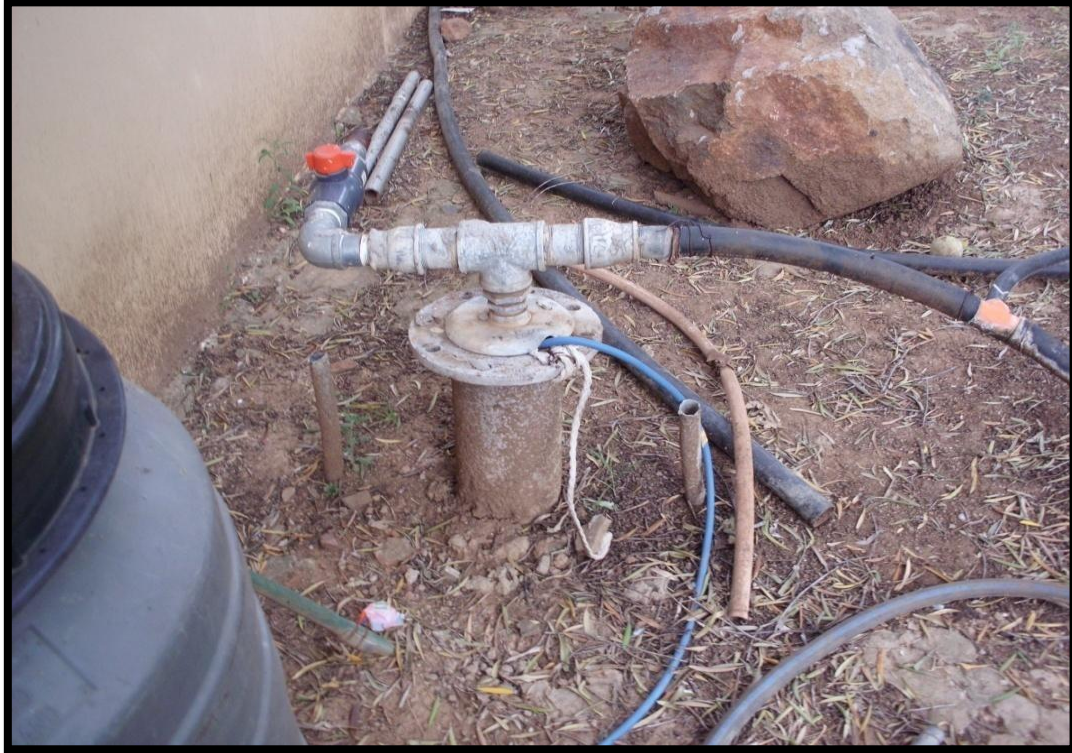
Figure C 5: 10 Voortrekker Borehole

Figure C 6: Mineshaft

Figure C 7: TPB1 borehole

Figure C 8: Itumeleng

Figure C 9: Charlesville

Figure C 10: TPB2

Figure C 11: Palmerston borehole

Figure C 12: Jagersfontein Borehole 1

Appendix D

Other cross plots

Figure D 1: As versus Mg, Ca, Na, K, Si and Cl

A Geohydrological Assessment of Arsenic as a Contaminant in the Jagersfontein area and
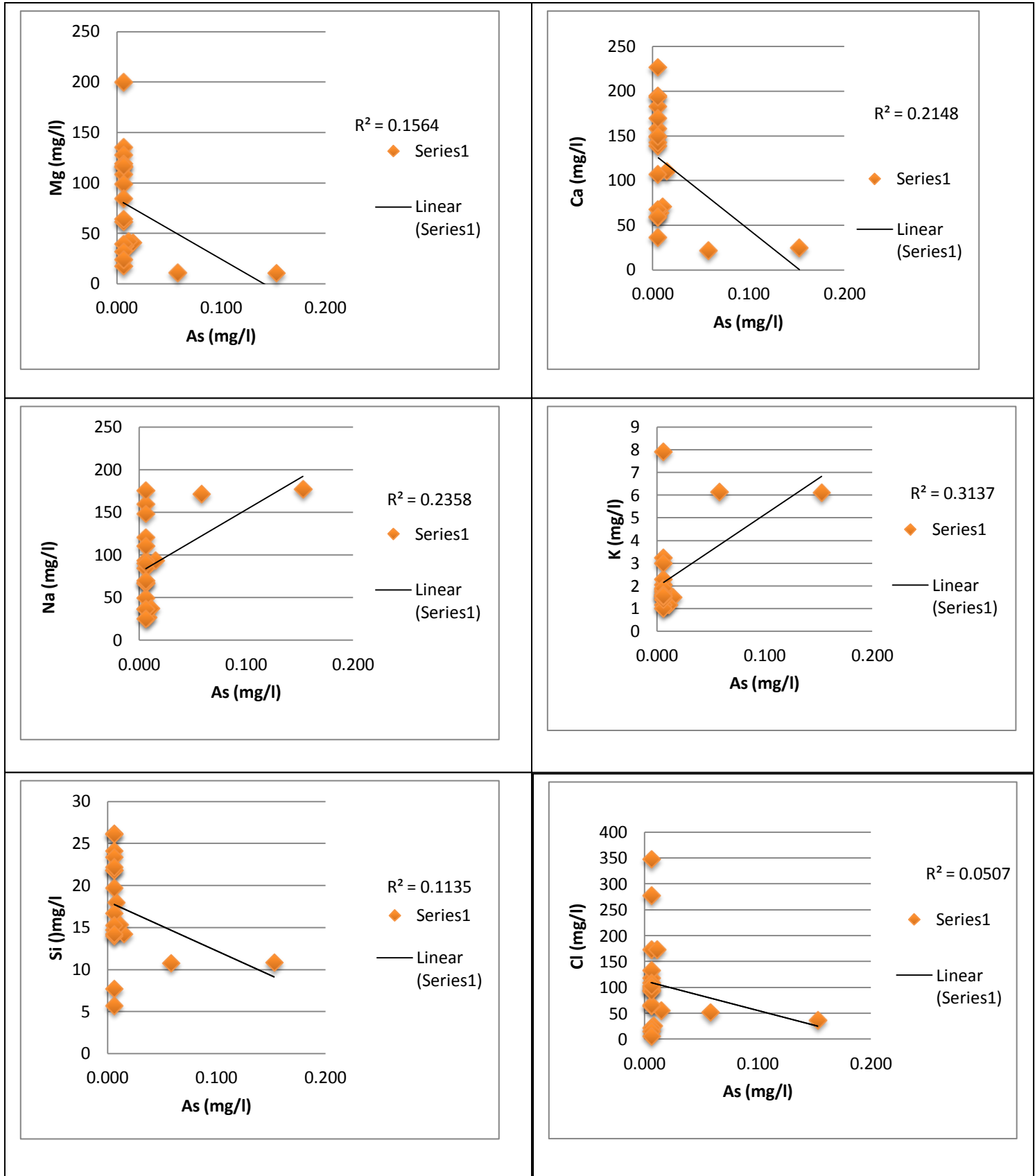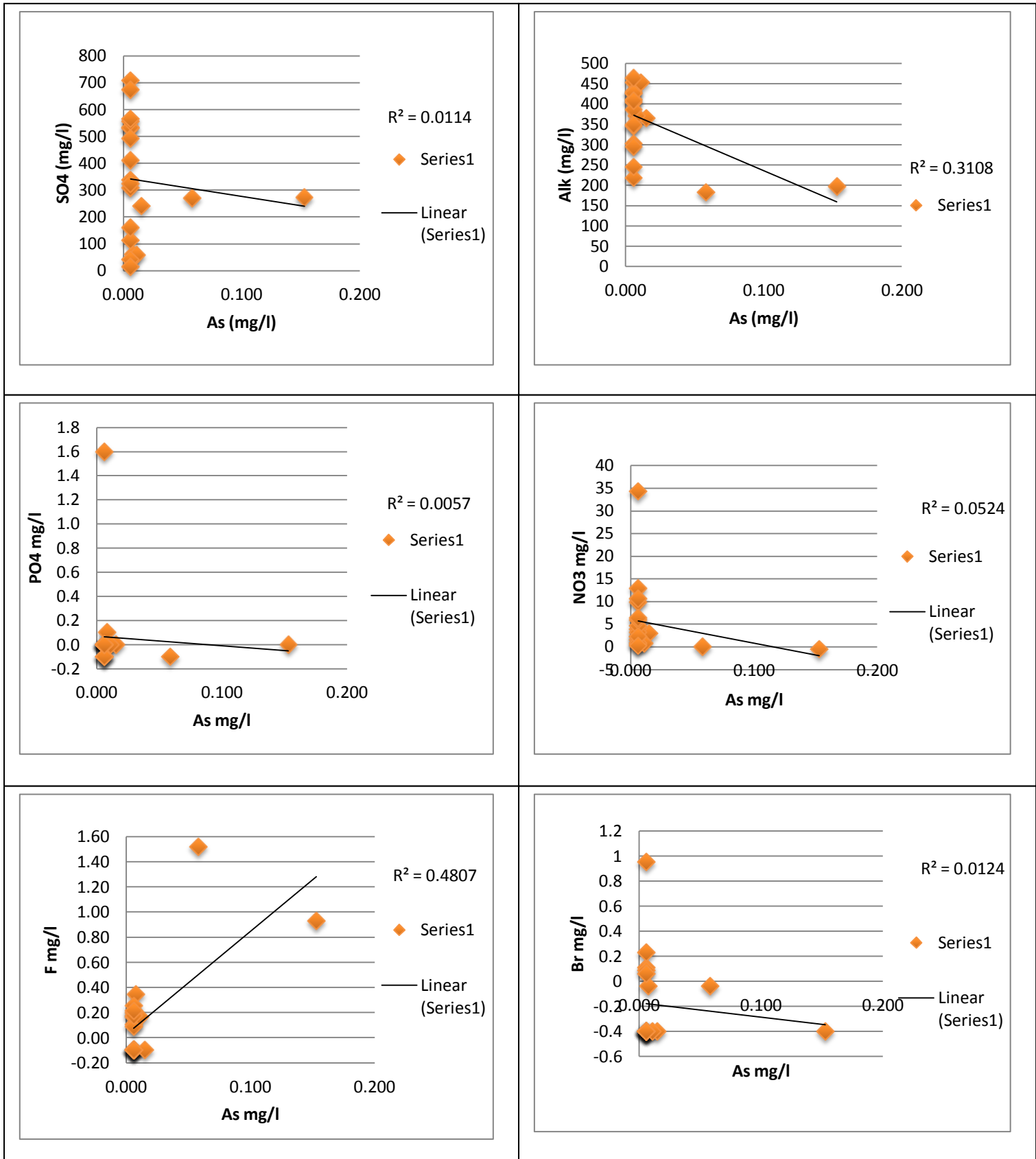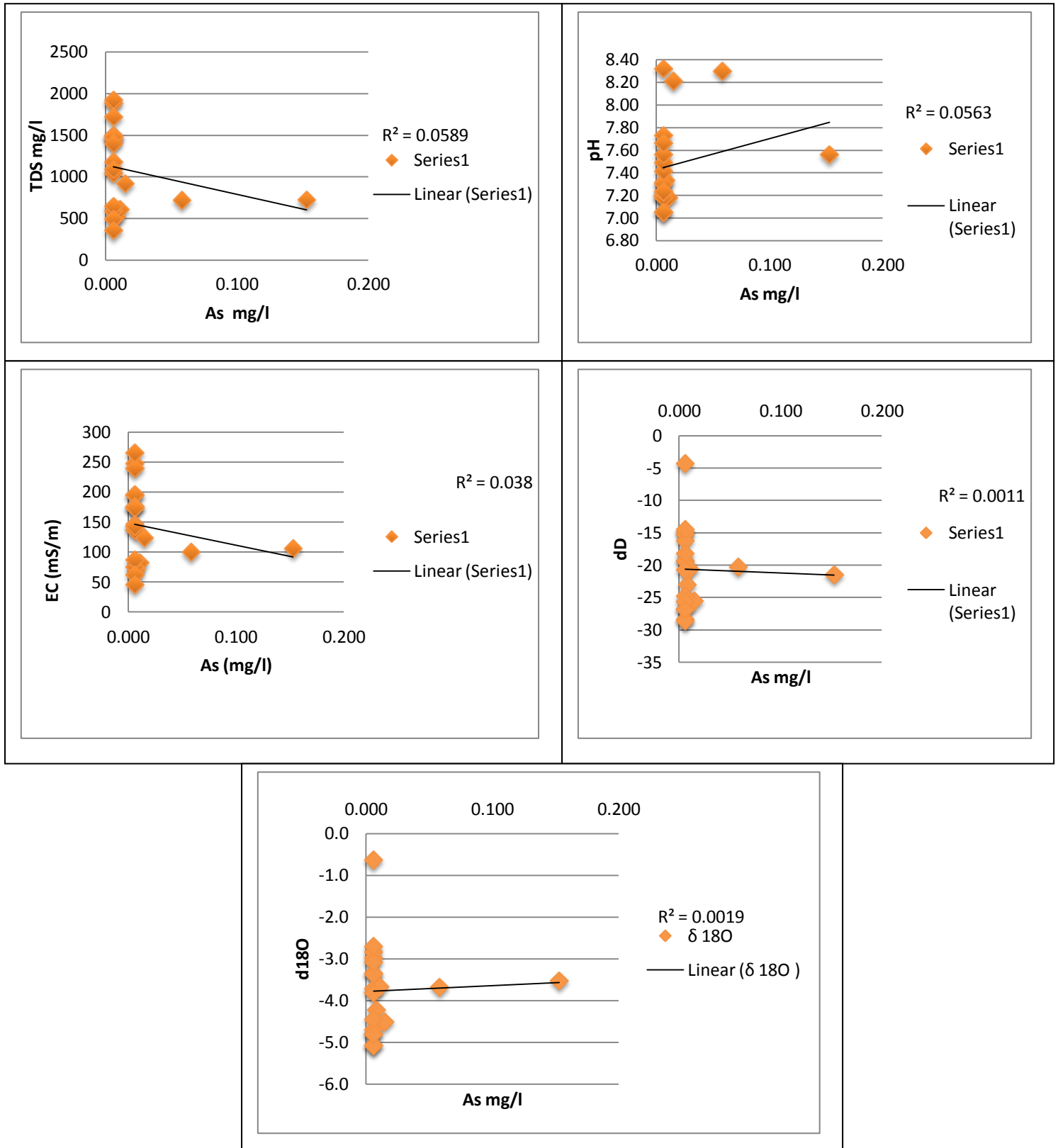remediation options

Figure D 2: As versus SO4, Alk, PO4, NO3, F and Br

Figure D 3: As versus TDS, pH, EC, dD, d18O
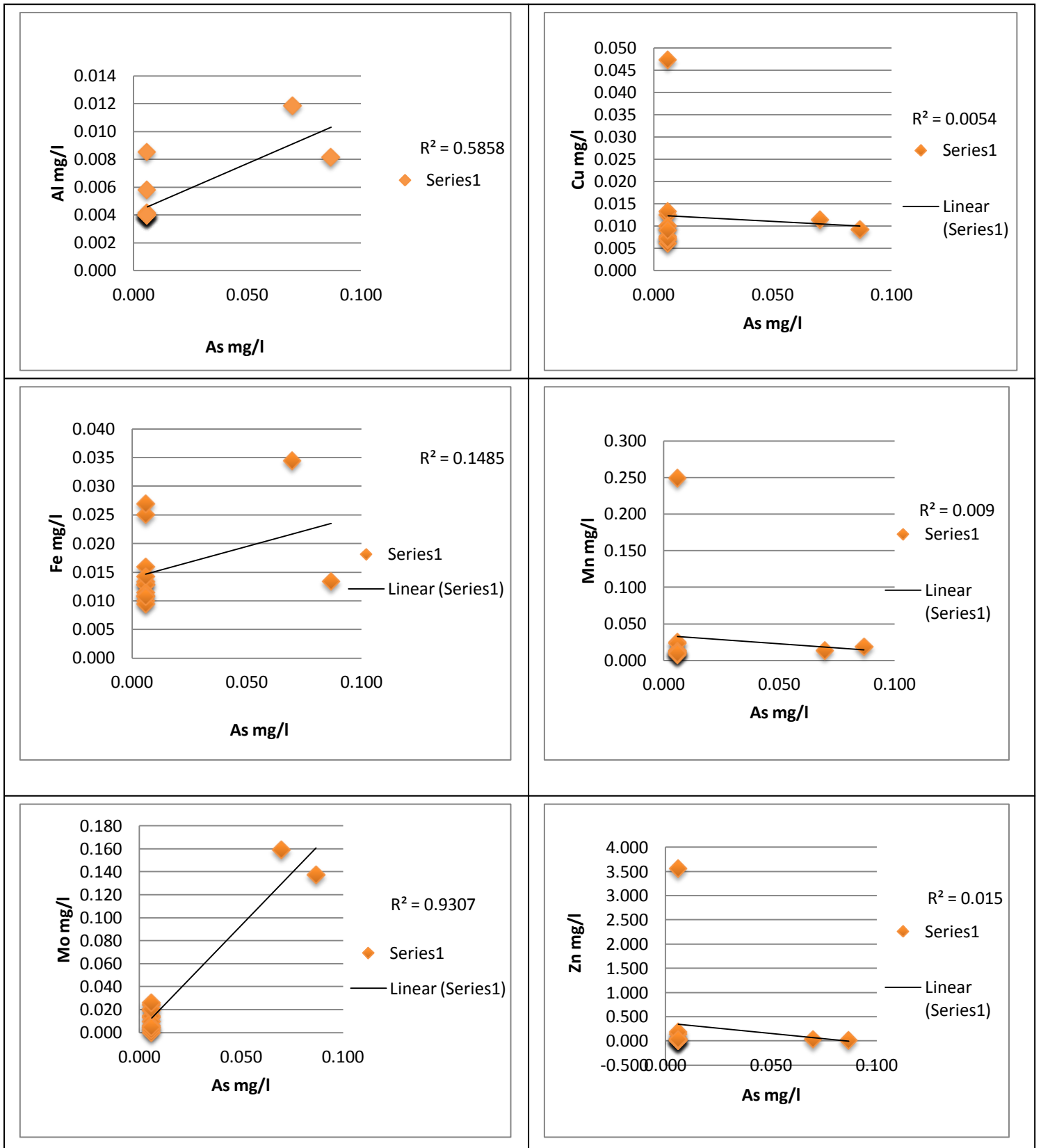
Figure D 4: As versus Al, Cu, Fe, Mn, Mo and Zn

Table D 1: As(III) and As(IV) species mineshaft sample

As specie	Concentration
As(3)	2.54E-38
HAsO2	1.19E-38
As(OH)3	1.04E-38
H2AsO3-	1.60E-39
AsO2-	1.53E-39
AsO2OH-2	0.00E+00
As(5)	5.53E-06
AsO3F-2	5.52E-06
HAsO3F-	1.29E-08
HAsO4-2	1.45E-25
H2AsO4-	2.74E-27
AsO4-3	1.49E-28
H3AsO4	1.92E-33

Table D 2: As(III) and As(IV) species Jagersfontein borehole 1 sample

As specie	Concentration
As(3)	1.19E-16
H3AsO3	1.17E-16
H2AsO3-	2.49E-18
H4AsO3+	2.51E-24
HAsO3-2	1.93E-25
AsO3-3	1.93E-33
As(5)	2.00E-07
HAsO4-2	1.46E-07
H2AsO4-	5.44E-08
AsO4-3	1.65E-11
H3AsO4	3.61E-13
H3AsO4	3.61E-13

Table D 3: As(III) and As(IV) species NG Kerk sample

As specie	Concentration
As(3)	3.68E-18
H3AsO3	3.42E-18
H2AsO3-	2.60E-19
HAsO3-2	7.00E-26
H4AsO3+	2.00E-26
AsO3-3	2.37E-33
As(5)	7.75E-07
HAsO4-2	6.99E-07
H2AsO4-	7.50E-08
AsO4-3	2.65E-10
H3AsO4	1.39E-13

Table D 4: As(III) and As(IV) species 20 Ostr sample

As species	Concentration
As(3)	5.55E-17
H3AsO3	5.44E-17
H2AsO3-	1.11E-18
H4AsO3+	1.17E-24
HAsO3-2	7.87E-26
AsO3-3	6.96E-34
As(5)	8.01E-08
HAsO4-2	5.70E-08
H2AsO4-	2.31E-08
AsO4-3	5.66E-12
H3AsO4	1.61E-13

Table D 5: As(III) and As(IV) species 6 Rstr sample

As species	Concentration
As(3)	1.45E-15
H3AsO3	1.44E-15
H2AsO3-	1.20E-17
H4AsO3+	8.40E-23
HAsO3-2	3.86E-25
AsO3-3	1.70E-33
As(5)	8.02E-08
HAsO4-2	4.23E-08
H2AsO4-	3.79E-08
AsO4-3	2.10E-12
H3AsO4	6.41E-13

Abstract

This thesis aims at geohydrologically assess arsenic in the Jagersfontein area and hence proposing remediation option.

The field procedure carried out involved hydrocensus and sampling where samples were collected and analysed for micro and macro parameters with emphasis on arsenic. Isotopic (^{18}O, D (deuterium) and Tritium ^{3}H) analysis was also carried out to characterise the water in terms of its origin, fate and age. A total of 20 boreholes were sampled. Historical data from Bloemwater was also incorporated in the study.

According to the chemical analysis, the most abundant cation is magnesium followed by calcium, and the most abundant anion is sulphate. Three different water types were classified; sodium/potassium sulphate, magnesium sulphate and calcium/magnesium bicarbonate. Hence they are from different sources. Sample collected from the mineshaft showed highest arsenic concentration which is higher than the South African National Standards (SANS 241, 2006) guideline for acceptable arsenic concentration in drinking water while all other individual boreholes in the main town of Jagersfontein showed low arsenic concentration (<0.006 mg/l); hence concluding that arsenic contamination comes from the mine. Mine water that has been treated in package plant (JFinal) still shows high arsenic concentration. Water from Kalkfontein dam is being treated in a bigger treatment plant (went operational in July 2012) and mixed with treated mine water. This reduces the arsenic concentration of water to an acceptable level before it is finally supplied to the community. Spearman's correlation coefficient calculated show a weak correlation between arsenic and other chemical parameters and so it is concluded that arsenic and these elements are not of same source implying the source of arsenic is not geogenic. Isotopic analysis shows the water samples plot very close to the global meteoric water line (GMWL) implying the groundwater is meteoric and is derived from the atmosphere. Clustering of the samples around the GMWL hints they might be of the same age. However one sample (surface water sample) plotted away from GMWL and it is attributed to effects of evaporation. The

hardness of the water samples is generally high. To solve this problem, individual owners of boreholes add water softeners (chlorine, crystals) to soften the water.

There are several techniques available for removal of arsenic from water in large conventional treatment plants. The basic principles of these technologies are based on physical-chemical processes such as oxidation, coprecipitation and adsorption on coagulated flocs, adsorption onto sorptive media, ion exchange, and membrane filtration. Most treatment options need the oxidation of As(III) to As(V) for efficient removal of arsenic.

For the case of Jagersfontein, coagulation and filtration technology ($FeCl_3$ as coagulant) will be the best option because it is very efficient in removing arsenic (V) which happens to be the dominant specie in the water. It is the cheapest technique compared to the others and it is also less sophisticated. However what is currently done in Jagersfontein to reduce the concentration of arsenic in water is dilution/mixing. Mine water treated in a package is mixed with treated water from Kalkfontein dam. Water (not arsenic contaminated) from Kalkfontein dam is treated in a bigger treatment plant which went operational in July 2012.

Key words; Arsenic, groundwater, assessment, remediation

Opsomming

Die doel van hierdie tesis is om arseen in die Jagersfontein-gebied te assesseer om sodoende remediërende oplossings te vind.

Die veldprosedures wat uitgevoer was, is hidrosensus en monsters wat geneem is vir analisering. Monsters is ontleed vir mikro- en makro-parameters met die klem op arseen. Isotoop- (^{18}O, D (deuterium) en Tritium ^{3}H) analise is ook uitgevoer om die water te karakteriseer in terme van oorsprong, toekoms en ouderdom. 'n Totaal van 20 boorgate is geëvalueer. Historiese data van Bloemwater is ook ingesluit in die studie.

Volgens die chemiese analise is magnesium die volopste katioon gevolg deur kalsium, en sulfaat is die volopste anioon. Drie verskillende watertipes is geklassifiseer, naamlik natrium-/kaliumsulfaat, magnesiumsulfaat en kalsium-/magnesium bikarbonaat. Die watertipes het dus verskillende oorspronge. Monsters wat uit die mynskag geneem is, het die hoogste arseenkonsentrasies getoon. Die konsentrasies is hoër as die riglyne van die Suid-Afrikaanse Nasionale Standaarde (SANS 241, 2006) vir aanvaarbare arseenkonsentrasie in drinkwater, terwyl al die ander individuele boorgate in Jagersfontein lae arseenkonsentrasie (<0,006 mg/l) getoon het. Daar is dus tot die slotsom gekom dat arseenbesmetting nie van die myn afkomstig is nie. Mynwater wat in die pakket-plant (JFinaal) behandel is, toon steeds hoë arseenkonsentrasies. Water van die Kalkfonteindam word behandel in 'n groter behandelingsplant (wat vanaf Julie 2012 in werking is) en word dan gemeng met behandelde mynwater. Dit verminder die arseenkonsentrasie in die water tot 'n aanvaarbare vlak voordat dit finaal aan die gemeenskap verskaf word. Spearman se korrelasiekoëffisiënt toon 'n swak korrelasie tussen arseen en ander chemiese parameters en vandaar is tot die gevolgtrekking gekom dat arseen en hierdie elemente nie van dieselfde bron is nie. Dit impliseer ook dat die bron van arseen nie geogenies is nie. Isotoopanalise toon dat die watermonsters baie naby aan die globale meteoriese waterlyn (GMWL) plot, wat impliseer dat die grondwater meteories is en 'n atmosferiese afkoms het. Groepering van die monsters om die GMWL toon dat hulle miskien dieselfde ouderdom kan hê. Daar is wel een monster

(oppervlakwatermonster) wat weg plot van GMWL en dit word toegeskryf aan die effek van verdamping. Die hardheid van die watermonsters is oor die algemeen hoog. Om hierdie probleem op te los, voeg individuele eienaars van boorgate, waterversagters (chloor, kristalle) by om die water te versag.

Daar is verskeie tegnieke beskikbaar vir die verwydering van arseen in water by groot konvensionele behandelingsplante. Die basiese beginsels van hierdie tegnologie is gebaseer op die fisies-chemiese prosesse soos oksidasie, ko-presipitasie en adsorpsie op gekoaguleerde vlokkies, adsorpsie op absorbeerbare media, ioonuitruiling en membraanfiltrasie. Vir die doeltreffendste verwydering van arseen word oksidasie van As (III) na As (V) gebruik.

In die geval van Jagersfontein, sal koagulasie en filtertegnologie ($FeCl_3$ as stollingsmiddel) die beste opsies wees, want dit is baie effektief in die verwydering van arseen (V), wat in dié geval die dominante spesie in die water is. Dit is die goedkoopste tegniek in vergelyking met die ander en dit is ook minder gesofistikeerd. Wat tans in Jagersfontein gedoen word om die konsentrasie van arseen in water te verminder, is verdunning/menging met ander water. Mynwater wat behandel is in 'n pakket word gemeng met behandelde water uit die Kalkfonteindam. Water (nie arseenbesmette) van die Kalkfonteindam word in 'n groter behandelingsplant behandel wat in Julie 2012 in werking getree het.

Sleutelwoorde; Arseen, grondwater, assessering, remediëring