Influence of mining on groundwater quality in the Johannesburg area, South Africa: an integrated approach

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Abstract:

An integrated approach has been used in order to explore the impact of mining activity on the groundwater quality which is highly needed by communities for diverse economic activities. The study area is underlain by Precambrian crystalline rocks of granitic gneisses and the Witwatersrand Supergroup rocks as well as dolomites and shales of the Transvaal Supergroup (Meta sedimentary rocks). These are covered by Karoo sediments and intruded by Bushveld igneous complex. The groundwater-surface water interaction is dynamic in nature within the carbonate rocks (dolomites) that are characterized by wide spread karst structures due to rebounding of regional water table and consequent acid mine decant. The nature of water quality has been thoroughly assessed based on the results from hydrogeochemical characteristics and environmental isotopes. The results show that the SO_4/Cl ratio has a wide range of values that falls between 0 and 306.37, while Fe/Ca ratio falls between 0 and 5.59. High SO_4/Cl values potentially indicate the interference of acid mine decant with the groundwater system as a result of sulphate concentration from acid mine water. Similarly, high Fe/Ca ratio also indicates the impact of acid mine decant on the groundwater system where iron is derived from acid mine water. In this regard the ratios above 0.25 (with the assumption of 1 to 4 natural abundance for Fe:Ca in water) could potentially represent the mixing of acid mine water with potable groundwater. Hierarchical Cluster Analysis revealed the presence of four distinct hydrogeochemical clusters that are related to different aquifers where pristine groundwater still occurs within the dolomites that contain old (low ^3H) groundwater with depleted $\delta^{18}O$ and δ^2H indicating high altitude recharge with deep groundwater circulation.

Key words: Crystalline aquifer, Environmental isotopes, Groundwater-surface water interaction, Johannesburg, Mining

Introduction

In the mining areas, mixing of highly mineralized and acidic water with fresh water could have tremendous impact on aquatic and groundwater dependent ecosystems. The Johannesburg area (Fig. 1) is characterized by the large-scale urbanization and industrial activity with substantial water demand by various sectors. The main water supply for the area is derived from Vaal Dam in the south. However, numerous rural communities rely on groundwater for domestic, small scale agricultural and large irrigation activities in the area. In the vast West Rand Gold fields of Johannesburg, acid mine decant first occurred in 2002 due to the closure of mines, while dewatering effluents and acid mine drainage was taking place for over a century which impacted both the quality of surrounding streams and of the dolomitic aquifer.

The Witwatersrand Basin hosts one of the world's largest gold and uranium mining districts where deep groundwater was pumped out at a rate of about 110 x 10^6 l/day until 2008 in some areas for more than a century to make underground mining possible (Ferret Report, 2005). Discharge of largely mineralized water pumped from underground mines into dams, reservoirs and streams has considerably increased recharge to the shallow aquifer (AGES, 2005). This activity is likely to have a direct impact on surface water quality by increasing its mineral content (salinity). There is also a considerable evidence confirming that the deep underground mine pumping has lowered the regional water table and led to drying out of springs while mining was active in the area (Ferret Report, 2005). After mine closures in 1980's in some part of the area, large number of springs start emerging due to a rise in the groundwater table.. The groundwater in the area has also maintained base flow to streams through out a year leading to the restoration of perennial flow.

(FIGURE 1)

The study area encompasses the Cradle of Human Kind World Heritage Site (CHKWHS) which hosts numerous hominid and other fossils located within caves in the Pretoria Group quartizites and Malmani dolomites. The CHKWHS is a prime receiver of acid mine decant derived from the gold mines in the West Rand area. Ground and airborne geophysical surveys have also identified subsurface acid mine discharge pathways in the area (Coetzee et al., 2009). In the closed mines, gradual recovery of regional water table through natural and cross basin recharge processes now generates a continuous discharge of acidic water loaded with heavy metals from the mine shafts (Witthüser and Holland 2008; Abiye et al., 2011).

With growing water supply demand in the area, the groundwater resource is assuming increasing importance and needs protection by the users and decision makers to ensure long term sustainability. Therefore, proper management intervention of the acid mine water could improve water availability in the area such as through treatment and re-use. Currently there is a buffering process to raise the pH and precipitate iron from acid mine decant, however, the stock of trace metals still mixes with the surrounding water resources besides the rising in the regional water table due to recovery. The continuous discharge of acidic water into the environment compromises the available fresh water resources both due to pollution load that threatens dolomitic groundwater and increase water levels in the karst structures. Thus, it is important to understand the extent of mining impact on the groundwater quality and the degree of groundwater-surface water interaction in order to properly manage the water resource which is also aggravated due to rebounding of regional water table. In the current investigation, hydrogeochemistry, environmental isotopes and discharge measurement data have been used to interpret the groundwater facies and quality. The results of this work could help groundwater users to plan for targeted exploitation of uncontaminated and less susceptible aquifers and subsequent protection and management of the aquifers. For hydrogeochemical interpretation, groundwater quality data were obtained from the National Department of Water Affairs (DWA) of South Africa database and have been interpreted using multivariate statistical method.

By virtue of its position within the subtropical belt of high pressure, South Africa is characterized by a semi arid to arid climate (D'Alberto and Tyson, 1996). Therefore, the Johannesburg area has a mean annual rainfall ranging from 600 to 700 mm/year (DWAF, 1992; Barnard, 2000). The estimated mean rainfall from 24 years of data (data obtained from South African Meteorological Service for central Johannesburg station) is 711.63mm, (Fig. 2). Most of rainfall occurs between October and March, mostly as a frontal type characterized by frequent thunderstorms, while winter months (June to August) are characterized by cold dry weather; these months are non productive from groundwater recharge perspective. According to D'Alberton and Tyson (1996), analysis of divergent water vapour transport reveals that transport to the South-West from tropical Indian Ocean is the most important source for water vapour in wet Januaries over South Africa.

The pan evaporation as reported by Hobbs (2011) for the West Rand area is in the rage of 2200 mm/yr.

(FIGURE 2)

Geological and Hydrogeological overview

The study area predominantly is underlain by crystalline basement rocks of granitic gneisses, the meta-sedimentary rocks of Witwatersrand Supergroup as wells as dolomites of the Transvaal Supergroup (Barton et al., 1999; Barnard, 2000; Anhaeusser, 2006) (Fig. 3). The general hydrogeological aspect of the area has been well described in the Johannesburg hydrogeological map and associated explanatory note (Barnard, 1999 and 2000).

The hydrogeology of the area is characterized by secondary aquifers especially within the weathered and fractured crystalline rocks (granitic gneiss and quartzite); karst aquifers in the dolomite and intergranular aquifers in alluvial deposits along river valleys and low land areas. In general, the complex hydrogeological setting of the area is as a result of crystalline nature of the metasedimentary and basement rocks, secondary structures and weathering processes.

Most of the fractured and weathered granitic rocks that outcrop in the study area have generally low and variable groundwater productivity (borehole yield varies between 0.01 l/sec and 0.98 l/sec), while the yield in the dolomitic aquifers ranges from 15 l/sec to 124 l/sec as estimated from DWA groundwater database (Abiye et al., 2011, Abiye 2011). It has been reported that dolomites are well known productive aquifers in different parts of South Africa (Bredenkamp et al., 1986; Buttrick et al., 1993; Bredenkamp and Xu, 2003; Holland and Wittüser, 2009). These aquifers are intersected by impervious and semi-pervious syenite and dolerite dykes, which divide them into compartments (Coetzee et al., 2009; Holland and Wittüser, 2009; Abiye et al., 2011). Due to the soluble nature of dolomitic rocks they potentially provide good recharge sites which eventually generate high yielding springs that are associated with dykes and tectonic depressions. During the field survey it was observed that the presence of dykes within the meta-sedimentary rocks is marked by patches of springs and wetlands. High yield springs have also been observed in association with karst structures in the dolomites such as the Ngosi spring in the CHKWHS (Malapa area) with an approximate discharge rate of more than 100 l/s. Alluvial deposits which are found along the stream valleys yield as much as 16 l/sec (Barnard, 2000).

(FIGURE 3)

The extensive gold mining operation to a depth of few kilometres in the Witwatersrand Supergroup play paramount role in connecting different groundwater basins both at shallow and deep horizons as well as for inter-basin groundwater transfer. Evidence of hydrogeological connectivity within the study area is the presence of continuous decanting of acidic water from the Randfontein area into the CHKWHs, where a measured discharge of 1.19 m^3/s is recorded in front of Krugersdorp game reserve. It was observed that networks of dissolution cavities have developed along linear tectonic lines in the dolomitic areas where sinkholes frequently exist. In the Malapa area, for example, disappearance of springs through sinkholes is a common feature that are aligned along a linear fracture line.

The consequence of acid mine decant on dolomitic rocks has a far reaching impact through the expansion of dissolution cavities that may threaten valuable archaeological evidence of the origin and evolution of humanity besides water quality deterioration. The impact of the acid decant on the groundwater quality has already been clearly noted with high total iron (≈1200 mg/l) and SO_4 (≈5000 mg/l) (Abiye, 2011). The continuous discharge of acidic water through out a year indicates the presence of regional groundwater circulation that maintains the base flow and recharges springs. According to Hobbs and Cobbing (2007), the rate of acid mine decant in the area ranges between 18,000 m^3/day and 36,000 m^3/day.

Materials and Methods

A literature review and field surveys were carried out in order to conceptualize the geological setting and hydrogeology of the area which resulted the compilation of the geological map presented on Fig. 3. From the field surveys, it was noted that the groundwater of the area is under strong influence of mining activities. In order to ascertain the influence of century long mining on the water quality monitoring program was developed in order to quantify the loss and gain in the streams that contain AMD. During the field investigations, digital Crison and Orion instruments were used to capture pH, EC, TDS and ORP values of water. These measurements were undertaken at different seasons for over five years.

Fifty eight water samples were collected from July 2008 to April 2012 using a 1-litre HDPE bottles and immediately covered with black plastic to avoid direct sunlight and were stored in a cooler box at 4^0C before being submitted to the isotope laboratory (iThemba Labs, Gauteng) for analysis.

For the D/H ($^2H/^1H$) and $^{18}O/^{16}O$ the equipment used consists of a PDZ Europa GEO 20-20 gas mass–spectrometer connected to peripheral sample preparation devices. A PDZ water equilibration system (WES), working in dual inlet mode is employed for hydrogen and oxygen isotope analysis of water. Equilibration time for the water sample with hydrogen is about one hour and CO_2 is equilibrated with a water sample in about eight hours. Laboratory standards, calibrated against international reference materials, are analysed with each batch of samples. The analytical precision is estimated at 0.1‰ for O and 0.5‰ for H. which applies to D/H ($^{2}H/^{1}H$), accordingly.

$$\delta^{18}O(‰) = \left[\frac{(^{18}O/^{16}O)_{sample}}{(^{18}O/^{16}O)_{standard}} - 1 \right] \times 1000$$

These delta values are expressed as per mil deviation relative to a known standard, in this case standard mean ocean water (SMOW) for $\delta^{18}O$ and δD. The stable isotope analyses for all samples data could be well reproduced within the expected analytical error limits.

For 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. About 500 ml of the water sample, having first been distilled and containing sodium hydroxide, is introduced into the cell. A direct current of 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 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.

Environmental isotopes are widely used to gain an insight into the groundwater flow dynamics, mixing and recharge conditions using the relative deviation from the Global Meteoric Water Line (GMWL) and the Local Meteoric Water Line (LMWL). Locally, isotopes have been successfully used to study recharge condition in other sedimentary basins in South Africa (Sami, 1992; Adams et al., 2001) to characterize recharge mechanism and geochemical processes in semi-arid and arid environments.

Stream flow measurement along Riet stream (West Rand area) and its major tributaries (Blougat stream and Tweelopie stream) that are likely to contain acid mine decant from Randfontein gold mine areas, has been carried out using a Global Water flow meter on

25/08/2011 and on 25/02/2012. Most of the streams in the area traverse the CHKWHS and join the Crocodile River which flows towards Hartebeespoort dam.

Selected groundwater quality data from the National groundwater database of the Department of Water Affairs (DWA) have been used for hydrogeochemical interpretation using Hierarchical Cluster Analysis based on the Ward's Minimum Variance cluster method.

Results and discussion

The $\delta^{18}O$, $\delta^{2}H$ and ^{3}H data are presented in Table 1 for different sampling points including springs, rains, streams, dam and boreholes. Selected groundwater quality data for the area which were obtained from DWA have been presented in Table 2 (more inclusive results are available from DWA).

Stream discharge within the study area

Figure 4 presents the measured flow rate along the Riet stream and its tributaries as measured on 25/08/2011 and 25/02/2012. The main-stem of the Riet stream shows variable discharge. The increase between P3 and P4 is related to base flow contribution and the presence of additional small tributaries. The measured seepage of acid mine water into dolomites ranges from 0.78 m^3/s (24.5 Million m^3/yr) in winter to 1.764 m^3/s (55.6 million m^3/yr) in summer. P2 contains acid mine decant and drains the Krugersdorp Game Reserve and contributes to higher discharge values at P4 as a result of springs in the game reserve in combination of major upstream tributaries (P1 and P3).

(FIGURE 4)

Environmental isotopes within the study area

The last column in Table 1 contains the calculated *d-excess* which is defined as an excess deuterium in a global precipitation ($d=\delta^{2}H-8\delta^{18}O$) (Dansgaard, 1964). D-excess is basically a measure of the relative proportions of ^{18}O and ^{2}H contained in water, and can be visually depicted as an index of deviation from the global meteoric water line (d=10) in $\delta^{18}O$ versus $\delta^{2}H$ space.

Stable isotopes of oxygen and hydrogen have been plotted with reference to the Global Meteoric Water Line (GMWL) and the Local Meteoric Water Line (LMWL) of Pretoria established from the IAEA GNIP data that has a regression line of $\delta^2H = 6.7\delta^{18}O + 7.2$ (IAEA GIS Global Mapping for Isotopes) (Fig. 5).

(TABLE 1)

Clark and Fritz (1997) suggest that for local investigation, it is important to compare surface and ground water data with the LMWL. Most of the data plot below the Pretoria Local Meteoric Water Line (LMWL) which indicate infiltration that took place after evaporation. The stable isotope plot also portrays a mixing trend where the end members are deep circulating water in dolomites (depleted with $\delta^{18}O$ and δ^2H) and stream (relatively enriched) where shallow boreholes lie in between and could be a mixing product (Fig.5). The mean values for $\delta^{18}O$, δ^2H and ^3H for the rain samples in the area is -4.11(‰), -17.26(‰) and 5.32±0.4 T.U, respectively. The mean value calculated from three rain samples plots above the LMWL which, according to Clark and Fritz (1997), could be due to low humidity in the vapour.

(FIGURE 5)

In addition to the $\delta^{18}O$ and δ^2H plot (Fig. 5), the graph on Fig. 6 is also useful in identifying the source of acid mine decant from deep water horizon. In Fig. 6, at least three groups of water can be identified based on $\delta^{18}O$ and ^3H distribution. Group 1 (G1) represents both shallow and deep circulating groundwater in weathered aquifers and dolomites where the tritium value is lower than the current mean rain value in the area. G2 represents shallow groundwater or water in streams except for few samples with depleted $\delta^{18}O$ due to deep water mixing. G3 represents samples collected from the Hartebeespoort dam with exceptionally high tritium value.

(FIGURE 6)

The environmental isotope signal for the acid mine decant shows an average value of -5.6‰ for $\delta^{18}O$, -22.0‰ for δ^2H, and 1.8 T.U. for ^3H. The relatively low ^3H compared to rain water and lower values of $\delta^{18}O$ and δ^2H than corresponding data of shallow boreholes could be interpreted as acid mine water receiving large proportion of the water from deep circulating groundwater originated from a wider hydrogeological basin. The isotope signature of the acid mine decant refers to depleted ^{18}O and high (positive) redox potential values that plot on the right quadrant of Fig. 7 and provides an important evidence for its composition as a result of highly oxidizing minerals and impact on associated water system.

(FIGURE 7)

The plot illustrates the presence of different aquifer systems (shallow weathered, fractured and karstified) in the area with variable recharge and circulation dynamics. It is also evident that perennial streams and shallow boreholes are enriched with respect to heavy isotopes which is due to infiltration after evaporation. Whereas, deep circulating karstic springs contain depleted isotope levels which may be due to recharge from high altitude and/or mixing of different water sources (Fig. 7 left quadrant). The isotope signal of the Malapa springs (dolomitic) represents relatively old water with more than five decades in circulation on the basis of the low ^{3}H, suggesting longer circulation time inside the aquifer. It is also possible to suggest that the relatively low values of $\delta^{18}O$ and $\delta^{2}H$ demonstrate high altitude recharge and/or recharge from wetter climates. The city of Johannesburg is located at 1745 m a.m.s.l where the water divide between the Limpopo and Vaal River is passing E-W direction through the city. However, there are areas that lie above 2200 m a.s.l., e g. in the NW part, Magaliesburg quartzites constitute high elevation areas, or any other high rising zones in the area. Winter season in the area is dry and cold (lies under the influence of cold South Atlantic air mass) that fails to generate evaporation effect on isotopes and, hence, is depleted in 18-O.

Data interpretation of deuterium excess (*d-excess* = $\delta^{2}H-8\delta^{18}O$), which characterizes the isotopic composition of meteoric water in a $\delta D/\delta^{18}O$ space, a parameter influenced by conditions prevailing in the oceanic regions which are known moisture sources to the continental regions, was undertaken to characterize the likely source of recharge to the aquifers. The $\delta^{18}O$ value was plotted against *d-excess* (Fig. 8) and the distribution has a range of variation from 2‰ to 24‰, which shows the influence of both local and regional moisture circulation in the area except for samples with high *d-excess* that most likely indicate local moisture source derived from a very low vapour humidity. Globally, *d-excess* averages at about 10‰, but varies due to variations in humidity to the source of formation of the vapour, wind speed and sea surface temperature during evaporation (Clark and Fritz, 1997). Therefore, data with low d-excess values show high humidity during formation of vapour mass signifying the short distance of the rain from the vapour source (Dansgaard, 1964; Rozanski et al., 1993; Clark and Fritz, 1997; Jouzel et al., 2007).

(FIGURE 8)

Hydrogeochemical and Hierarchical Cluster Analysis (HCA)

Based on the water quality data obtained from the Department of Water Affairs of South Africa,(selected data are given Table 2), ratio-distribution has been used to discriminate the extent of mine water impact in the crystalline aquifers. From the chemical data, the two well known acid mine decant components (Fe and SO_4) have been considered with respect to Ca and Cl. Accordingly, the ratio for SO_4/Cl has resulted a wide range of values that fall between 0 and 306.37 while for that of Fe/Ca the ratio falls between 0 and 5.59. It is obvious that in dolomitic aquifers do not generate sulphate into the water unless impacted by AMD, and, hence, the SO_4/Cl ratio would be close to Zero, indicating the dominance of bicarbonate in the groundwater system. On the other hand, high SO_4/Cl values show the interference of AMD with the groundwater system. Even though Fe is a minor chemical constituent in the groundwater, the Fe/Ca ratio is considered as an indicator for the impact of AMD on the groundwater system. In this regard values above 0.25 (with 1 to 4 natural abundance for Fe:Ca) could potentially represent the impact of acid mine decant.

More significant hydrogeochemical facies have also been identified which indicate mixing of bicarbonate water and acidic mine decant (sulphate type) generated intermediate water (Fig. 9). The plot further shows the presence of hydrogeochemical evolution that goes through HCO_3-SO_4-Cl facies.

(FIGURE 9)

(TABLE 2)

Hierarchical clustering is applied to group similar hydrogeochemical data into “clusters” that have been controlled by similar geochemical process or derived from same source. There is a vast literature on validity of cluster analysis in the case of vast data points where applications were tested based on permutations. In hierarchical clustering, the two most similar clusters are combined and continue to combine until all data points are in the same cluster. Hierarchical clustering produces a tree (called a dendogram) that shows the hierarchy of the clusters. This allows for exploratory analysis to see how the microarrays group together based on similarity of hydrochemical features like in the case of Johannesburg where more than 1000 data points were considered for statistical analysis.

The dendogram on Fig. 10 shows four clusters of specific hydrogeochemical groupings presumably due to similar geochemical processes within the aquifer or similar sources. The cumulative variance of the four clusters is 99.32% with the maximum and minimum semi-partial R^2 (complete linkage) of 0.3705 and 0.0607, respectively, indicating dominant hydrogeochemical clusters in the area. The identified clusters clearly show the hydrogeochemical footprints in the area due to lithological control and AMD impact.

(FIGURE 10)

The detailed hydrogeochemical characteristics of the groundwater are interpreted as follows:

- Cluster A has high Na, Ca, Mg, HCO_3 and SO_4 concentrations which could be attributed water resident within dolomitic aquifer. The high sulphate content could be derived from acid mine decant. This group is identified as sodium bicarbonate-sulphate and calcium bicarbonate type water.
- Cluster B has high Ca, Mg and HCO_3 with low Na and SO_4 concentration and it is attibuted to the relatively uncontaminated groundwater within the parts of the dolomitic aquife (could be deep circulation system). This group is identified as calcium – magnesium bicarbonate type water.
- Cluster C has low Na, Ca, Mg, SO_4, HCO_3 (Max ≈ 150 mg/L) concentration and low Si concentration. This cluster indicates groundwater belonging to fractured/weathered crystalline rocks such as granitic gneiss with predominantly shallow circulation. This group is identified as sodium bicarbonate type water
- Cluster D has low Na, Ca, Mg, SO_4 (very low) and high Si (max ≈ 29 mg/L) concentrations. This cluster could belong to quartizte and alluvial aquifers. This group is identified as Sodium sulphate type water

HCA has identified different hydrogeochemical groupings within the groundwater of the study area with variable chemistry which reveals an indication of the impact of acid mine decant on groundwater quality which could be considered as an important geochemical agent in controlling the regional groundwater quality.

Conclusions

The study shows that the century long gold mining activity in the area has intensively altered the quality of shallow groundwater. Environmental isotope data reveals the presence of predominantly shallow groundwater circulation within the fractured crystalline rocks and deep circulation within the dolomitic aquifers. Moreover, stable isotope data (δ^2H and $\delta^{18}O$) as well as tritium data demonstrate that significant proportion of the acid mine drainage is contributed from relatively old (low ^3H value) and deep circulation water (low $\delta^{18}O$) which affects the dolomitic aquifer. Mixing of old water from deep circulating groundwater, shallow groundwater and water from direct precipitation is widely taking place in the area. It was also discovered that about 56 million m3 of acid mine decant seeps into the fresh dolomitic groundwater.

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References

Abiye TA (2011) Provenance of groundwater in the crystalline aquifer of Johannesburg area, South Africa. Int. J. Physical Science **6(1):**98-111.

Abiye TA, Mengistu H, Demlie MB (2011). Groundwater resource in the crystalline rocks of the Johannesburg area, South Africa. *J. Water Resources and Protection* **3(4):** 199-212

Adams S, Titus R, Pietersen K, Tredoux G, Harris C 2001. Hydrochemical characteristics of aquifers near Sutherland in the Western Karoo, South Africa. *J. Hydrology*. **241**:91-103.

Africa Geo-Environmental Services (AGES) Report. 2005. Numerical modeling of seepage potential at three ingress areas of the Central Rand Basin of the Witwatersrand Goldfields. Council for Geosciences, Pretoria, South Africa.

Anhaeusser CR (2006). Ultramafic and mafic intrusions of the Kaapvaal craton. In "The Geology of South Africa". Johnson M.R; Anhaeusser, C.R, Tomas, R.J (editors). Council for Geosciences, p95-134.

Barnard HC (1999). Hydrogeological map of Johannesburg 2526. 1:500,000." Department of Water Affairs and Forestry, Pretoria, Johannesburg, South Africa.

Barnard HC (2000). An explanation for the 1:500,000 Hydrogeological map of Johannesburg 2526," Department of Water Affairs and Forestry, Pretoria, RSA.

Barton Jm, Barton Esw, Kroner A. (1999). Age and isotopic evidence for the origin of the Archaean granitoid intrusive of the Johannesburg Dome, South Africa. *J. African Earth Sciences*. **28** (3):693-702.

Bredenkamp DB, Xu Y (2003) Perspectives on recharge estimation in dolomitic aquifers in South Africa. In Groundwater recharge estimation in Southern Africa. Xu, Y and Beekman H.E., (editors). UNESCO, p207.

Bredenkamp DB, Van Der Westhuizen C, Wiegmans FE, Kuhn C (1986) Groundwater supply potential of dolomite compartments West of Krugersdorp." Directorate of Geohydrology. DWAF, Report no. GH 3440. Pretoria, South Africa.

Buttrick DB, Van Root JL, Ligthelm R (1993). Environmental geological aspects of the dolomites of South Africa**.** *J. African Earth Sciences*, **16**:53-61.

Clark ID, Fritz P (1997) Environmental isotopes in Hydrogeology. CRC Press LLC. P328

Coetzee H, Chirenje E, Hobbs P, Cole J (2009) Ground and airborne geophysical surveys identify potential subsurface acid mine drainage pathways in the Krugersdorp Game Reserve, Gauteng Province, South Africa." Proceedings of the 11th SAGA meeting and exhibition, Swaziland, 16-18 Sept. 2009, pp 461-470.

Craig H (1961) Standard for reporting concentrations of deuterium and oxygen-18 in natural water. *Science,* **133**:1833-1834

D'Alberton PC, Tyson PD (1996) Three-dimensional kinematic trajectory modelling of water vapour transport over Southern Africa. *WaterSA.* **22** (4): 297-308.

Dansgaard, W (1964) Stable isotopes in precipitation. Tellus 16, 436-468.

DWAF (Department of Water Affairs and Forestry) 1992. Hydrology of upper Crocodile River sub-system. Report no. PA200/00/1492. Vol 1 and 2, Pretoria, South Africa.

Ferret Report (2005) Derivation of a numerical model for a cumulative water balance of the Central Rand Basin. Council for Geosciences, Pretoria, South Africa.

Hobbs PJ (ED) (2011). Situation assessment of the surface water and groundwater resource environments in the Cradle of Humankind World Heritage Site. Report prepared for the Management Authority. Department of Economic Development. Gauteng Province. South Africa.

Hobbs PJ, Cobbing JE (2007) A hydrogeological assessment of acid mine drainage impacts in the West Rand Basin, Gauteng Province, South Africa. Report No. CSIR/THRIP.

Holland M, Wittüser KT (2009) Geochemical characterization of karst groundwater in the cradle of humankind world heritage site, South Africa. *Environ Geol*. **57**: 513-524.

IAEA. (2011) Global Network of Isotopes in Precipitation. The GNIP database. Web address: http://www.naweb.iaea.org/napc/ih/GNIP/userupdate/description/1stpage.html.Data accessed: 02/03/2012

Jouzel R, Stievenard M, Johnsen SJ, Landais A, Masson-Delmotte V, Sveinbjornsdottir A, Vimeux F, Von Grafenstein U, White, JWC (2007) The GRIP deuterium-excess record. *Quaternary Science Reviews* **26**:1-17.

Rozanski K, Araguas-Araguas L, Gonfiantini R (1993) Isotopic patterns in modern Precipitation. *Geophysical Monograph* **78**:1-35.

Sami K (1992) Recharge mechanisms and geochemical processes in a semi arid sedimentary basin, Eastern Cape, South Africa. *J. Hydrology*. **139**:27-48.

Witthüser KT, Holland M (2008) Hydrogeology of the Cradle of Humankind World Heritage Site, South Africa." *The 12th International Conference of International Association for Computer Methods and Advances in Geomechanics (IACMAG),*1-6 October, 2008, Goa, India.

Figure

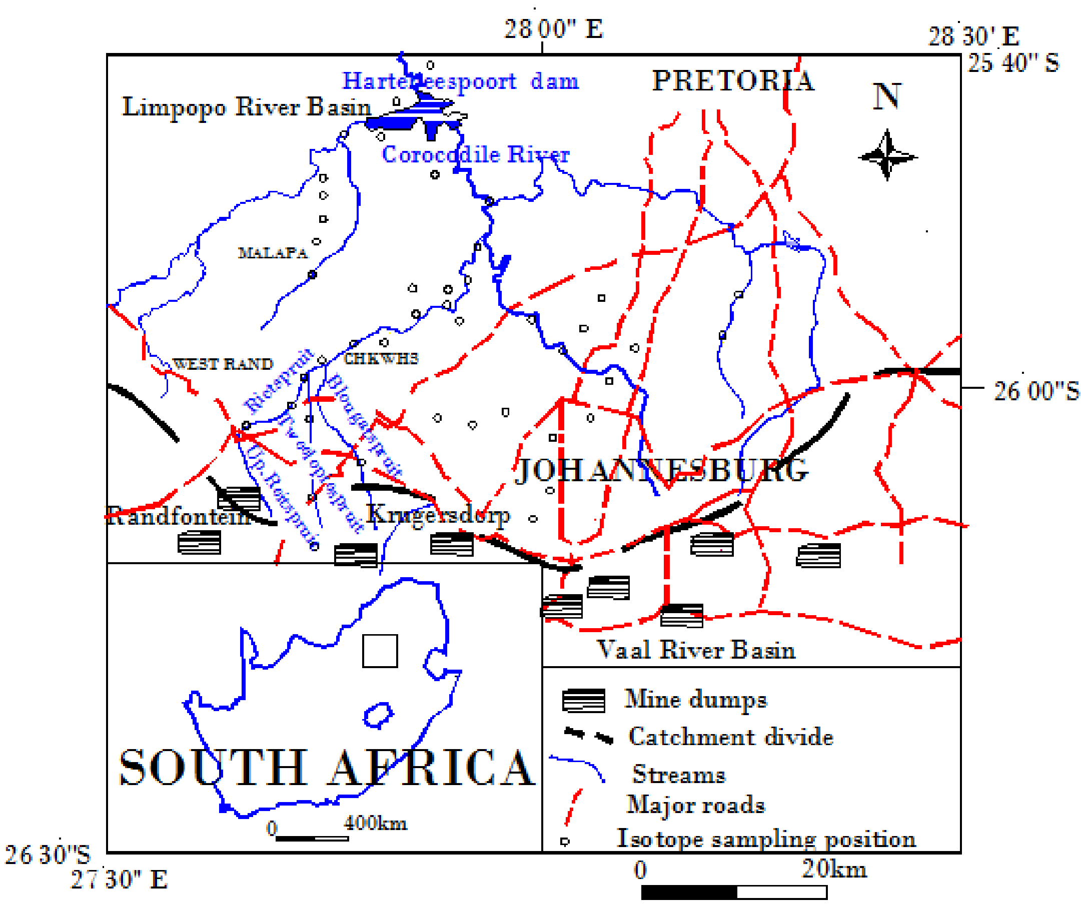
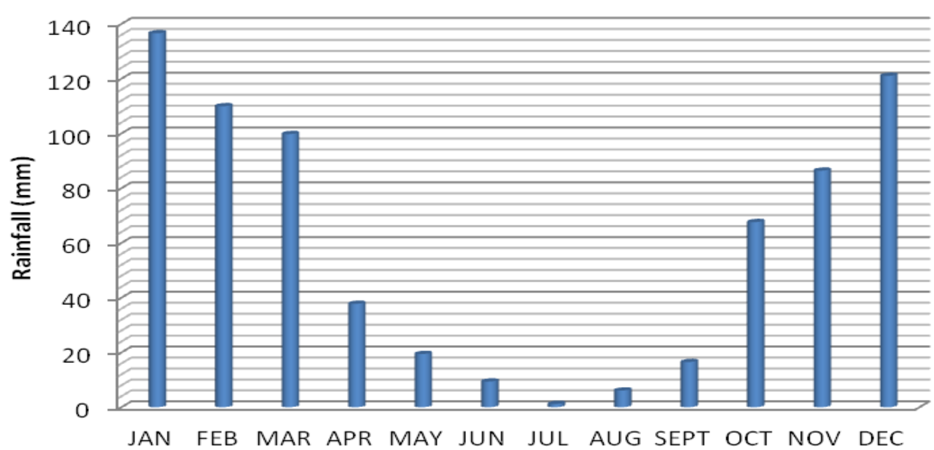


Figure 1. Location map of the upper Crocodile River basin (CHKWHS stands for the Cradle of Human Kind World Heritage site), and isotope sampling points are indicated in small circles.



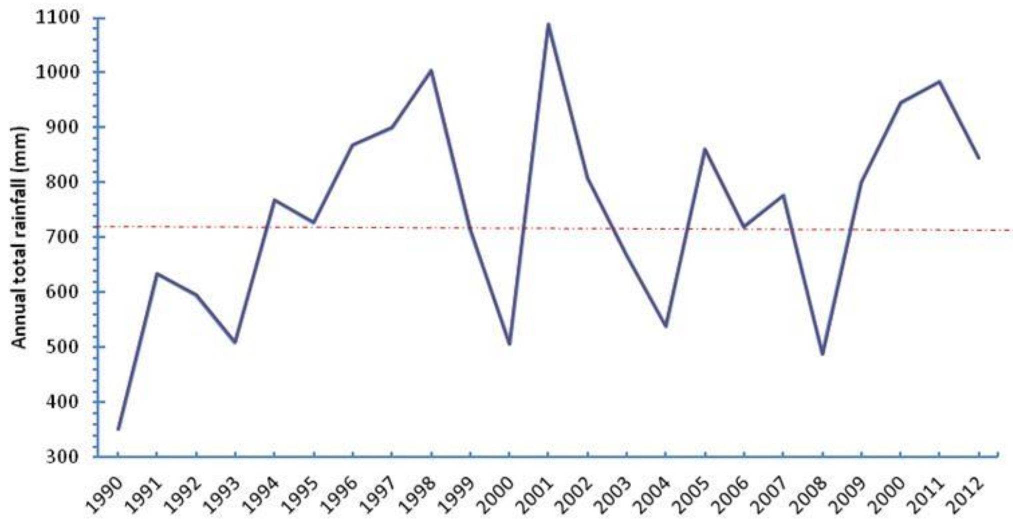


Figure 2. Mean monthly and annual total precipitation in the Johannesburg area (Data source: South African Meteorological Service)

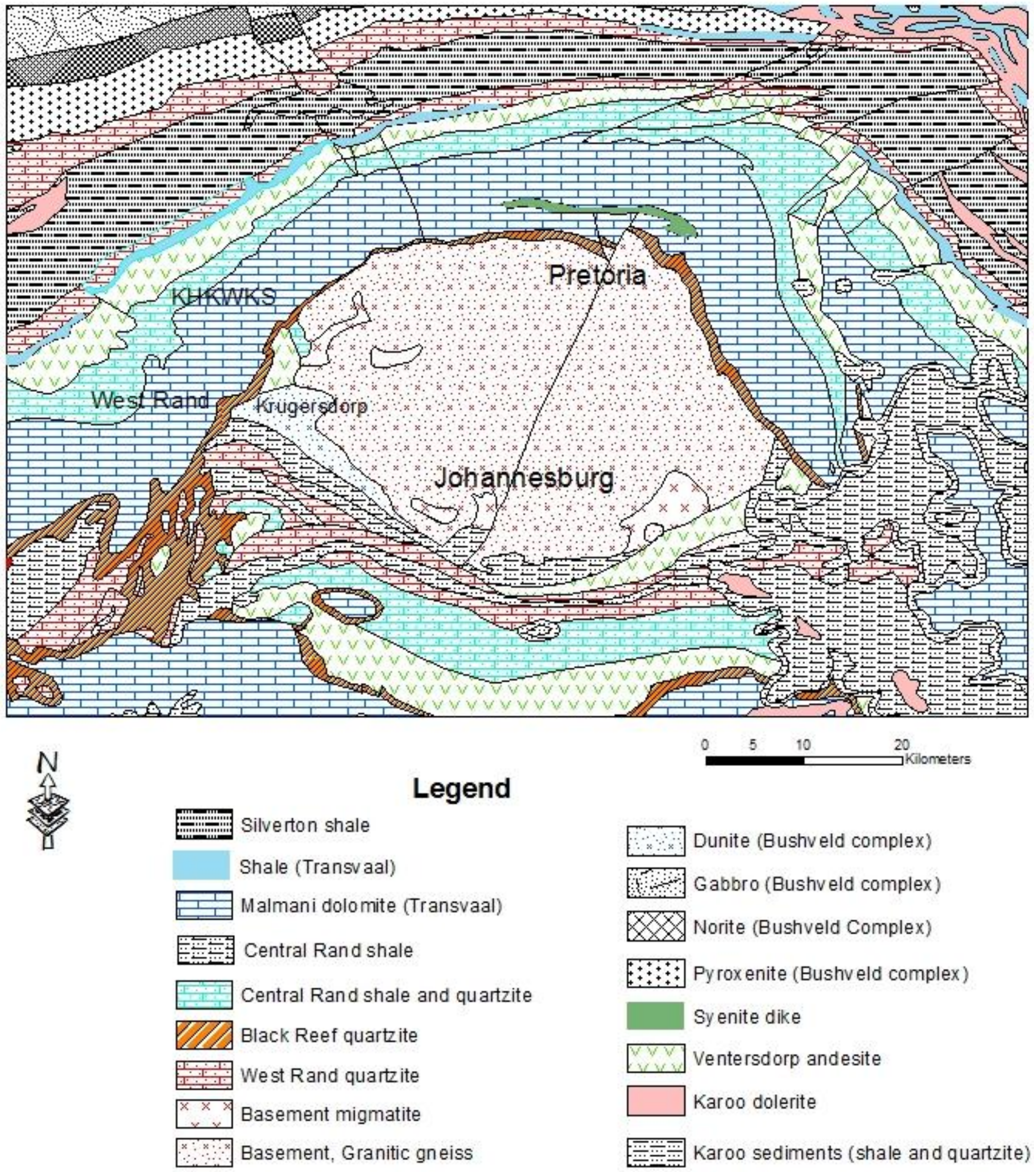


Figure 3. Geological map of the study area (Source: Council for Geosciences).

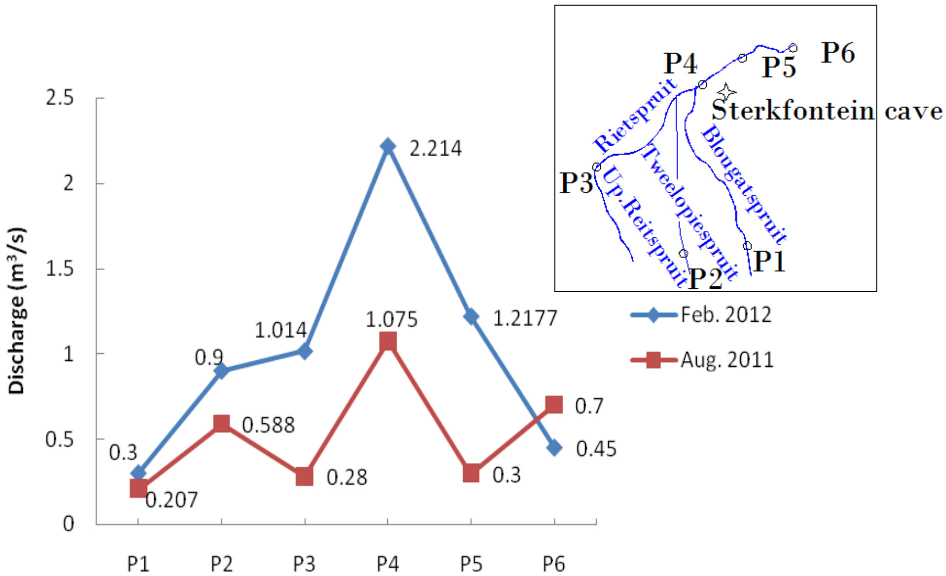


Figure 4. Discharge variation along Riet stream and its tributaries in the CHKWHS (x- axis represent measurement positions along Riet stream and its tributaries)

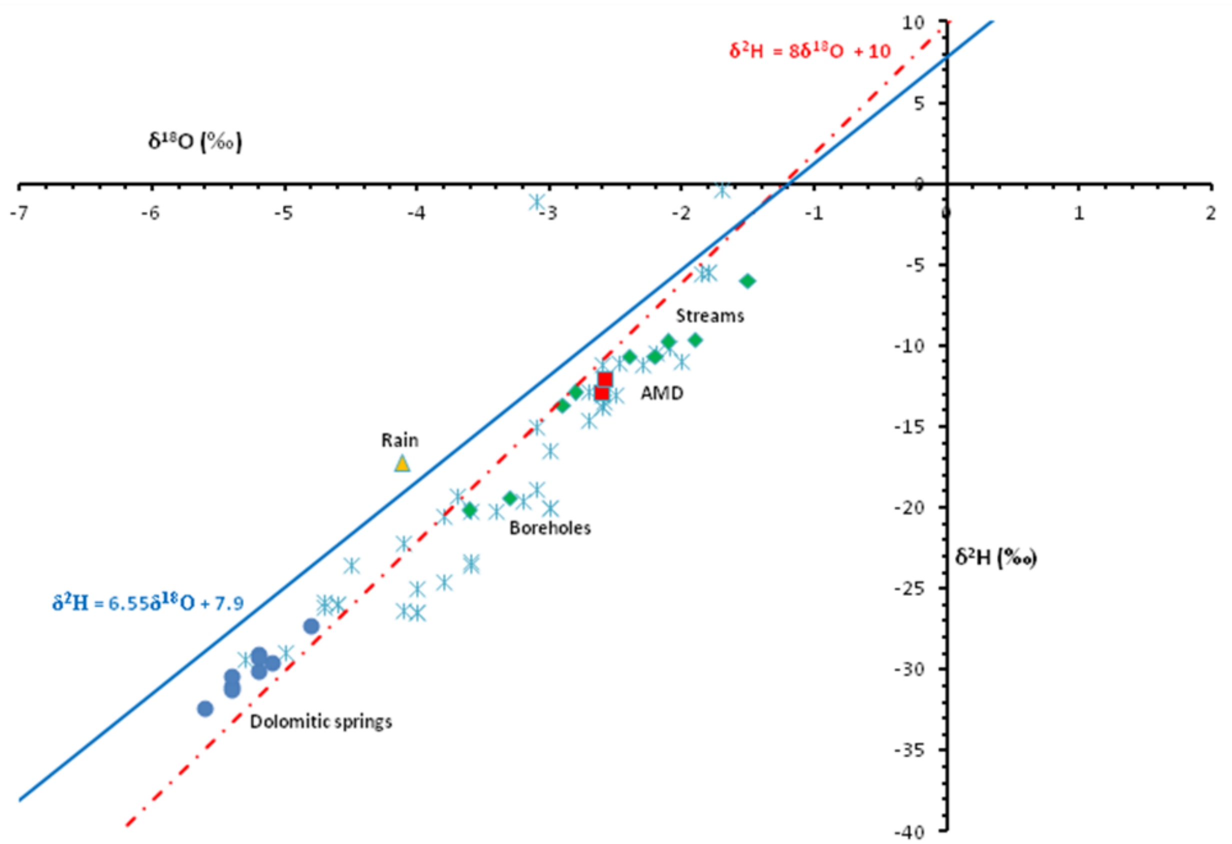


Figure 5. Stable isotope plot for the water samples taken in the upper Crocodile River Basin. (Global Meteoric Line (Craig, 1961), Local Meteoric Water Line (www.IAEA.org/gnipmain.htm)

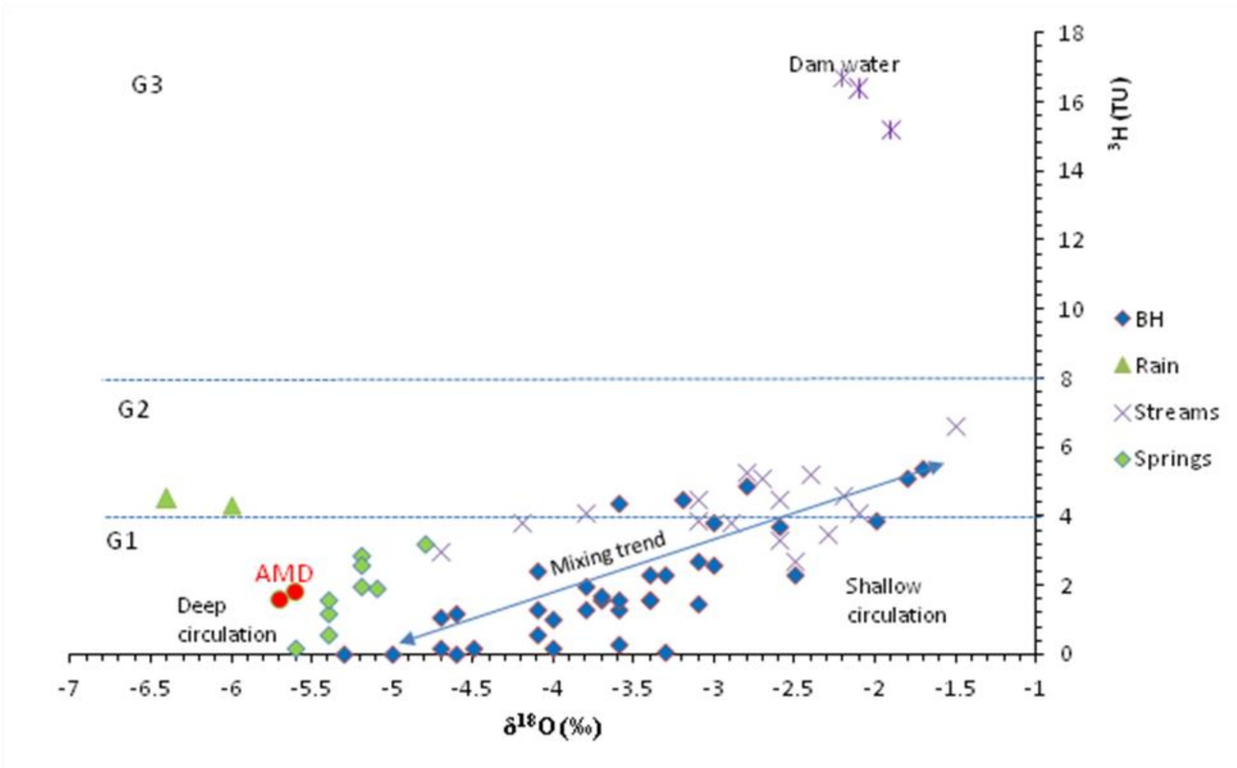


Figure 6. Tritium distribution with respect to $\delta^{18}O$ that shows mixing and provenance of circulation.

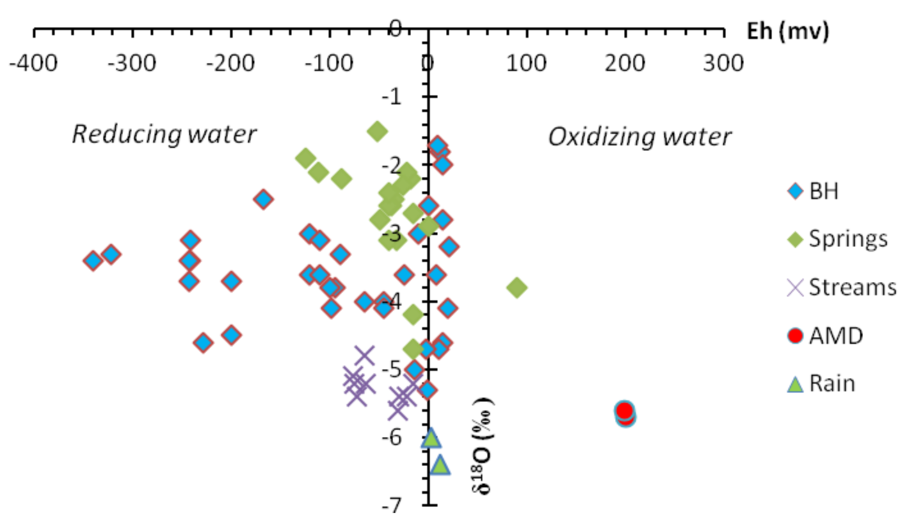


Figure 7. $\delta^{18}O$ vs Eh plot for different redox environment

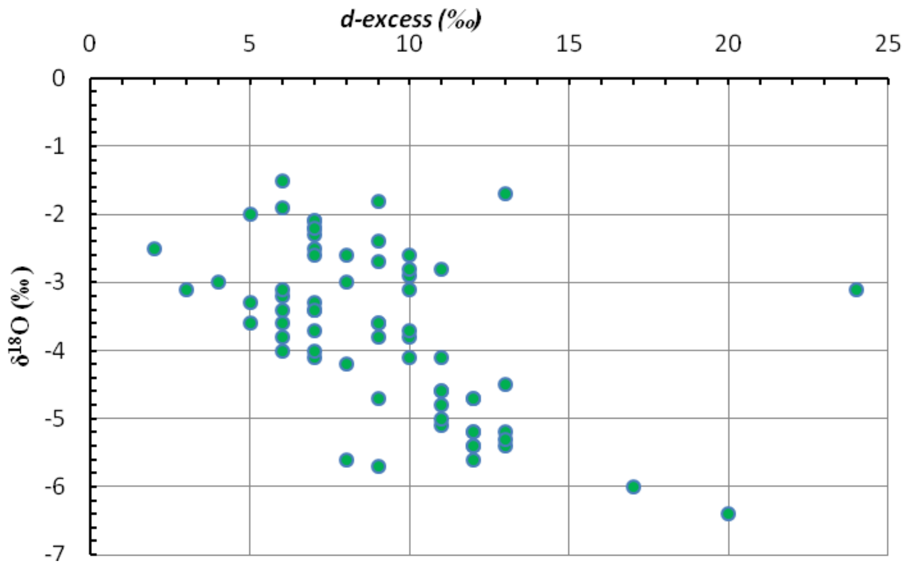


Figure 8. Plot of *d-excess* versus $\delta^{18}O$ for water samples within the study area.

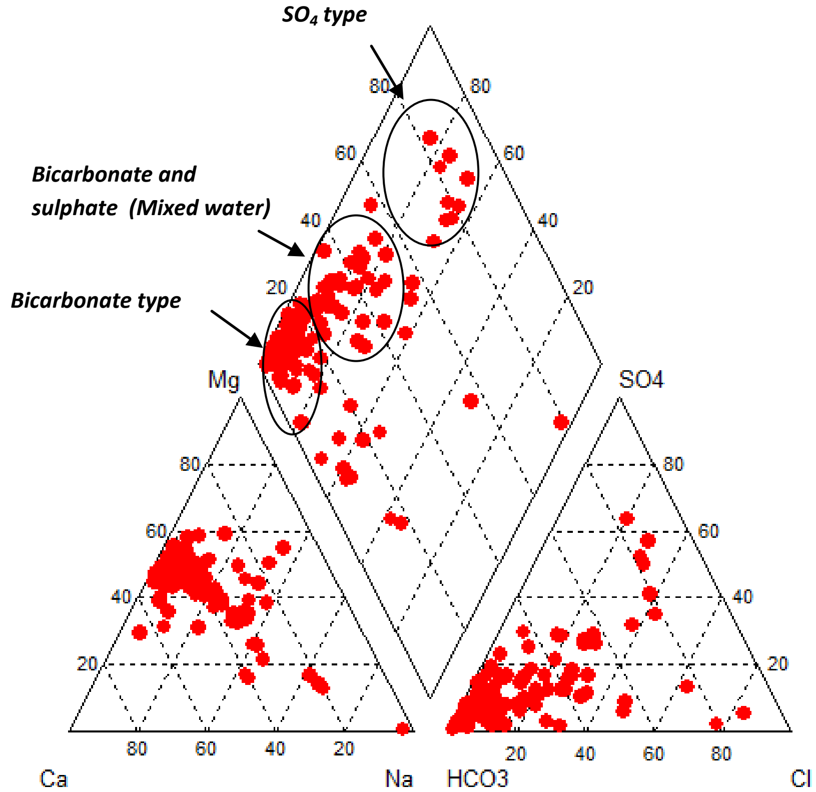


Figure 9. Piper plot of chemical data indicating main hydrogeochemical facies

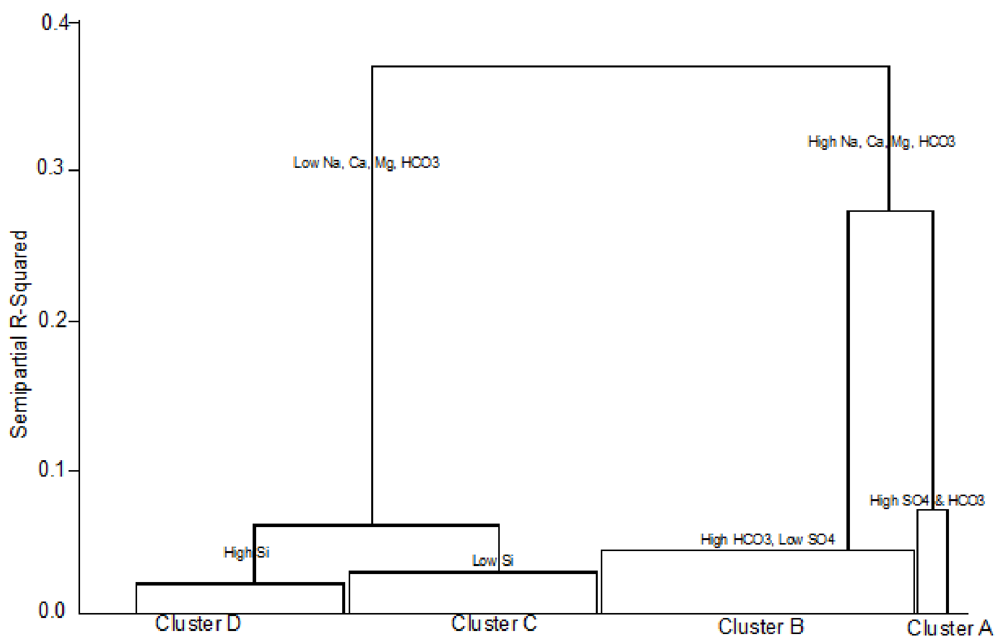


Figure 10. Four major hydrogeochemical clusters in the area

Table 1. Environmental isotope results

Code	Source	Lat(S)	Long (E)	pH	TDS (mg/l)	EC (μS/cm)	Eh(mv)	δ18O (‰)	δ2H (‰)	3H (T.U.)	d excess (‰)
JHB1	Spring (dolomite)	-25.9012	27.8098	7.5	116.2	181.4	-15.7	-5.17	-29.0	2.9±0.3	12.36
JHB2	Spring (dolomite)	-25.8715	27.8091	8.5	120.7	188.9	-64.5	-4.75	-27.3	3.2±0.3	10.70
JHB3	Spring (dolomite)	-25.8716	27.7809	7.7	140.2	220.0	-22.2	-5.42	-31.0	0.6±0.2	12.36
JHB4	Spring (dolomite)	-25.8798	27.7992	7.8	145.5	228.0	-29.5	-5.40	-31.2	1.2±0.2	12.00
JHB5	Spring (dolomite)	-25.8652	27.7878	8.5	110.6	172.6	-73.2	-5.39	-30.4	1.6±0.3	12.72
JHB6	Spring (dolomite)	-25.8625	27.7869	8.6	87.4	136.5	-75.2	-5.23	-30.1	2.0±0.3	11.74
JHB7	Spring (dolomite)	-25.8678	27.7869	8.5	77.8	121.4	-76.5	-5.11	-29.6	1.9±0.3	11.28
JHB8	Spring (dolomite)	-25.8601	27.7869	8.4	108.1	168.9	-63.1	-5.17	-29.2	2.6±0.3	12.16
JHB9	Spring (dolomite)	-25.8701	27.78	7.7	110.0	172.3	-31.0	-5.64	-32.4	0.2±0.2	12.72
JHB10	Stream (winter)	-26.0911	27.7598	7.5	118.8	185.3	-0.1	-2.89	-13.7	3.8±0.3	9.42
JHB11	Acid mine decant	-26.1101	27.7267	3.6	1502.0	2350.0	198.1	-5.61	-22.0	1.8±0.3	22.88
JHB12	Stream (winter)	-26.0401	27.7298	7.5	216.0	337.0	-18.2	-2.22	-10.7	4.6±0.4	7.06
JHB13	Stream (winter)	-26.0223	27.7278	7.6	217.0	339.0	-21.9	-2.09	-9.8	4.1±0.4	6.92
JHB14	Stream (winter)	-26.0911	27.7765	7.8	225.0	352.0	-35.3	-2.49	-13.0	2.7±0.3	6.92
JHB15	Stream (winter)	-26.231	27.78	7.9	194.3	303.0	-38.1	-2.61	-12.9	3.3±0.3	7.98
JHB16	Stream (winter)	-26.0102	27.74	7.8	229.0	358.0	-25.4	-2.31	-11.2	3.5±0.3	7.28
JHB17	Stream (winter)	-26.1501	27.99	8.1	135.8	212.0	-48.9	-2.80	-12.9	5.3±0.4	9.50
JHB18	Stream (winter)	-26.1523	28	8.2	112.6	176.0	-39.8	-2.63	-11.2	4.5±0.4	9.84
JHB19	Stream (winter)	-26.1841	27.99	7.4	171.9	269.0	-32.6	-3.11	-15.0	3.9±0.3	9.88
JHB20	Stream (winter)	-26.1626	28.1198	7.2	106.0	167.0	-15.0	-2.72	-12.8	5.1±0.4	8.96
JHB21	Stream (winter)	-26.0421	28.0519	8.0	149.1	233.0	-40.5	-2.44	-10.7	5.2±0.4	8.82
JHB22	Dam	-25.8001	27.8923	8.2	181.4	284.0	-52.0	-1.51	-6.0	6.6±0.4	6.08
JHB23	Dam	-25.7623	27.7925	9.6	146.4	229.0	-125.1	-1.89	-9.6	15.2±0.7	5.52
JHB24	Dam	-25.7201	27.8515	9.4	148.9	232.0	-111.5	-2.13	-10.1	16.4±0.7	6.94
JHB25	Stream (winter)	-25.71	27.8462	8.8	158.1	247.0	-87.7	-2.24	-10.4	16.7±0.7	7.52
JHB26	Stream (winter)	-25.919	27.8109	18.7	328.0	210.0	-39.9	-3.14	-1.1	4.5±0.4	24.02
JHB27	Stream (summer)	-26.1784	28.0908	7.1	110.0	180.0	-15.0	-4.71	-28.8	3.0±0.3	8.88
JHB28	Stream (summer)	-26.1584	28.0909	7.2	106.0	167.0	-15.0	-4.24	-25.3	3.8±0.3	8.62
JHB29	Acid mine decant	-26.02	27.721	3.0	1502.0	2350.0	200.0	-3.65	-20.4	1.6±0.3	8.8
JHB30	Stream with AMD	-26.6789	27.7821	4.6	1200.0	1750.0	89.0	-3.77	-20.5	4.1±0.4	9.66
JHB31	Rain 12/2010 JHB	-26.11	27.72	6.0	72.0	120.0	12.0	-6.37	-31.6	4.5±0.4	19.36
JHB32-1	Rain 01/ 2011 JHB	-26.0984	27.7815	6.0	69.0	120.0	2.5	-5.98	-30.8	4.3±0.4	17.04
JHB32-2	Rain 01/ 2012 JHB	-26.0984	27.7815	6.7	30.0	19.0	2004.0	-0.23	3.5	8.0±0.5	5.34
JHB33	Borehole	-25.89821	27.45948	7.0	143.2	224.0	14.0	-4.64	-26.0	1.2±0.3	11.12
JHB34	Borehole	-25.89236	27.45772	7.4	111.2	173.4	-14.6	-5.01	-28.9	0.0±0.2	11.18

JHB35	Borehole	-25.8908	27.45905	6.8	71.5	111.2	10.8	-4.72	-26.1	1.1±0.3	11.66
JHB36	Borehole	-25.89471	27.47216	7.2	89.9	140.5	-3.1	-4.7	-25.8	0.2±0.2	11.8
JHB37	Borehole	-25.8971	27.45948	6.8	207.0	323.0	19.8	-4.13	-22.2	2.4±0.3	10.84
JHB38	Borehole	-25.89236	27.45872	7.6	6720.0	8400.0	-1.2	-5.33	-29.3	0.0±0.2	13.34
DOL1	Borehole	-25.21	28.21	7.7	5160.0	6450.0	-10.0	-3.04	-20.0	2.6±0.3	4.32
DOL2	Borehole	-25.96	28.21	7.4	944.0	1180.0	-25.0	-3.61	-20.2	1.3±0.2	8.68
DOL3	Borehole	-25.95	28.2	7.7	8184.0	10230.0	-45.0	-4.01	-26.4	0.2±0.2	5.68
DOL4	Borehole	-25.95	28.21	7.7	4352.0	5440.0	0.2	-2.61	-13.8	3.7±0.3	7.08
DOL5	Borehole	-25.96	28.22	8.1	2224.0	2780.0	12.0	-1.82	-5.4	5.1±0.4	9.16
DOL6	Borehole	-25.94	28.22	8.1	3632.0	4540.0	8.0	-3.59	-23.5	4.4±0.4	5.22
DOL7	Borehole	-25.93	28.21	7.6	6240.0	7800.0	-45.0	-4.11	-26.3	0.6±0.2	6.58
DOL8	Borehole	-25.94	28.2	7.2	4528.0	5660.0	-94.3	-3.83	-24.6	2.0±0.4	6.04
DOL9	Borehole	-25.95	28.23	7.7	5920.0	7400.0	-120.6	-3.02	-16.5	3.8±0.4	7.66
DOL10	Borehole	-25.98	28.23	7.7	1888.0	2360.0	9.0	-1.73	-0.3	5.4±0.5	13.54
DOL11	Borehole	-25.96	28.1912	7.7	1632.0	2040.0	14.0	-2.03	-10.9	3.9±0.4	5.34
DOL12	Borehole	-25.9612	28.2221	7.7	5760.0	7200.0	-339.5	-3.42	-20.2	1.6±0.3	7.16
DOL13	Borehole	-25.9831	28.2412	7.4	3480.0	4350.0	-120.4	-3.63	-23.3	0.3±0.2	5.74
DOL14	Borehole	-25.9712	28.2391	8.1	5360.0	6700.0	20.1	-3.09	-19.6	4.5±0.4	5.12
DOL15	Borehole	-25.9231	28.2111	7.9	2736.0	3420.0	-65.0	-4.03	-25.0	1.0±0.2	7.24
DOL16	Borehole	-25.9552	28.2222	6.8	3936.0	4920.0	-321.1	-3.34	-19.4	0.1±0.2	7.32
DOL17	Borehole	-25.9651	28.2489	7.5	5120.0	6400.0	-228.9	-4.61	-25.9	0.0±0.2	10.98
DOL18	Borehole	-25.9882	28.2112	7.7	3528.0	4410.0	-199.3	-4.50	-23.5	0.2±0.2	12.5
DOL19	Borehole	-25.9773	28.2446	7.8	4552.0	5690.0	-243.1	-3.70	-19.3	1.6±0.2	10.3
DOL20	Borehole	-25.9776	28.2439	7.6	5440.0	6800.0	-110.7	-3.09	-18.8	1.5±0.3	5.92

Site id	Orig site name	Latitude	Longitude	Altitude	EC mS/cm	K mg/l	Na mg/l	Ca mg/l	Mg mg/l	Cl mg/l	TAL mg/l	SO4 mg/l	Si mg/l
2627BA00194	STERKFONTEIN	-26.03611	27.7	1520	112.5	1.36	62.5	93.3	53.3	94.3	97.6	227.1	6.3
2528CC00162	CEN. GED. BRONBERRIK	-25.85639	28.16695	1430	66	1.63	6.8	69.6	38.9	15.4	263.3	20.4	
2528CD00007	RIETVALLEI	-25.89639	28.3125	1487	53.9	0.54	16.1	45.4	31.1	20	172.4	32.1	8.39
2528CC00026	OLIFANTSFONTEIN	-25.9275	28.21945	1480	87.6	1.76	61.3	63.6	30.1	78.2	209.7	59.1	9.83
2627BA00021	ZWARTKRANS	-26.0174	27.71136	1463	98	1.51	46.1	87.8	49.1	70.2	119.8	229.7	6.44
2627BA00063	WOLVEKRANS	-26.08056	27.57639	1545	83	0.7	1	7.1	4	1.5	42.4	9.9	6.01
2528CD00028	RIETVALLEI	-25.89861	28.30278	1519	37.1	1.38	5.8	35.2	20.6	6.6	121.3	21.6	0.86
2528CD00155	HARTEBEESTFONTEIN	-25.96945	28.28056	1586	40.1	0.43	4.9	39.4	23.9	6.4	168.8	11.4	6.22
2528CD00049	GROOTFONTEIN	-25.91689	28.33856	1500	24.6	0.15	1	23.8	12.8	1.5	118.7	5.5	6.01
2528CC00016	DOORNKLOOF GED. 2	-25.88916	28.20888	1460	56	0.92	9.3	46	37.7	18.1	224.2	7	4.44
2528CD00044	RIETVALLEI	-25.89222	28.32195	1524	255	0.62	5.6	24.2	15	4.6	92.3	8.1	4.5
2627BA00106	VLAKPLAATS	-26.06825	27.64736	1573	373	0.54	14.2	30.5	19.8	26	115.2	15.8	5.78
2627BA00082	VLAKDRIFT	-26.0508	27.67248	1546	34.4	1.6	7.6	35.1	21.2	39	98.5	47.3	6.09
2528CD00078	DOORNKLOOF GED. 106	-25.88222	28.25666	1460	44.8	0.65	11	41.4	25.9	11	192.5	12.6	10.7
2628AB00032	HARTEBEESFONTEIN	-26.01667	28.28555	1570	50.2	1.28	12.7	39.8	31.4	28.5	158.6	33	14.12
2528CD00043	RIETVALLEI	-25.90861	28.31695	1501	64	0.86	51	39.9	24.1	41.3	153.2	76.1	4.5
2627BA00081	STERKFONTEIN	-26.04625	27.67872	1543	31.6	0.4	3.2	30.8	19.3	10.9	125.8	8.3	6.13
2528CC00013	DOORNKLOOF GED. 5	-25.85694	28.23333	1490	60.4	2.73	6.4	62.3	35	3	265.9	15.6	15.43
2528CD00050	GROOTFONTEIN	-25.94961	28.34194	1580	20.4	0.38	1	21.3	11	1.5	106	6	5.14
2528CD00086	STERKFONTEIN	-25.95	28.26806	1559.77	36	0.79	5.4	36.1	21.6	4.2	157.3	9.8	

Table 2. Sample water quality data for some water supply wells in the Johannesburg area (Data source: DWA)

Supplementary Material

Click here to download Supplementary Material: groundwater chemical data Johannesburg.xls