Assessment of Ingress Areas/Points in the Witwatersrand Basin using Environmental Isotopes as Tracers

Lufuno Ligavha-Mbelengwa[1], Lerato Mokitlane[1], Godfrey Madzivire[1,2], Humberto Saeze[1], Pamela Nolakana[1], Henk Coetzee[1]

[1]*Council for Geoscience, Water and Environment Unit, 280 Pretoria Street, Silverton, Pretoria, South Africa, lligavhambelengwa@geoscience.org.za*

[2]*University of South Africa, Department of Environmental Science, 28 Pioneer Ave, Roodepoort, South Africa*

Abstract

This study investigated the use of environmental isotopes as tracers to identify sources of water that enters mine voids. Water samples were collected from surface, boreholes and shafts. The findings indicated depleted $\delta^{18}O$ and $\delta^{2}H$ to be related to groundwater and shafts showing recharge by precipitation. Heavy isotopic signature is linked to surface water open to evaporation. Most groundwater and shafts displayed recent recharge by modern rainfall as deduced from tritium, although other sites gave no indication of recent recharge. Findings gave an indication that surface water ingress into the subsurface. Deduced main water types were $Na\text{-}HCO_3$, $Mg\text{-}Cl\text{-}HCO_3$ and $Ca\text{-}Mg\text{-}SO_4$.

Keywords: Groundwater, Water Interaction, Isotopes, Mine Water, Surface Water, Water Types

Introduction

Jasechko (2019) describes isotope hydrogeology as the measuring of stable or radioactive isotope compositions of river, spring and groundwater, then interpreting the isotopic measurements to quantify or conceptualise groundwater flow paths, velocities and biochemical. The most widely used isotopes in hydrogeology are of hydrogen (^{1}H, ^{2}H and ^{3}H), oxygen (^{16}O, ^{17}O and ^{18}O) and carbon (^{12}C, ^{13}C and ^{14}C). There are a number of uses of groundwater isotopes; among others is the identification of recharge areas and quantifying the recharge rates, which in turn can be used as input for water budget analysis. Isotopes can also be used for dating groundwater.

Stable isotopes of oxygen (^{16}O and ^{18}O) and hydrogen (^{1}H and ^{2}H or deuterium - D) are used to determine whether groundwater is derived from precipitation or local meteoric waters. Stable isotopes undergo fractionation, kinetic and equilibrium fractionation. Meteoric water lines (MWL) which are linear regressions describe the variations of $\delta^{18}O$ and $\delta^{2}H$. Global meteoric water lines (GMWLs) are widely used to describe $\delta^{18}O$ and $\delta^{2}H$ relationship; although at a regional scale a local meteoric water line (LMWL) can be used. The comparison of stable isotopes has been applied to identify whether aquifer systems are recharged by overlying water bodies. The similarities of the values between groundwater and that of the river water is indicative of the river replenishing the local aquifer.

Environmental tritium (^{3}H) is also widely applied as a useful tracer in the hydrological studies. It is a radioactive isotope that decays through low energy beta ray emission and has a half-life of 12.43 years (Abiye 2013). Tritium can be used to measure the age of groundwater regarded as modern groundwater. This is often encountered in shallow groundwater and are more likely to contain anthropogenic contaminants than older waters. The concentration of tritium in the rainwater varies with geographical location, however, these goes up to 5.0 tritium units (TU) (Abiye 2013).

This study assessed the use of environmental isotopes as tracers to map ingress areas in the Witwatersrand Goldfields. Piper diagrams were done to determine the water types from various sources. Stable and radioactive isotopes were used to determine the origin of the water and to measure its age respectively.

Methods

Study area

The study was conducted in the Witwatersrand Goldfields, Eastern Basin as depicted by fig.1.

Sample collection and preparation

Water samples were collected from surface water bodies, boreholes and shafts for the analyses of stable (oxygen and hydrogen) and tritium isotopes and water chemistry. Prior collecting groundwater samples, boreholes were purged to remove the stagnant water in the borehole with the aim of introducing fresh water from the aquifer into the borehole for representative sample.

Stable and radioactive isotopes

A 1 L polyethylene bottle was filled at each sampling site and used to contain the collected sample for both stable (^{2}H and ^{18}O) and radioactive (^{3}H) analyses. Water analyses were done at the Environmental Isotope Laboratory (EIL) of iThemba LABS, Johannesburg.

The equipment used for stable isotope analysis consists of a Los Gatos Research (LGR) Liquid Water Isotope Analyser. Laboratory standards, calibrated against international reference materials, are analysed with each batch of samples. The analytical precision is estimated at 0.5‰ for O and 1.5‰ for H. Analytical results are presented in the common delta-notation:

$$\delta^{18}O(‰) = \left[\frac{\left(^{18}O/_{16}O\right)_{sample}}{\left(^{18}O/_{16}O\right)_{standard}} - 1\right] \times 100 \qquad 1$$

which applies to D/H ($^{2}H/^{1}H$), accordingly (Butler *et al* 2020). 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 (Eddy-Miller and Wheeler 2010).

The tritium samples were distilled and subsequently enriched by electrolysis. Samples of standard known tritium concentration are run in one cell of each batch to check on the

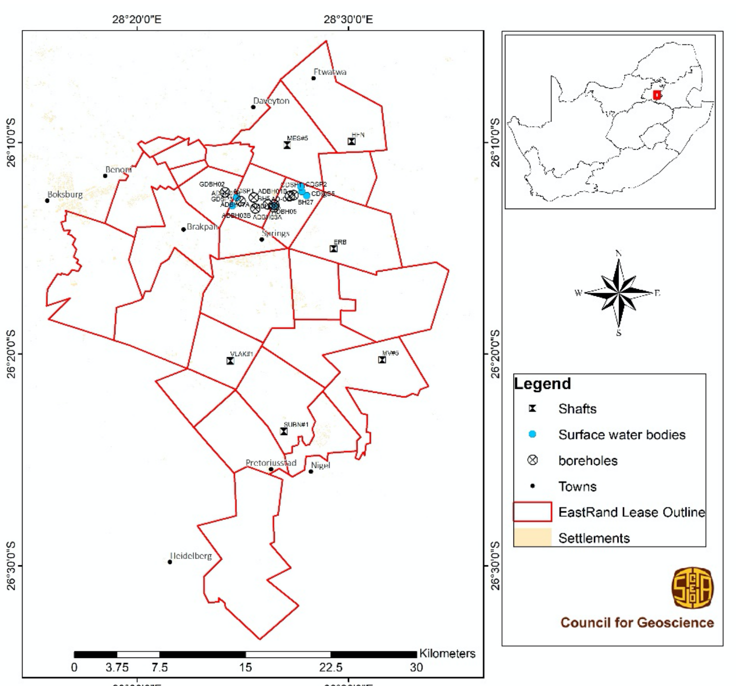

***Figure 1** Locality map displaying surface water, boreholes and shafts of the Eastern Basin.*

enrichment attained. Detection limits are 0.2 TU for enriched samples (Butler *et al* 2020).

Water chemistry

Samples to be analysed for metals/metalloids were preserved by adding 3 drops of concentrated HNO_3, whilst an unpreserved sample was collected for analyses of anions. Polyethylene bottles (100 mL and 250 mL) were used to store samples for metals/metalloids and anions analyses. These were then analysed using inductively coupled plasma mass spectrometry (ICP-MS) and ion chromatography (IC) respectively.

Data interpretation

Stable isotopes

Interpretation of the results that were obtained from the laboratory was done using the Global Meteoric Water Line (GMWL) developed by (Craig 1961) and the long-term measurements of precipitation at Pretoria station (1961-2018) from the International Atomic Energy Agency's Global Network of Isotopes in Precipitation (GNP) program as Local Meteoric Water Line (PMWL) using equation 2 and 3 respectively. The lines were then plotted on the meteoric water plot that displays ^{18}O on the x-axis, whilst ^{2}H plots on the y-axis. This data is then interpreted with reference to the MWL.

$$\delta D = 8 \times \delta^{18}O + 10 \qquad 2$$

$$\delta D = 6.7126 \times \delta^{18}O + 7.175 \qquad 3$$

Radioactive isotopes (^{3}H)

Tritium results are presented as tritium units (TU). South African rainwater has natural tritium of about 3.0 TU, thus determination of recharge by recent water can be done with reference to that of present-day rainfall. Zero tritium is an indication of low to no recharge, whilst measurable tritium will indicate recharge in that particular source (Abiye 2013).

Hydrogeochemical analysis

Results were processed using AquaChem 3.70 and are interpreted using Piper diagrams where various water types are categorised.

Results and discussion

Water types

Chemistry data was plotted on the Piper diagram (fig.2) to determine various water types in the area. The findings from these assisted in the selection of sites to be analysed

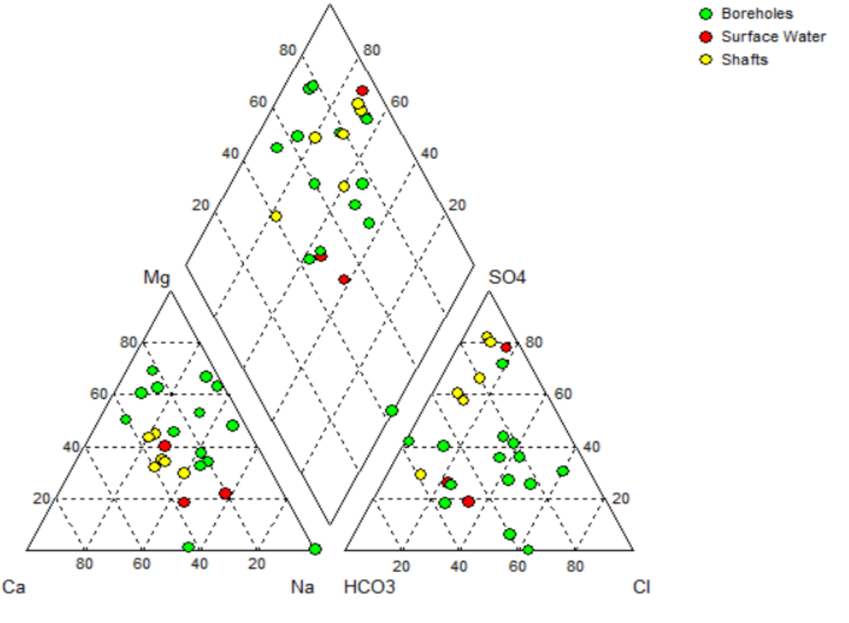

Figure 2 *Piper diagram displaying sampled sites.*

for isotopic composition, especially for sites that are situated in the same vicinity.

Application of hydrochemistry simultaneously as other tracer methods may give an indication of surface water-groundwater interaction. The diagram (fig.2) was plotted using surface, boreholes and shaft water samples. The water types that were deduced from the Piper plot are Na-HCO_3, Mg-Cl-HCO_3, Na-SO_4, Mg-HCO_3, Ca-Mg-SO_4 and mixed type (no dominant ions). In the cation triangle, water from the boreholes show a trend from a more Mg-rich content, presumably due to interaction with the dolomitic aquifer in the area, to a mixed water and to Na-rich (Mg-Cl-HCO_3, Mg-SO_4, Mg-HCO_3, Na-HCO_3 types). In the anion triangle, the trend is from HCO_3-rich content, to Cl and SO_4-rich water.

Shafts display a Ca-Mg-SO_4 water type, except for HFN that displays water that is mostly enriched in HCO_3. Surface and borehole water from CDSP2 and ADBH03A respectively, matches that of shafts with high dominance in Mg and SO_4. ADBH03A has a water signature that differs from that of other boreholes in the same vicinity. CDSP1 on the one hand plots with borehole BH8 and BH32 in the same vicinity. Furthermore, surface water ADSP1 plotted along with ADBH01A, ADBH07A, GDB02 at close proximity as well as shaft HFN, all displaying a more Na-HCO_3/Na-SO_4 water type. The Na-HCO_3 is dominant in surface water and borehole BH8, BH15 and BH32. All the boreholes around Cowles Dam proximity except BH32, BH1, BH15 and BH19 displayed Mg-Cl-SO_4/HCO_3 water type. The variation could be due to water-rock interaction leading to mineral dissolution and water quality evolution. Some boreholes showed water with high concentrations of Na than Ca and vise versa giving an indication of ion exchange.

Deductions from the water types indicate that the Eastern Basin mine voids (shafts) water represents a mixture of water from various sources, with geological influence on the water chemistry.

Meteoric water plots

All surface water samples plotted along the evaporation zone because they are exposed to the atmosphere displaying enrichment in $\delta^{18}O$ and $\delta^{2}H$ isotopes.

Shafts SUBN#1, ERB and MV#5 also plotted along the evaporation line. All these shafts are situated in the southern part of the study site and could be receiving recharge from both precipitation and surface evaporated water (fig.3 and fig.4), indicating the possibility of surface water ingress into the subsurface. All the shafts that are situated

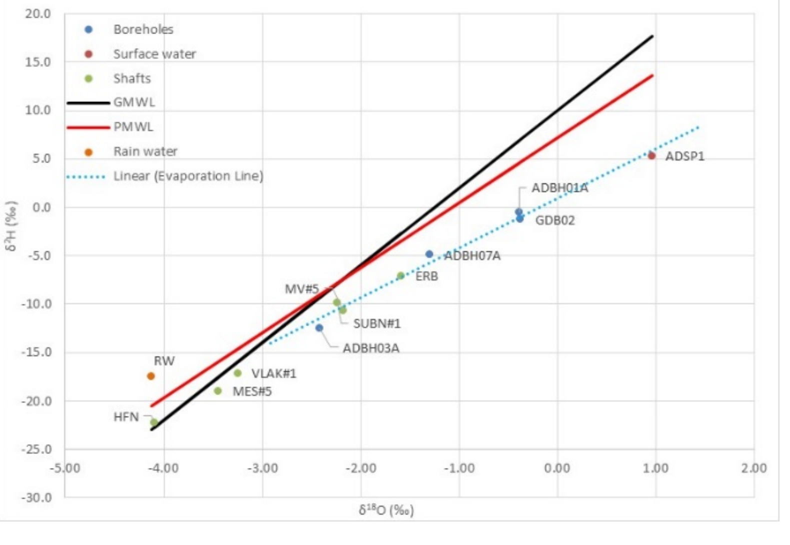

Figure 3 *Meteoric water plot for surface water, boreholes (Alexander Dam) and shafts.*

in the north of Blesbokspruit (MES#5 and HFN) plotted along the meteoric water line showing a possibility of recharge by surface or groundwater that was not prone to evaporation (depletion in $\delta^{18}O$ and $\delta^{2}H$ isotopes). Thus, these shafts might not be linked to surface water bodies that were sampled in this study since they all plotted along the evaporation line.

The meteoric water plot shows groundwater around Alexander Dam plotting along the evaporation line together with shafts SUBN#1, MV#5 and ERB and surface water ADSP1 (fig.3). These sites may be receiving their water from precipitation and evaporated water. Unlike the rest of the boreholes water, ADBH03A is more depleted in $\delta^{18}O$ and $\delta^{2}H$ isotopes.

All surface water (CDSP1 and CDSP2) plot along the evaporation line (fig.4), although CDSP1 is more enriched in $\delta^{18}O$ and $\delta^{2}H$. This could be because of the distance this water travels from CDSP2 where it becomes prone to evaporation. CDSP1 and CDSP2 further plots close to BH32 and BH33 respectively. CDSP2 could be receiving recharge from both surface and groundwater. Whereas, BH33 and BH32 could be receiving recharge from water that underwent a high degree of evaporation as opposed to water from precipitation. BH1, BH27, BH4, BH15, BH19 and BH18 (fig.4) show recharge by precipitation or water that did not undergo long period of evaporation and plots along the meteoric water line. These sites are situated in the same vicinity.

Tritium dating

Tritium was measured in TU with the water signatures ranging between 0.2 – 5.2 TU. According to Murray *et al* (2015), this is an indication of old water (<1.0 TU) that was recharged before 1960, recent water (1.0 – 4.0 TU) and possibly waste contaminated water (>4.0 TU). It is explained that South African rain water have a natural tritium concentration of about 3 TU, as also observed on the acquired tritium results in tab.1 (rainwater sample). Almost all the water sampled from surface, boreholes and shaft appeared to be of recent recharge period because of tritium content that matches one of present-day rainfall. Measurable tritium concentration in these sites gives an indication of surface water-groundwater interaction confirming the ingress of surface water to groundwater and mine voids. However, other sites displayed tritium concentration of less than 1.0 TU. These are shafts MES#5 and HFN and groundwater from ADBH03A, BH33, BH19, BH4 and BH18. Lastly, surface water from CDSP1 displayed tritium amount of 5.2 TU.

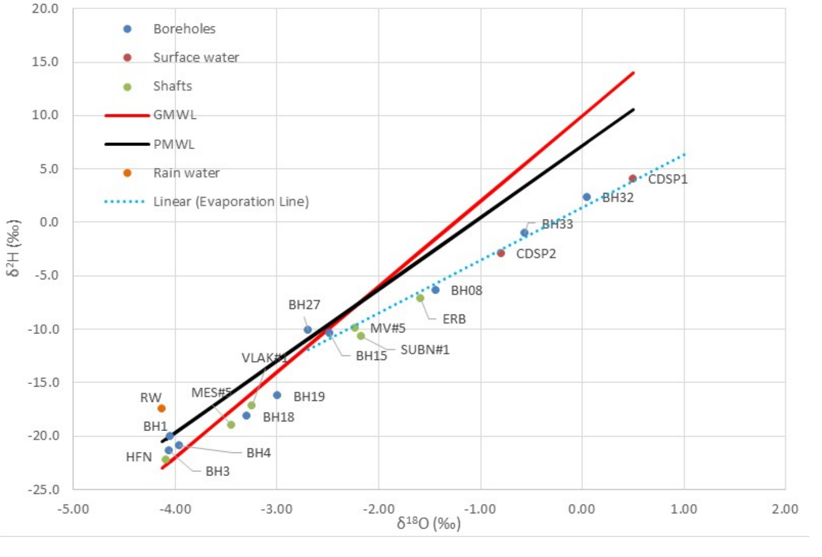

__Figure 4__ Meteoric water plot for surface water, boreholes (Cowles Dam) and shafts.

Table 1 Tritium results for surface water, groundwater, shafts and rainwater in the Eastern Basin.

Sample ID	Tritium (T.U.)			Sample ID	Tritium (T.U.)		
ERB	1.0	±	0.3	BH33	0.7	±	0.3
VLAK#1	1.3	±	0.3	BH27	1.8	±	0.3
MES#5	0.9	±	0.3	BH32	1.1	±	0.3
HFN	0.2	±	0.2	BH08	3.2	±	0.4
SUBN#1	2.0	±	0.3	BH19	0.9	±	0.3
MV#5	1.5	±	0.3	BH3	1.2	±	0.3
ADSP1	2.4	±	0.4	BH1	1.1	±	0.3
CDSP1	5.2	±	0.4	BH4	0.7	±	0.3
CDSP2	1.9	±	0.3	BH18	0.3	±	0.3
ADBH07A	2.5	±	0.3	BH15	2.6	±	0.4
ADBH01A	2.9	±	0.3	GDB02	2.9	±	0.4
ADBH03A	0.7	±	0.3	Rain Water	3.3	±	0.4

Conclusions

Water types as deduced from the Piper plot are; Na-HCO_3, Mg-Cl-HCO_3, Na-SO_4, Mg-HCO_3 and Ca-Mg-SO_4. The findings indicated that groundwater displayed Na-SO_4 and Mg-Cl-SO_4/HCO_3 water types, whereas mine voids water showed Ca-Mg-SO_4 water type. The water compositions are assumed to be influenced by both geological and anthropogenic activities.

The application of environmental isotopes is useful in tracing the source and pathway of the water. Further, to measure the age of modern water. The application of environmental isotopes in this study gave an indication that surface water ingress the subsurface. This was experimented at Alexander and Cowles Dam where groundwater and shafts were showing recharge by meteoric water and water that has undergone evaporation. Additionally, as obtained from tritium results, most shafts and groundwater appeared to be receiving modern recharge with reference to the modern rainfall in South Africa.

However, shafts MES#5 and HFN that displayed different water type and plotted along the meteoric water line apart from other shafts displayed tritium concentration of less than 1.0 TU, which is an indication of old water in these sites. Moreover, most boreholes that plotted along the meteoric water line also displayed water of less than 1.0 TU.

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