Determination of isotopic composition of rainwater to generate local meteoric water line in Thohoyandou, Limpopo Province, South Africa

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ABSTRACT

Hydrogen (D) and oxygen (^{18}O) isotopic compositions of precipitation are useful tools to delineate the nature of precipitation, groundwater recharge and climatological investigations. This study investigated the isotopic composition of 12 rainfall occurrences at Thohoyandou, with the objective of generating the local meteoric water line (LMWL) and determining the factors controlling the isotopic composition of the rain. The delta (δ) values for D and ^{18}O of the samples were determined using a Thermo Delta V mass spectrometer connected to a Gasbench. Thohoyandou rainwater showed a wide range of stable isotope values; δD values of the rainwater varied from −76.3‰ to +22.7‰ (SMOW) with a weighted mean of −9.8‰ and $\delta^{18}O$ values ranged from −10.78‰ to +3.07‰ (SMOW) with a weighted mean of −2.7‰. δ-values of rainwater were more enriched during winter and more depleted during summer, due to the amount of rainfall and seasonal effect. The LMWL in Thohoyandou is defined by $\delta D = 7.56\delta^{18}O + 10.64$, which shows a similar slope to the global meteoric water line (GMWL) but with a slightly higher intercept, of 10.64‰ instead of 10‰. This implies that the process of rain formation in Thohoyandou occurred under equilibrium conditions which are not significantly affected by evaporation. The slightly higher d-intercept value above the GMWL reflects an additional supply of recycled moisture across the regions. This implies that there is no continental effect but inland moisture from various water bodies and vegetation.

Keywords: evaporation effect, hydrogen and oxygen isotopes, local meteoric water line, rainwater, Thohoyandou

INTRODUCTION

Thohoyandou is one of the fastest growing towns within the Soutpansberg Group in Thulamela Local Municipality of Vhembe District in Limpopo Province, South Africa (Vhembe District Municipality, 2007). Increasing urbanisation in Thohoyandou is putting pressure on water supplies. The district comprises of a few catchment areas which are stressed due to high demand for water for developmental activities such as agriculture, human consumption and mining, due to a limited supply of both ground and surface water. Water management in the district faces the following challenges: imbalance between supply and demand for water, alien invasion, inappropriate land uses in the river valleys, the impact of fertilizers and pesticides, inadequate monitoring, poorly managed sewerage systems, high concentrations of pit latrines, flood events and droughts (Vhembe District Municipality, 2007).

Groundwater is a major source of water supply to most households in Thohoyandou. Groundwater recharge in Thohoyandou needs to be assessed and monitored as an important part of water resource management. Variation in stable isotopes of hydrogen (D) and oxygen (^{18}O) in precipitation forms the primary background data for groundwater recharge investigations (Ingraham, 1998; Gupta and Deshpade, 2003; Gat, 2010; Kortelainen, 2009). These include the sources and timing of recharge, retention time and circulation of groundwater (Kortelainen, 2009). Such a study will require long-term data for stable isotopes in rainfall (IAEA/WMO, 2015). Unfortunately, there are limited and non-coherent datasets for δ^2H and $\delta^{18}O$ of rainwater in the Province, which provide incomplete information. This necessitated the short-term monitoring of rainfall for one hydrological cycle in Thohoyandou; to assess the stable isotope composition of the rainwater to generate the local meteoric water line (LMWL), which is crucial to the evaluation of groundwater recharge.

Precipitation is the ultimate source of groundwater in most systems. However, knowledge of the factors that control the isotopic composition of precipitation before and after recharge enables the use of oxygen and hydrogen isotopes as tracers of water sources and processes. The natural processes that cause variation of isotopic composition of precipitation are (i) the temperature of the condensation of the precipitation and (ii) the degree of rainout of the air mass at phase change (Gat, 2010). Thus, the change in the isotopic composition of natural water occurs during its passage into the atmosphere or when it is subjected to a chemical reaction (Yurtsever and Araguas, 1993; Criss, 1999). The light molecules of water are more volatile than the heavier ones. Then cooling of the atmospheric moisture enhances the heavy molecules' condensation preferentially, leaving a residual vapour more and more depleted in heavy isotopes. Such sequential condensation occurs as air masses move inland from the sea or rise to higher altitude (Criss, 1999).

On a regional scale, the distribution of isotopic composition is controlled by several factors, such as altitude effect, latitude effect, continental effect and amount effect (Yurtsever and Araguas, 1993). Rivers might be depleted in heavy isotopes due to their precipitation from higher altitudes. In ponds or lakes, the water might be considerably enriched in heavy isotopes through evaporation, and will deviate from a linear relationship between D and ^{18}O usual for precipitation (Yurtsever and Araguas, 1993). This linear relationship between D and ^{18}O was derived by Dansgaard (1964). It was referred to as the 'global meteoric water line' (GMWL), upon which stable isotope interpretation of hydrological processes is based.

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Therefore, this study aimed to measure the stable isotope composition of rainwater in Thohoyandou in order to determine its origin (meteoric or continental). There is a need to have sound knowledge of the factors that control the isotopic composition of rainwater; hence, hydrogen and oxygen isotopes were used as tracers of water sources and processes. This study investigated occurrence of D and ^{18}O values of rainwater at the University of Venda, Thohoyandou, from May 2016 to May 2017. The study was aimed at generating the local meteoric water line and determining the conditions that control the isotopic composition of rainwater in Thohoyandou. The generated equation (TLMWL) will be an essential reference for future studies, particularly in this area. The stable isotopes of δD and $\delta^{18}O$ can be used to determine sources of groundwater recharge, determine water-mineral exchange, evaluate surface-water and groundwater interaction, and to analyse other geochemical and hydrologic problems within the region.

STUDY AREA

Climatic characteristics

Rainwater samples were collected at the University of Venda in Thohoyandou within Thulamela Municipality, Vhembe District of Limpopo Province, South Africa (Fig. 1). Thohoyandou is the major town in the municipality. The municipality is situated in the eastern subtropical region of the province, and is categorised as falling within the hot semi-arid region (Kottek et al., 2006). It receives much of its rainfall during summer (November to February), as the area is within the northward and southward oscillation of the inter-tropical convergence zone (ITCZ) and associated southerly monsoon winds (Kabanda, 2004). The mean annual rainfall of Nzhelele ranges from 350–400 mm (Makungo et al., 2010). More than 80% of rainfall occurs in summer (DWAF, 2001). The average temperature ranges from 35°C in summer to 18°C in winter (Kabanda, 2004). Figure 2 shows the rainfall and temperature data obtained from the South African Weather Service for the period from May 2016 to May 2017. The land use of the municipality includes residential, subsistence agriculture and commercial uses in Thohoyandou town. Informal businesses within and around the town play a significant role in the community's economic and social life.

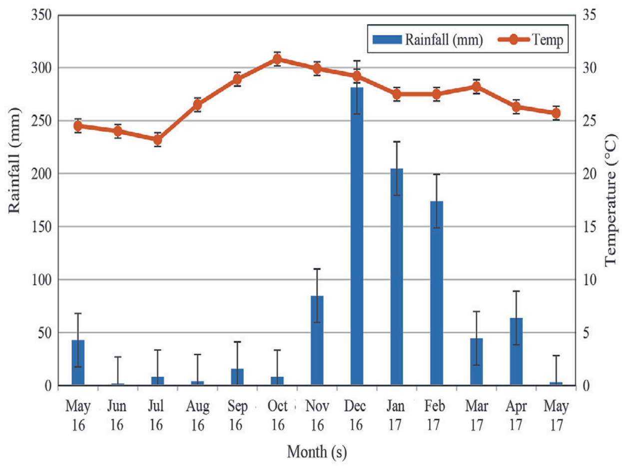

Figure 2
Monthly variation of the rainfall and temperature from May 2016 to May 2017 (obtained from the South African Weather Service)

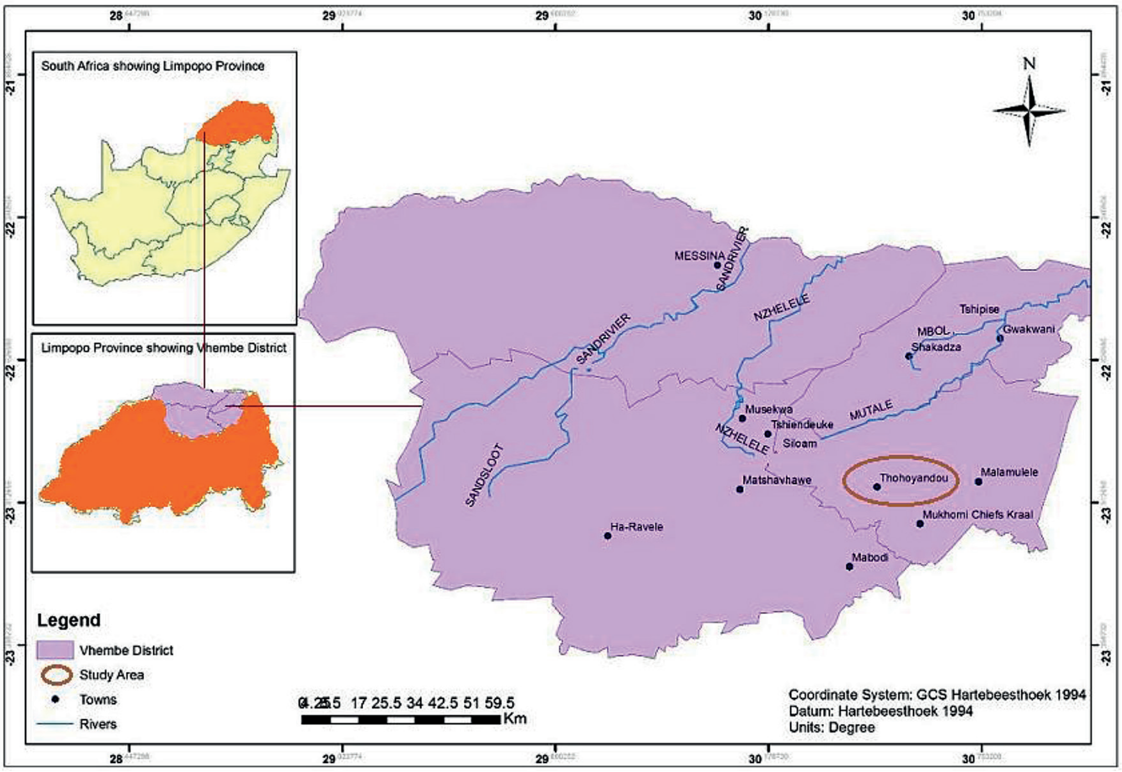

Figure 1
Map of Vhembe District showing Thohoyandou town and other towns, Limpopo Province, South Africa

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Geology and hydrogeology

The rock of the Soutpansberg Group shows a 30° dipping towards the north-northwest direction, with pronounced extensional faults categorised as the dominant east-north-east to west-south-west and the less-dominant north-west to north-west-north (Fig. 3) (Brandl, 1986; Brandl, 2002; Johnson et al., 2006; Barker et al., 2006). The dominant ENE trending fault is believed to be old and started occurring as far back as the formation of Soutpansberg strata. The Soutpansberg strata, though foliated, are not regionally strongly fractured but are often found to be locally fractured (Brandl, 2002). There is a heavy presence of fault planes, intruded diabase dykes and shale-quartzite interface intruded sill (Brandl, 2002). Due to the nature of the geological formation in the study area, groundwater is stored and transmitted through fractures and faults (Brandl, 1986). The geology and soil of the sites consist of fertile clay soil, sandy soil and clay loam soil. The Soutpansberg Group comprises of a volcano-sedimentary succession which is subdivided into 7 formations (Fig. 3); Tshifefe, Sibasa, Fundudzi, Willies Poort, Nzhelele, Stayt and Mabiligwe (Brandl, 2002; Johnson et al., 2006). Thohoyandou falls under the Sibasa Formation, which is dominantly a volcanic succession, with rare discontinuous intercalations of clastic sediments, having a maximum thickness of about 3 000 m. The volcanic succession comprises basalts, which were sub-aerially extruded and minor pyroclastic rocks. The basalts are amygdaloidal, massive and generally epidotised. The clastic sediments, which include quartzite, shale and minor conglomerate, can reach a maximum thickness locally of 400 m. A radiometric age of 1 749 ± 104 Ma was obtained (Johnson et al., 2006).

Thohoyandou falls under the Sibasa Formation within Soutpansberg Group

EXPERIMENTAL SECTION

Sampling and analysis

Twelve rainwater samples (ME 01 to ME12) were collected from May 2016 to April 2017 at the University of Venda, Thohoyandou. ME01 to ME05 and ME12 were collected from May to October 2016 and May 2017 (winter) while ME06 to ME11 were collected from November 2016 to April 2017 (summer). The samples were collected by attaching a funnel to a high-density polyethylene bottle and kept in an open area for direct collection of rainwater. Immediately after the rain the bottle was unscrewed from the funnel and sealed with a plastic cone cap (Muhammed and Sadiq, 2014). The samples were preserved and stored in the refrigerator at 4°C before being taken to the laboratory for isotopic analysis.

Stable isotope analyses of the samples were performed using Thermo Delta V mass spectrometer connected to a Gasbench at Environmental Isotope Group (EIG) iThemba Laboratories Gauteng, Johannesburg, South Africa. The water samples were equilibrated in preparation for measurement. The standard side of the dual inlet system was connected to a tank of reference hydrogen (δD) and reference carbon dioxide ($\delta^{18}O$). The equilibration time of the water samples with hydrogen gas was 40 min; whereas carbon dioxide gas was equilibrated with water samples in about 20 h. Laboratory standards, calibrated against international reference materials, were analysed with each batch of the samples. The samples were prepared in duplicate and run to obtain average values which are presented in Table 1.

Conventionally, the isotope ratios of $^{2}H/^{1}H$ and $^{18}O/^{16}O$ in the water samples were expressed as per mil (‰) deviation relative to the Standard Mean Ocean Water (SMOW) as follows:

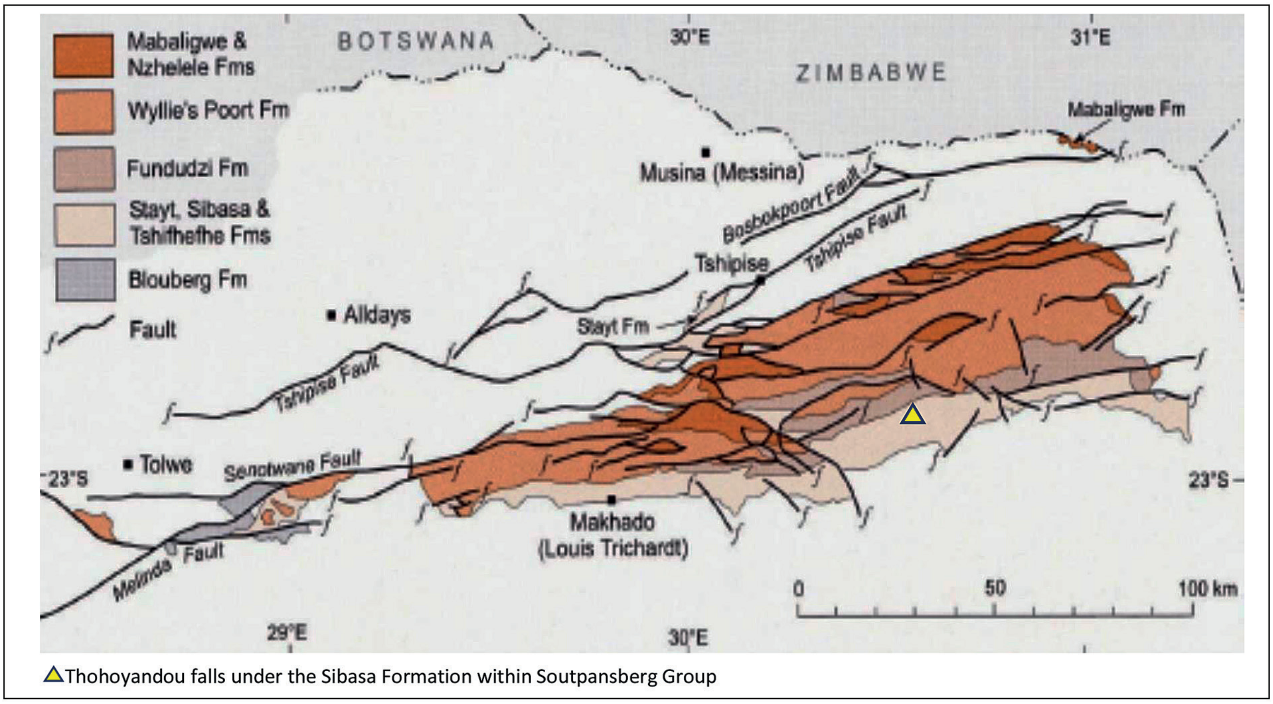

Figure 3
Distribution of the formations in the Soutpansberg Group as well as the Blouberg Formation (modified after Barker, 1979)

$$\delta\ (‰) = \frac{R_{sampLe} - R_{smow}}{R_{smow}} \times 1\ 000 \quad (1)$$

where: R represents the ratio of heavy to light isotopes (D/H or $^{18}O/^{16}O$) in the sample and standard, respectively. The oxygen and hydrogen isotopic ratios were henceforth expressed individually as $\delta^{18}O$ and δD, respectively, or collectively as δ values. Total analytical precisions were estimated at 0.2 ‰ for $\delta^{18}O$ and 0.8‰ for δD. Deuterium excess (d-excess) was calculated from the following equation (Dansgaard, 1964):

$$d = \delta D - 8 \times \delta^{18}O \quad (2)$$

RESULTS AND DISCUSSION

ME01 to ME05 and ME12 were collected from May to October 2016 and April 2017 (winter) while ME06 to ME11 were collected from November 2016 to March 2017 (summer). Table 1 shows the isotopic composition of rainwater occurrences between May 2016 and April 2017 at the University of Venda, Thohoyandou. According to the International Atomic Energy Agency (IAEA) (IAEA-IMO 2015), warm regions are characterised by more enriched isotopic values (+ve) of D and ^{18}O while cooler regions are characterised by more depleted isotopic values (-ve). The study area falls under the hot semi-arid region of the country and it is expected to have more enriched isotopic values of D and ^{18}O in the rainwater samples, but the seasonal effect is observed in the study. Figure 4 shows that the area has most of its rainfall from November 2016 to February 2017, which constitutes the part of the summer when samples (ME06 – ME011) were taken and the isotopic values were more depleted (Fig. 4; Table 1), whereas more enriched isotopic values were obtained from May to October 2016 (ME01 – ME05) and in April 2017 (ME12).

This could be because of the 'amount' effect, i.e., the lower the volume of rainfall, the higher the $\delta^{18}O$ or δD content (Dansgaard, 1964; Coplen et al., 2000) (Fig. 4). This proves that there is a strong negative correlation between the rainfall amount and the isotopic composition (δD or $\delta^{18}O$). The amount effect, which is a profound characteristic of tropical low-latitude precipitation, has also been observed in Thohoyandou, South Africa (this study) and in studies in other locations, such as Cameroon (Njitchoua et al., 1999; Kuitcha et al., 2012; Wirmvem et al., 2014), Nigeria (Mbonu and Travi, 1994), Niger (Taupin et al., 2000; Risi et al., 2008), Ghana (Adomako et al., 2015), Ethiopia (Kebede and Travi, 2012; Kebede, 2013), Costa Rica (Sa'nchez et al., 2013) and India (Rai et al., 2013).

The rainwater samples collected from the area of study show a wide range of stable isotope composition (Table 1); the δD values of the rainfall varied from −76.3‰ to +22.7‰ (SMOW) with a weighted mean of −9.8‰, and $\delta^{18}O$ values ranged from −10.78 ‰ to +3.07‰ (SMOW) with a weighted mean of −2.7‰ (n = 12). This indicates the degree of evapotranspiration in the study area. The d-excess values varied widely, from −6.60 to 21.09‰ with a mean d-excess value of 11.8‰. As shown in Table 1, the annual mean d-excess values in rainwater were above 10‰ of the ocean moisture (Dansgaard, 1964), which is the primary source of most rainfall, although transpired moisture can be an important moisture source for many terrestrial regions (Brubaker et al., 1993). High d-excess values (>10‰) suggest an additional source of moisture, such as moisture recycling, among others (Wirmvem et al., 2017).

TABLE 1
Stable isotope composition of contemporary rainwater in Thohoyandou

Sample code	δD (‰)	δ¹⁸O (‰)	d-excess (‰)
ME01	16.0	−0.48	19.81
ME02	22.1	1.94	6.58
ME03	15.2	−0.74	21.09
ME04	1.3	−1.81	15.78
ME05	18.0	3.07	−6.60
ME06	−49.6	−7.22	8.14
ME07	−76.3	−10.78	9.93
ME08	−4.2	−2.18	13.25
ME09	−41.9	−6.75	12.03
ME10	−15.9	−3.89	15.22
ME11	−24.5	−5.19	17.06
ME12	22.7	1.61	9.77
Mean value (s)	−9.8	−2.7	11.8

Weather and climate differ from place to place with variation of rainfall, temperature, and wind, and these factors contribute to shifts in the local meteoric water line (LMWL) relative to the GMWL (Fig. 5). From this study, the 'amount' effect yielded isotopically light rainfall; suggesting that the weather is responsible for determining where on the meteoric water line the data fall. However, the meteoric water line also shifts from a point to an outlier position below/above the GMW line, due to kinetic effects associated with evaporation (Gat, 1996; Sa'nchez et al., 2013; Rai et al., 2013; Wirmvem et al., 2017). This accounts for the slight differences in the LMW lines for Cape Town, Pretoria and Thohoyandou (Fig. 6).

The observed wide range of stable isotope compositions of rainwater in one hydrological year in Thohoyandou could be as a result of seasonality (basically winter and summer). The distinctive variations in isotopic signatures based on rainfall occurrence offer a tool to determine the timing of groundwater recharge within the Soutpansberg Group. Most of the rainfall occurs during the hot season (summer). There is evidence of

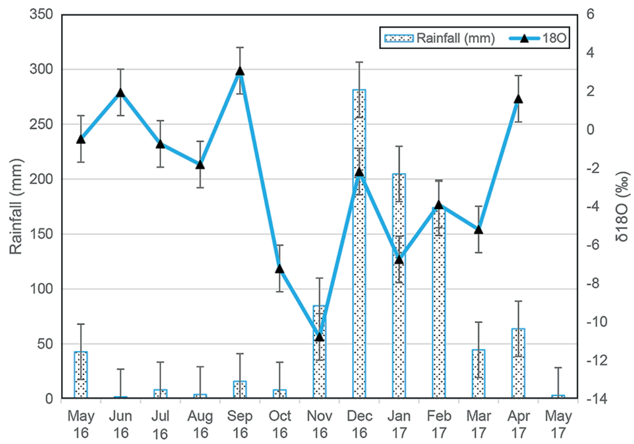

Figure 4
Variation of $\delta^{18}O$ as a function of the monthly rainfall from May 2016 to May 2017 in Thohoyandou

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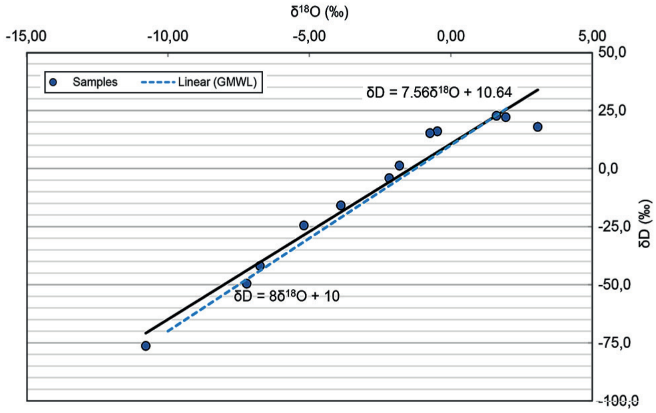

Figure 5
Conventional $\delta^{18}O$–δD relationships of rainwater from May 2016 to May 2017 at Thohoyandou. The relationships show the Thohoyandou local meteoric water line (TLMWL) in comparison with the global meteoric water line (GMWL).

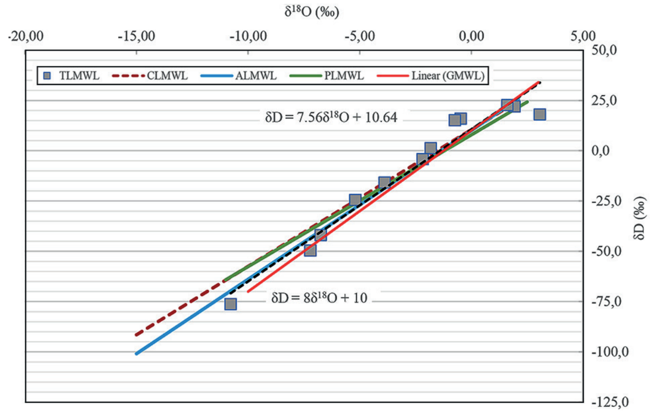

Figure 6
The relationships show the Thohoyandou local meteoric water line (TLMWL) in comparison to the global meteoric water line (GMWL), Africa local meteoric water line (ALMWL), Cape Town local meteoric water line (CLMWL) and Pretoria local meteoric water line (PLMWL)

depleted values with heavy rainfall, but enriched values are associated with low rainfall (Fig. 4) (Wirmvem et al., 2017). The observed depleted $\delta^{18}O$ values in the rainwater within the period (Fig. 3) could possibly be associated with the higher vertical velocity of ascending air masses and smaller effect of exchange between atmospheric air leading to more rainout fractionation effect (Joseph et al., 1992). Meanwhile, enriched isotopic values at the edges of the rainy season are likely due to large exchange with atmospheric vapour, and partial evaporation of the raindrops during rainfall (Gat, 2010; Taupin et al., 2000; Rai et al., 2013).

The $\delta^{18}O$–δD plot of the one-hydrological year data gave the regression line that represents the local meteoric water line for Thohoyandou (TLMWL):

$$\delta D = 7.56\delta^{18}O + 10.64 \quad (3)$$

Equation 3 shows a similar slope to the GMWL of Craig (1961) but with a relatively high d-intercept. This implies that the process of rain formation in Thohoyandou within the Soutpansberg Group, Limpopo Province, occurs in equilibrium conditions with a minor evaporation effect when raining. The slightly high d-excess value is an indication that the rainwater is formed from water vapour evaporation near the land surface, i.e., either by re-condensation of the evaporated rainfall or evaporation of surface waters such as the Limpopo River and Nzhelele River, among others (Russel and Johnson, 2006). The slope also suggests that the raindrops were not notably affected by evaporation (Dansgaard, 1964; Craig, 1961; Rozanski et al., 1993), including the small and enriched rain events from May to August 2016 with high d-excess values (Table 1).

The stable isotopic composition (δD and $\delta^{18}O$) of the rainwater samples for Thohoyandou were compared to the global meteoric water line (GMWL) ($\delta D = 8\delta^{18}O + 10$; Craig, 1961), Africa local meteoric water line (ALMWL) ($\delta D = 7.4\delta^{18}O + 10.1$; Cohen et al., 1997), Cape Town local meteoric water line (CLMWL) ($\delta D = 6.8\delta^{18}O + 10.5$; Harris et al., 1999) and Pretoria local meteoric water line (PLMWL) ($\delta D = 6.55\delta^{18}O + 7.9$; Abiye et al., 2011) (Fig. 6). Slight differences in the d-intercept of the meteoric lines (10 for GMWL; 10.1 for ALMWL; 10.5 for CLMWL; 7.9 for PLMWL and 10.64 for TLMWL) may be attributed to changing conditions in the source of atmospheric moisture (Gonfiantini et al**.**, 2001) and local climatic effects such as re-evaporation (Taupin et al., 2000; Salati et al., 1979 and Liu et al., 2014). From the ALMWL, it can be deduced that rain formation in Africa occurs under equilibrium, with a minor evaporation effect during rain droplet formation. A study by Joseph et al. (1992) reported that there was no continental effect (effect due to distance from the coast) in Africa, which was supported by studies from Cameroon, Nigeria, Ethiopia, and Kenya (Wirmvem et al., 2017; Muhammad and Sadiq, 2014: Kebede and Travi, 2012; Kebede, 2013). Hence, this finding supports the lack of a continental effect suggested by other studies in Sub-Saharan Africa.

Climatic and geographic factors play a vital role in the differences between the LMW lines and GMWL. For instance, Cape Town gets most of its rainfall in winter, compared to Thohoyandou that receives mostly summer rainfall. The generated local meteoric water line (TLMWL) is useful in assessing the origin and mechanism of groundwater recharge in the locality. The recharge value can be obtained by integrating the rainfall value with the stable isotope values (D and ^{18}O). Integrated recharge values are calculated by multiplying the $\delta^{18}O$ and δD values recorded for each month, by the fraction of rainfall that fell in that month, the fraction being calculated as a rainfall fraction for all of the months in which data were collected (Diamond, 1997).

Salati et al. (1979) explained that, during evaporation high d-excess values are obtained when the increase in evaporated moisture is such that precipitation from such moisture decreases in residual moisture. In the study, about 60% of the samples had d-excess values greater than 10 ‰ (Table 1). The d-excess value is useful for the determination of the relative contributions of inland moisture and oceanic moisture to groundwater recharge, as well as the conditions of recharge. This depletion effect has been called the 'continental effect' and results in lighter stable isotope ratios furrther away from the ocean. The higher d-intercept further reflects a possibility of an additional supply of recycled regional moisture across the region. The results of this study imply that there is no continental effect, due to the added inland moisture from vegetation and numerous water bodies in the region to precipitation. The generated TLMWL will be used to determine sources of groundwater recharge,

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determine water-mineral exchange, evaluate surface-water and groundwater interaction, and to analyse many other geochemical and hydrologic problems within the region.

CONCLUSION

Stable isotope composition for the rainwater occurrences between 2016 and 2017 at Thohoyandou (peri-urban settlement) was investigated. Results showed wide and distinctive isotopic variations that ranged from −10.78 to +3.07 ‰ for $\delta^{18}O$ and −76.3 to +22.7‰ for δD. Rain formation processes at Thohoyandou occurred under isotopic equilibrium condition with a minor evaporation effect during the precipitation, as reflected by the slope of the local meteoric water line of $\delta D = 7.56\delta^{18}O + 10.64$. The LMWL is then used as reference to understand isotopic composition leading to the formation of the water resources within the specific location. The higher d-intercept value above the GMWL (10 ‰) reflects a possibility of an additional supply of recycled moisture across the region. This implies that there is no continental effect but inland moisture from various water bodies and vegetation. Also, it could be attributed to changing conditions at the source of atmospheric moisture, and local climatic effects such as re-evaporation. There is a need for long-term stable isotopic records in the study area and across South Africa, which will be used as a tool for improved water resource evaluation and climatic studies, especially in a changing climate.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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