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Determination of local meteoric water lines along a precipitation gradient, Namibia

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ABSTRACT

Precipitation is the main input parameter in the hydrological balance and plays important role in groundwater recharge. Isotopic fingerprints are a tool to trace this component. In this study, isotopic composition of precipitation was determined along a precipitation gradient at three sites namely: Tsumeb ($600 mm/a$ precipitation; Waterberg ($450 mm/a$) and Kuzikus/Ebenhaezer ($240 mm/a$ precipitation). Precipitation samples from Tsumeb and Waterberg were collected during the rainy season from 2017 to 2018, while Kuzikus/Ebenhaezer samples were collected between 2014 and 2015. A total number of 83 precipitation samples were collected. Precipitation samples were analysed using a Los Gatos water stable isotope spectro-analyser at the University of Namibia. Precipitation isotopic values for $\delta^{18}\mathrm{O}(‰)$ range from -9.08 to 5.19 for Tsumeb, -15.96 to 5.09 for Waterberg and -12.54 to 4.75 for Kuzikus/Ebenhaezer, while $\delta^{2}\mathrm{H}(‰)$ isotopic values for Tsumeb, Waterberg and Kuzikus/Ebenhaezer range from -73.30 to 46.70; -117.50 to 40.60 and -82.50 to 47.80, respectively. Scattering of rain samples along the global meteoric water line in the areas could be attributed to a seasonal effect. Local meteoric water line equations for Tsumeb, Waterberg and Kuzikus/Ebenhaezer were obtained using a linear regression method and are $\delta^2\mathrm{H} = 7.78\,\delta^{18}\mathrm{O} + 6.74$, $R^2 = 0.95$; $\delta^2\mathrm{H} = 7.37\,\delta^{18}\mathrm{O} + 5.77$, $R^2 = 0.97$; $\delta^2\mathrm{H} = 7.16\,\delta^{18}\mathrm{O} + 9.88$, $R^2 = 0.96$ correspondingly. All the slopes obtained from three study sites are lower than that of a global meteoric water line equation. A lower slope could be an indication that the local precipitation has experienced some subcloud evaporation, leading to enrichment of heavy isotopes. The effect is more pronounced at Kuzikus/Ebenhaezer where the slope is 7.16. Our findings could serve as baseline for these three study sites with regards to further isotopic investigations in the study areas especially in tracing the origin of groundwater.

1 Introduction

Precipitation is the main input parameter in the hydrological cycle and plays a major role in groundwater recharge. To understand the process of groundwater recharge based on its isotopic fingerprint, it is important to first understand the isotopic composition of precipitation that serves as the parent source of groundwater through recharge processes. Craig (1961) derived an equation for the Global Meteoric Water Line (GMWL) based on meteoric water from many places around the world as follows: $\delta^2\mathrm{H} = 8\,\delta^{18}\mathrm{O} + 10‰$ SMOW, Whereby $\delta^2\mathrm{H}$ is the concentration of deuterium relative to protium in unit of per mill ($‰$) of a sample compared to a standard; $\delta^{18}\mathrm{O}$ is the concentration of oxygen-18 relative to oxygen-16 in unit of per mill ($‰$) of a sample compared to a standard, and the standard is SMOW (standard mean ocean water).

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Isotopic composition of precipitation ($\delta^2\mathrm{H}$ and $\delta^{18}\mathrm{O}$) is controlled by factors and processes such as meteorological conditions that are controlling evaporation of water from the ocean; rainout mechanisms, which influence the fraction of precipitable water; second-order kinetic effects such as snow formation or evaporation below cloud base and admixture of recycled water from evapotranspiration over the continents (Araguás-Araguás *et al.*, 2000; Gat, 2000; Gibson *et al.*, 2008). Variations in $\delta^2\mathrm{H}$ and $\delta^{18}\mathrm{O}$ values of precipitation water result from both equilibrium and kinetic fractionations depending on many factors and processes. These processes include conditions of air moisture source areas, air moisture transport trajectories, precipitation histories, weather systems leading to precipitation, and subcloud processes (Guan *et al.*, 2013).

A meteoric water line is characterized by two parameters, i.e. slope and intercept which is a deuterium excess (d-excess). The slope and d-excess for the meteoric water line depend on hydrological parameters (Singh, 2017). Generally, the slope of a meteoric water line should be close to 8 which is the theoretic Craig slope under equilibrium conditions. However, the slope value could be lower than 8 during non-equilibrium processes such as evaporation or be greater than 8 for condensation (Dansgaard, 1964). The d-excess equation was first formulated by Dansgaard (1964) as $d = \delta^2\mathrm{H} - 8\,\delta^{18}\mathrm{O}$ whereby $\delta^2\mathrm{H}$ and $\delta^{18}\mathrm{O}$ stand for the deuterium and oxygen-18 abundance relative to VSMOW (Vienna Standard Mean Ocean Water). It is used to constraint the source of precipitation as well as the conditions during vapour transport to the precipitating site (Aemisegger *et al.*, 2014; Bershaw, 2018; Pang *et al.*, 2011; Pfahl and Sodemann, 2014; Uemura *et al.*, 2008). The d-excess parameter has been shown to be a diagnostic tool for measuring the contribution of evaporated moisture to the downwind atmosphere (Gat, 1996). Craig (1961) derived the global d-excess value from the GMWL as $10‰$. Lower than $10‰$ d-excess values are likely due to enhanced subcloud evaporation of raindrops which is common in arid regions (Bershaw, 2018; Wang *et al.*, 2016). Higher d-excess of vapour is observed when relative humidity is low over evaporating water bodies. The more kinetic fractionation that occurs, the higher the d-excess is observed in vapor (Bershaw, 2018).

Although studies have been carried out to determine local precipitation lines such as those of Kaseke *et al.* (2016); Wanke *et al.* (2018); these studies focused on particular areas but have not identified a correlation between local meteoric water lines and the precipitation gradient in Namibia. Therefore a gap is identified to determine local meteoric water lines along a precipitation gradient. In this study, the $\delta^2\mathrm{H}$ and $\delta^{18}\mathrm{O}$ values of precipitation samples that were collected from Tsumeb, Waterberg and Kuzikus/Ebenhaezer are investigated with the main objective of determining local meteoric water lines along a precipitation gradient, and to understand isotopic variations.

2 General descriptions of study sites

The study was carried out along a precipitation gradient from Tsumeb in the northern part of Namibia, Waterberg in the central region and Kuzikus/Ebenhaezer in south-eastern Namibia. The study sites show a precipitation gradient from about $600 mm/a$ to $200 mm/a$ (Figure 1). Tsumeb area lies within the south-eastern part of Cuvelai-Etosha Basin (CEB). The area receives exceptionally high annual precipitation compared to the rest of the country with an annual precipitation rate of about $600 mm/a$ and an annual potential evaporation rate ranging between 2000 to $3000 mm/a$ (DWA, 1988). The Tsumeb area is known for its intensive agricultural activities as well as mining activities. The Waterberg area is found in the south-western part of Omatako Basin. The area receives an annual precipitation of about $450 mm/a$ and has a potential evaporation of about $2800 mm/a$ (DWA, 1988). The study area is part of the Waterberg Plateau National Park which is remarked by flowing springs at the foot of the plateau. The Kuzikus/Ebenhaezer area falls within the northern part of the Stampriet Basin, where the annual precipitation ranges between $175 mm$ to $240 mm$, with potential evaporation varying from $3000 mm/a$ to $3500 mm/a$ (DWA, 1988). The study area is associated with cattle and game farming activities.

The rainy season in Namibia starts in October and ends in April of the following year. Mean annual precipitation isohyets are presented in Figure 1a). Long-term climatic conditions thus mean monthly precipitation and mean monthly temperatures were obtained from nearest weather stations to the sites namely: Tsumeb station (for the Tsumeb site); Okakarara station (for the Waterberg site) and Leonardville station (for the Kuzikus/Ebenhaezer site). A summary of these climatic conditions are presented in Figure 1 b).

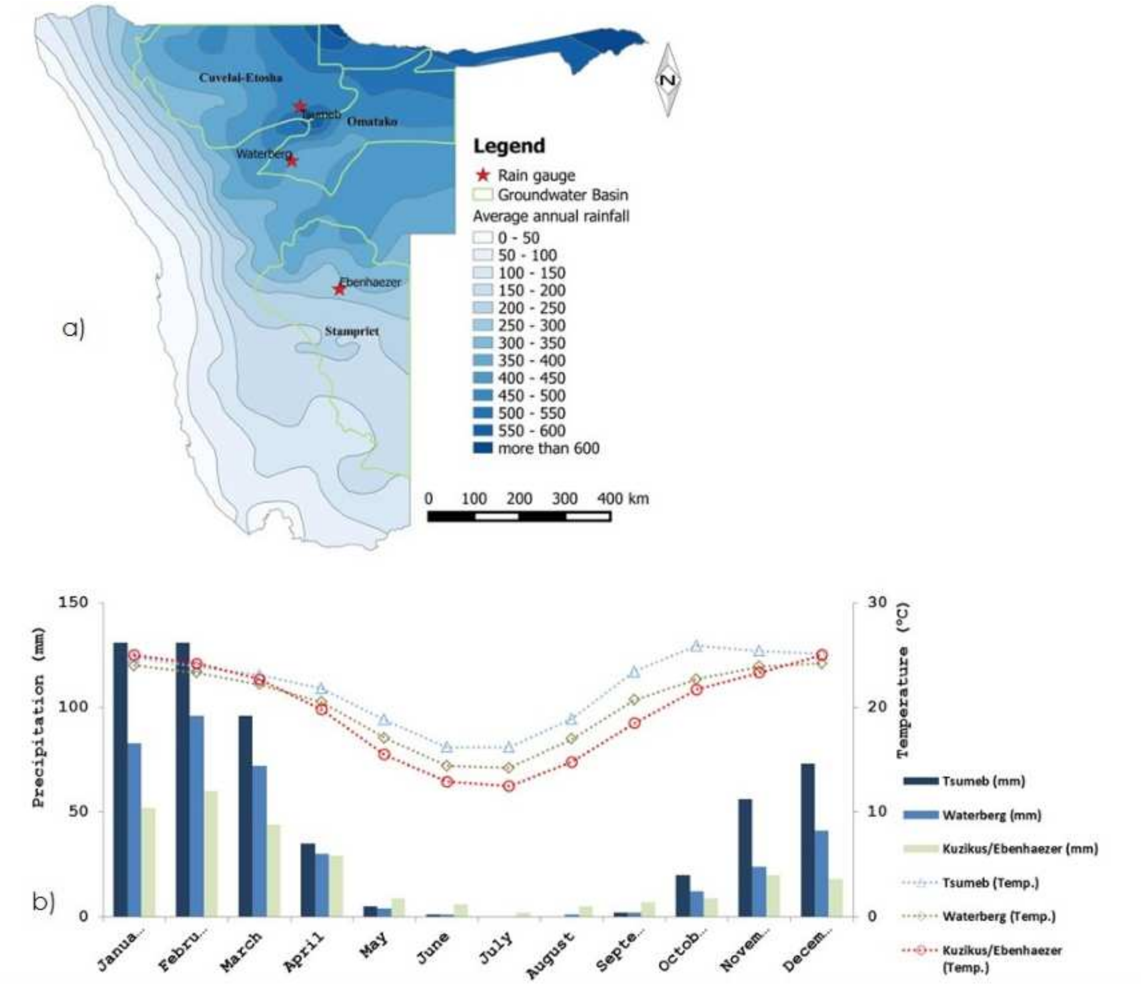

Figure 1: Climatic conditions: a) Precipitation gradient (Acacia Project E1); b) Mean monthly precipitation and temperature for Tsumeb, Waterberg and Kuzikus/Ebenhaezer from 1982–2012 (Climate-Data.Org, 2018).

3 Materials and methods

Precipitation stations were set up at respective study areas whereby a rain gauge was mounted to a pole about $2m$ long. Precipitation events were collected and tightly sealed in $50ml$ clear glass bottles as soon as the rain stops to prevent evaporation.

Precipitation samples from Tsumeb and Waterberg were collected during the rainy season from 2017 to 2018, while Kuzikus/Ebenhaezer samples were collected between 2014 and 2015. A total number of 83 precipitation event samples were collected (20 samples from Tsumeb, 29 samples from Waterberg, 34 samples from Kuzikus/Ebenhaezer). Precipitation event samples were analysed using Los Gatos Research Inc., LGR DLT 100 laser spectrometer at the hydro-lab, University of Namibia whereby the mean values of each sample were obtained.

All isotope ratios were reported in $\delta-$notation (‰) relative to the international Vienna Standard Mean Ocean Water (VSMOW) standard.

$$\delta \text{ sample } (‰) = \left(Rsample - \frac{Rvsmow}{Rvsmow} \times 1000 \right)$$

whereby δ sample is the deviation of the isotope ratio of a sample relative to that of the VSMOW, $Rsample$ is the ratio of $^{18}\mathrm{O}$ to $^{16}\mathrm{O}$ atoms in the sample, and $Rvsmow$ is the ratio of $^{18}\mathrm{O}$ to $^{16}\mathrm{O}$ atoms in the VSMOW.

D-excess values for each sample were obtained using an equation by (Dansgaard, 1964):

$$d = \delta^{2}\mathrm{H} - 8\,\delta^{18}\mathrm{O}.$$

The mean weighted isotopic values for $\delta^{2}\mathrm{H}$ and $\delta^{18}\mathrm{O}$ were obtained by multiply isotopic values by the precipitation amount added together and divided by the total precipitation amount. The arithmetic mean was obtained by adding isotopic values and then divided by the total number of samples. Local Meteoric Water Lines (LMWs) were generated using linear regressions for all precipitation samples collected at the specific site. Coefficients of determination of the regression lines have been determined as R^2. Annual arithmetic $\delta^{18}\mathrm{O}$ means have been calculated based on events and used in the plots for *altitude, latitude and continental effects*.

4 Results and Discussion

4.1 Characteristics of $\delta^{18}\mathrm{O}$ and $\delta^{2}\mathrm{H}$ values in precipitation

Precipitation isotopic values for $\delta^{18}\mathrm{O}(‰)$ range from -9.08 to 5.19 for Tsumeb, -15.96 to 5.09 for Waterberg and -12.54 to 4.75 for Kuzikus/Ebenhaezer, while $\delta^{2}\mathrm{H}(‰)$ isotopic values for Tsumeb range from -73.30 to 46.70, Waterberg -117.50 to 40.60 and Kuzikus/Ebenhaezer -82.50 to 47.80. These isotopic values are scattering along the GMWL (Figure 2). The scattering of isotopic values along a GMWL could be attributed to a seasonal effect.

A seasonal fluctuation of the stable isotope ratios is observed as a result of temperature effects, different trajectory of air masses, and varying fractionation processes in the source area of atmospheric moisture (Külls, 2000). A comparison of weighted mean values of both $\delta^{18}\mathrm{O}$ and $\delta^{2}\mathrm{H}$ (Table 1) to the precipitation isotopic isoscapes of Namibia by Kaseke *et al.* (2016) indicates that the mean values obtained in these study areas fall mainly within the $\delta^{18}\mathrm{O}$ and $\delta^{2}\mathrm{H}$ range values of their globally fitted isoscape model with an exception of Waterberg $\delta^{2}\mathrm{H}$ mean value that falls within the ranges of their cokriging isoscape model. Kaseke *et al.* (2016) have indicated a progressive isotopic depletion from east to west of Namibia which is attributed to the modification of the water vapour from the Indian Ocean along its trajectory. Furthermore, as marine air parcels move into the continents, they tend to mix and homogenize resulting in the scattering of isotopic values along meteoric water lines (Gat, 1996).

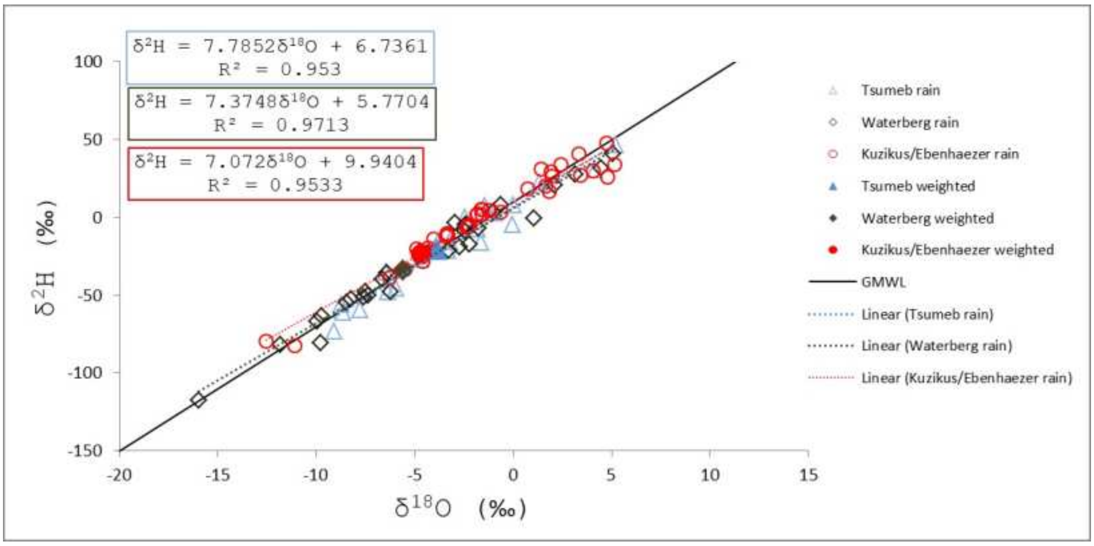

Figure 2: Dual plot of stable isotopes in the study areas.

Table 1: A summary of isotopic values in precipitation events

Site	Longitude (°)	Latitude (°)	Altitude (m)	Arithmetic Mean δ^{18}O (‰)	Arithmetic Mean δ^2H (‰)	Weighted Mean δ^{18}O (‰)	Weighted Mean δ^2H (‰)
Tsumeb	17.58215	-19.20610	1313	-2.99	-17.61	-3.88	-21.14
Waterberg	17.39876	-20.39602	1475	-4.36	-26.36	-5.60	-34.30
Ebenhaezer	18.45601	-23.21571	1340	-1.40	0.025	-4.67	-23.57

4.2 Slopes of the local meteoric lines

LMWL equations for Tsumeb, Waterberg and Kuzikus were obtained using a linear regression method and are: $\delta^2\mathrm{H} = 7.78\delta^{18}\mathrm{O} + 6.74,\ R^2 = 0.95$; $\delta^2\mathrm{H} = 7.37\delta^{18}\mathrm{O} + 5.77,\ R^2 = 0.97$; $\delta^2\mathrm{H} = 7.07\delta^{18}\mathrm{O} + 9.94,\ R^2 = 0.96$ correspondingly. Slopes of the defined LMWLs are noted to be decreasing along a precipitation gradient, whereby Tsumeb has the highest slope and Kuzikus/Ebenhaezer the lowest (Figure 2). All the slopes obtained from the three study sites are lower than that of the GMWL which is 8. The effect is most pronounced at Kuzikus/Ebenhaezer (slope $= 7.07$).

A slope which is less than 8 is usually attributed to evaporation from the falling rain that result into the enrichment of the heavy isotopes in the remnant drop along the so-called evaporation line (Gat, 1996). Kuzikus/Ebenhaezer site having the lowest slope correlates well with a higher potential evaporation value in the study area in comparison to Tsumeb and Waterberg; hence a pronounced evaporation effect. Our slopes are within the ranges of slopes that have been determined in Namibia by Kaseke *et al.* (2016) (GNIP based LMWL and observed LMWL both with a slope of 7.20), Wanke *et al.* (2018) (LMWL slope for CEB as 7.20) and JICA (2002) (LMWL for Stampriet Basin with a slope of 7.10) where they indicated that such a low slope implies a degree of dryness. Wanke *et al.* (2018) compiled slopes from 22 different sources in southern Africa whereby the minimum slope of 5.60 is from Lake Sibayi catchment, South Africa, and the highest value of 8.70 from central Mozambique. All in all, the average slope value from these 22 sources is 7.13 and comparable to our results. On a global scale, lower slopes were also found for the semi-arid region of the US Great Plains (Harvey and Welker, 2000) and an arid region in northwest China (Pang *et al.*, 2011).

4.3 Variation of Deuterium Excess in Precipitation

D-excess obtained from the LMWL equations are as follow: 6.74‰ for Tsumeb; 5.77‰ for Waterberg and 9.94‰ for Kuzikus/Ebenhaezer (Figure 2). D-excess value for Kuzikus/Ebenhaezer is very close to that defined by Craig (1961) which is 10. However, the same cannot be said for Tsumeb and Waterberg as they have lower d-excess values. D-excess obtained from each sample plotted against δ^{18}O (Figure 3) shows an insignificant negative correlation for all three sites with R^2 values of 0.02; 0.20 and 0.26 for Tsumeb, Waterberg and Kuzikus/Ebenhaezer, respectively.

The fact that d-excess values from the LMWLs for all the three sites are lower than that of GMWL, could be a result of subcloud secondary evaporation which also leads to enrichment of heavy isotopes in precipitation (Crawford *et al.*, 2017; Wang *et al.*, 2016). On the other hand, most of the d-excess values obtained from each sample are slightly higher than 10‰ and usually, the evaporated moisture's isotope composition is characterized by larger d-excess values, so precipitation derived from an air mass into which the re-evaporated moisture is admixed is also characterized by a large d-excess (Dansgaard, 1964; Gat, 1996).

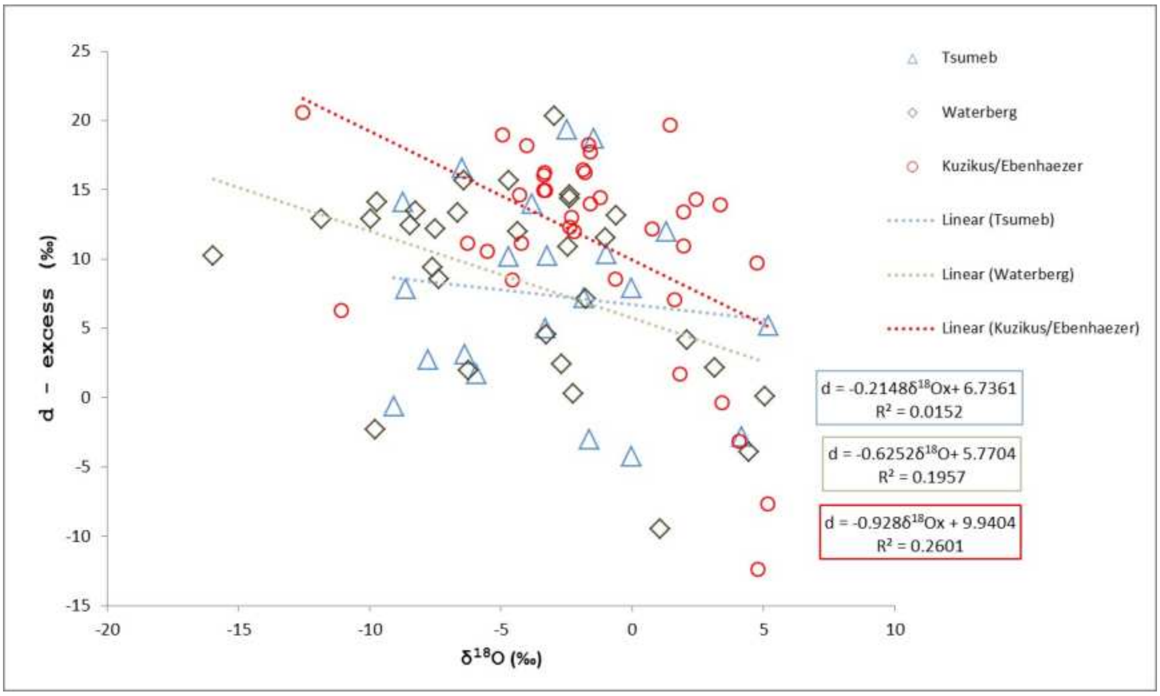

Figure 3: D-excess variations in the study areas.

4.4 Observed Isotopic Effects in Precipitation

4.4.1 Amount Effects

R^2 derived from regression lines were as follows: $R^2 = 0.08$ for Tsumeb; $R^2 = 0.09$ for Waterberg; $R^2 = 0.52$ for Kuzikus/Ebenhaezer (Figure 4). Very low R^2 values for both Tsumeb and Waterberg (0.08 and 0.09 respectively) is an indication that precipitation amount is not a controlling factor of the isotopic composition of precipitation at these two sites. It correlates well with findings by Wanke *et al.* (2018) and Crawford *et al.* (2017). However, the same cannot be said for Kuzikus/Ebenhaezer where R^2 value (0.52) shows that there is a significant negative correlation between isotopes and the amount of precipitation. Evaporation from falling rain drops and fractionation by isotopic exchange tend to enrich small amounts of rain in heavy isotopes (Dansgaard, 1964). A slightly pronounced amount effect at Kuzikus/Ebenhaezer could be attributed to such factors, especially that this area has the highest potential evapotranspiration and lowest monthly precipitation averages in comparisons to the other two study areas.

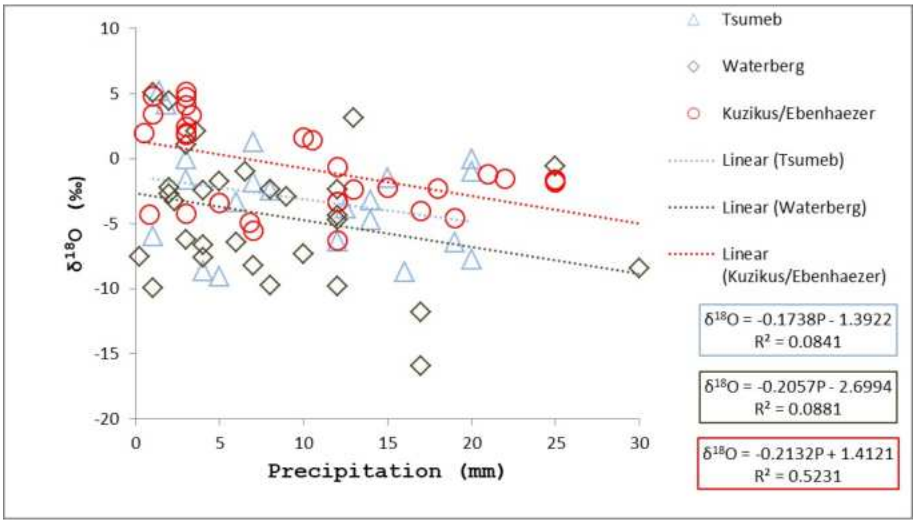

Figure 4: Amount effects in the study areas.

4.4.2 Altitude, Latitude, Continental and Seasonal Effect

For the altitude effect, there is a strong linear correlation with $R^2 = 0.90$ (Figure 5a). However, there is no correlation for latitude and continental effects as their R^2 values are 0.06 and 0.04, respectively (Figure 5b and 5c). A pronounced altitude effect could be attributed to the fact that the lowering of temperature with increasing elevation in mountainous regions usually leads to enhanced condensation and as a result to a progressive depletion in heavy isotopes of precipitation with altitude (Araguás-Araguás *et al.*, 2000). Dansgaard (1964) also indicated that heavy isotope concentrations in fresh water decreases with increasing altitude.

For the seasonal effect, the general trend for the three sites is that $\delta^{18}\mathrm{O}$ values are varying with months (Figure 5d). Values are enriched in $\delta^{18}\mathrm{O}$ at the beginning of the rainy season (October to January) and progressively become depleted during the rainy season. The most $\delta^{18}\mathrm{O}$ depleted value is from Kuzikus/Ebenhaezer of -10.79‰ in April followed by Waterberg with -10.35‰ in March. Kuzikus/Ebenhaezer received two heavy rain events thus $55mm$ and $65mm$ with more depleted $\delta^{18}\mathrm{O}$ values of -11.10‰ and -12.54‰ respectively. The heaviest rain event at Waterberg was recorded in March of $30mm$ with $\delta^{18}\mathrm{O}$ values of -8.44‰ and the most depleted $\delta^{18}\mathrm{O}$ value of -15.96‰ in the same month is associated with a $17mm$ rain event. High rain intensities are usually associated with depleted isotopic compositions (Gat, 2000).

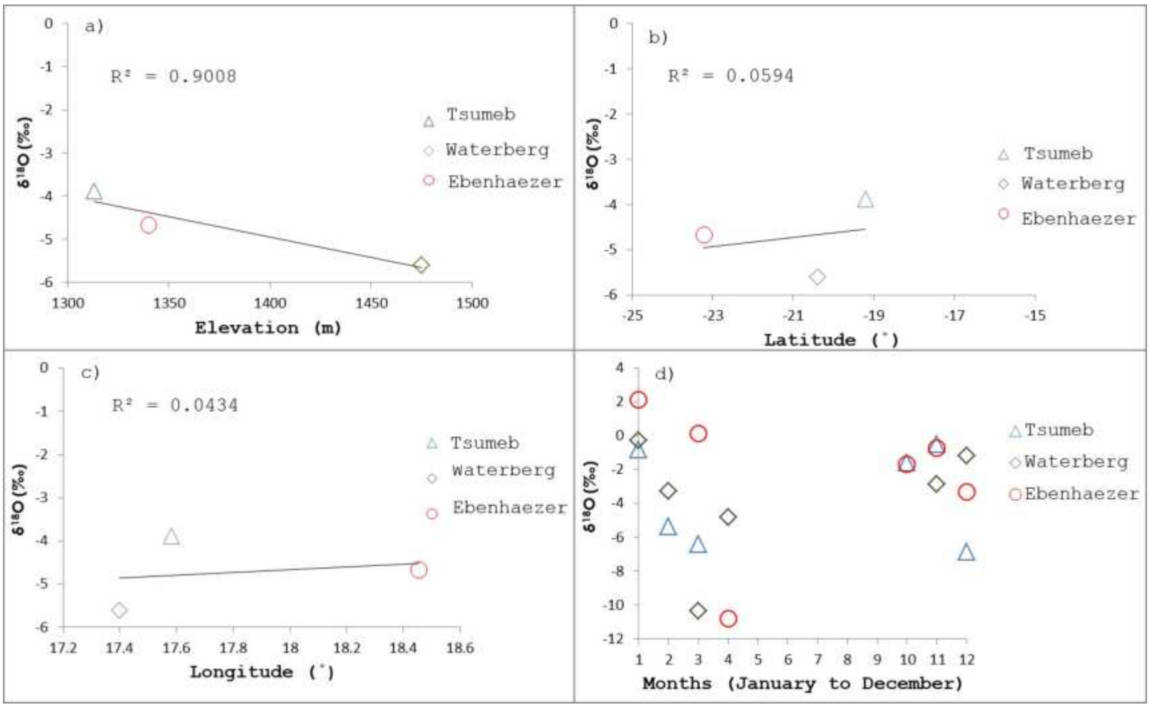

Figure 5: Effects across a precipitation gradient in Namibia: a) Altitude effect; b) Latitude effect; c) Longitude effect; d) Seasonal effect (based on weighted means δ^{18}O values).

5 Conclusion

The study has determined and shown local meteoric water lines that are varying along a precipitation gradient and their slopes were noted to be decreasing along a precipitation gradient. Such findings could be of importance for future studies along the precipitation gradient in between the study sites as one could use our generalized findings by extrapolations to give insight for the distribution across the entire country. Additionally, these findings serve as a baseline for those three study sites with regards to further isotopic investigations in the study areas especially in tracing the origin of groundwater since much of the isotopic composition of precipitation recharging groundwater is retained provided that there is no evaporation. However, this study was done for a yearlong period only and it would be ideally to record such measures over periods of at least one decade and obtain long term annual averages. It would also be more accurate to collect samples at the same time for the three sites for a longer period as this will be interesting to understand the impact of climate change over time.

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Declaration of conflict of Interest

The authors declare that there are no conflicts of interest.

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