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Isotopic Composition of Water Bodies in the Kuiseb and Cuvelai-Etosha Basin, Namibia

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ABSTRACT

This study aimed to investigate the isotopic composition of different water bodies in two basins. Water samples collected from open and undefined water sources such as the Etaka and Ruacana waterfall and an artificial spring in the Cuvelai-Etosha Basin; as well as the boreholes, Atlantic Ocean and fog from the Kuiseb Basin were analysed for stable isotopes namely, Deuterium (δ^2H) and oxygen 18 ($\delta^{18}O$)) and elemental composition. Stable isotope ratios were measured using the Picarro L2120–i Analyser (Cavity Ring-Down Spectrometry method) and trace elemental composition was assessed using the Inductively Coupled Plasma Mass Spectroscopy (ICP-MS). Open water bodies of the Cuvelai-Etosha Basin were found to be enriched with heavy isotopes, and also plotted along the evaporation line (below and away from the Global Meteoric Water Line (GMWL)), which is indicative of the high evaporation rates within the basin. Kuiseb boreholes were depleted of heavy isotopes and plotted along the Global and Local Meteoric Water Line, indicating direct recharge from precipitation and minimal, if any, evaporation effects. Trace elemental analyses indicated possible contamination of water bodies with high concentrations of Al and Fe, confirming the effect of sediment input in the flood prone basin (Cuvelai), and continual erosion/hard crust in the Kuiseb. Positive correlations with r^2 greater than 0.5, confirming increase in $\delta^{18}O$ and δ^2H with increase in trace elements including Strontium and Lithium in the Kuiseb Basin, and Molybdenum (Mo) and Manganese (Mn) in the Cuvelai-Etosha Basin were also observed.

1. Introduction

Internation Atomic Energy Agency (IAEA) (2004) emphasizes the key importance of stable isotopes in understanding the earth's water cycle in order to effectively manage water resources to address water availability and water demand issues. Heavy stable isotopes of water namely Deuterium (^2H) and Oxygen-18 (^{18}O) as investigated by numerous studies are ideal tracers in sustainable water resources development and management. Environmental tracers as documented in various studies have been used individually and also in combination to determine the origin of water, recharge patterns, age of water or residence time and water trajectories (Hydroisotop GmbH 2005; Gibson et al. 2005; Arigiriou and Lykoudis 2008).

Evaporation and precipitation are closely related in such a way that evaporation occurs when the air is under-saturated and precipitation occurs when the air is oversaturated (Gat, Mook and Meijer 2001). Gat et al. (2001) observed that evaporation from surface water bodies and ocean are the main sources of atmospheric water which under adiabatic conditions may condense forming precipitation. Thus lighter water isotopes are more enriched in volatile states compared to heavy isotopes which are more enriched in the liquid state. Hence, open water bodies and underground water are likely to be rich in heavy isotopes compared to atmospheric water.

With evaporation effects in groundwater, other factors such as permeability of the subsurface, type of soil and depth to the water level need to be considered. Evaporation that takes place during percolation or through a shallow water table has been attributed to the enrichment of underground water in some semi-arid regions of Southern Africa (Ploethner 1998). In the Kuiseb Basin, Ploethner (1998) observed that samples from evaporated water either before filtration or through shallow water table were enriched in δ^2H and $\delta^{18}O$. Ploethner (1998) further concluded that groundwater recharge in the Kuiseb Basin is confined to exceptionally intense rain even when the Kuiseb river flows. Similarly, studies in the Cuvelai-Etosha Basin also observed that evaporated water bodies were enriched in heavy isotopes and plotted along the evaporation line (Geyh 1994; Hamutoko, Uugulu and Wanke 2015; Schilling 2015).

In general, the values of δ^2H and $\delta^{18}O$ in precipitation decrease with an increase in the amount of precipitation (Dansgaard 1964). Thus heavy rain is likely to be depleted in heavy isotopes and the resulted directly recharged sources. Vogel and van Urk (1975) observed low isotope ratios in groundwater of semi-arid regions of the Southern Africa compared to precipitation, and further highlighted that it corresponds to the isotopic composition of exceptionally heavy rain events. The existing Cuvelai-Etosha Basin precipitation baseline (Turewicz 2013) did not record or measure the total amount of rain water for events from which the analyzed samples were obtained, thus conclusions on this are inconclusive.

The variation with the amount of water also applies when water is evaporating from a source, melting or percolating into the ground. For instance, shallow open water bodies are likely to be rich in heavy isotope compared to deep open water bodies due to the difference in mixing fluxes.

To fully understand water trajectories and chemical equivalence issues, a combination of environmental tracers such as isotope ratios, mineralogy and trace elements is crucial (Elliot 2014). Elliot (2014) further stressed that this could especially be beneficial in the study of groundwater systems where mixing and pumping from such sources is of importance, as this would help with the understanding of water flows and geochemical dynamics of such systems.

This study thus set out to investigate the isotopic composition of water bodies in the partly coastal Kuiseb Basin and the prone to flood and drought Cuvelai-Etosha Basin. The two basins share high evaporation rates and groundwater dependence, yet, their annual rainfall frequencies and intensity varies significantly. For the purpose of sustainable management of water resources, planning and adaptation in these two basins, understanding of the recharge and interaction processes that govern water availability is significantly important.

In this study, samples from open and closed water bodies were analysed for isotope ratios (Deuterium (^2H) and Oxygen-18 (^{18}O) and trace elements. The isotope ratios were further ploted along the Global Meteoric Water Line (GMWL) to determine the origin and correlated to trace elemens to assess the influence (or lack of thereof) of trace elements on the isotope ratios. In regions with no established LMWL, the GMWL as used in various studies dating back to 1960 remain the convenient reference for understanding and tracing the origin of water with isotopes in such regions (McGuire and McDonnel 2007).

The LMWL for the areas under investigation exists for the Cuvelai-Etosha basin (Turewicz 2013).

$$\delta^2H = (7.2195\ \delta^{18}O) + 4.1065$$

The Namibian LMWL has a lower slope compared to the GMWL (Figure 2.1). Schilling (2015) attributed the change in the slope of the LMWL to the change in evaporation line. Fractionation in relatively dry conditions of <25% relative humidity results in a low slop compared to fractionation in relatively humid environments between 25% - 75% (Clark and Fritz 1997). Clark and Fritz (1997) further noted that the GMWL is attained at a relative humidity of 95% and above.

Materials and Methods

Description of Study Sites

The Cuvelai-Etosha Basin is the most densely populated basin (Bäumle, et al. 2011) covering an area of approximately 5287 Km^2 (Amwaama et al. 2005). The basin is further divided into four sub-basins namely; the Cuvelai-Iishana, Tsumeb, Olushandja and Niipele Odila (Kluge, Liehr, Lux, Niemann and Brumer 2006).

Made up of gneissic and granitic basement, the basin is dominated by porous aquifers of moderate potential in the central Cuvelai and fractured or karst aquifers of high potential in the area of Otavi where groundwater recharge takes place (Figure 1). Groundwater is accessed through both shallow and deep wells depending on the level of the water table for domestic and farming purposes. Bäumle et al. (2011) noted that a major part of groundwater flow in the Cuvelai-Etosha basin is shallow and discharges through various springs along the south margin of the deep or low laying base of the Cuvelai-Etosha Basin, Etosha Pan.

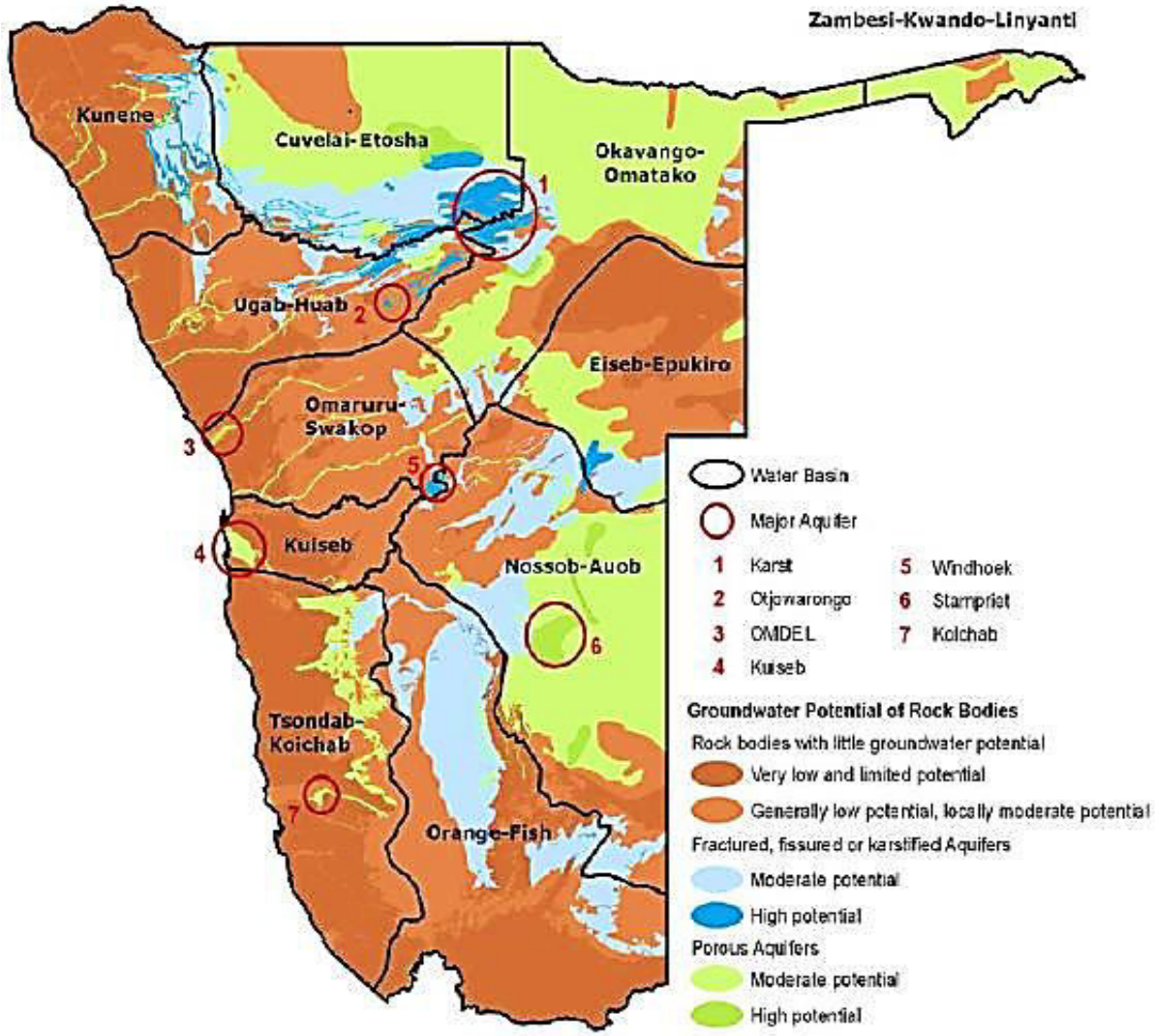


Figure 1 Map of Aquifers in Namibia (http://www.iwrm-namibia.info.na/iwrm)

The Kuiseb Basin stretches over parts of Erongo and Khomas region, covering the most arid part of the Namib Desert along the Atlantic Ocean (Shanyengana, Henschel, Seely and Sanderson 2002). The basin receives an annual rainfall ranging from 350 mm in the upper catchment to less than 50 mm at the coast (IWRM Joint Venture Consultants n.d). In addition to rainfall as a form of precipitation in this basin, there is regular occurrence of fog. The benefits of fog as estimated to occur for about 60-200 days annually (Henschel, Mtuleni, Grunkowski, Seely and Shanyengana 1998) extend to ecological sustainability (Soderberg 2010).

As shown in Figure 1, the moderately permeable alluvial aquifer is found in the lower catchment and the

high potential fractured or karst aquifer is in the upper catchment extending to the mountains of Khomas region. Groundwater is abstracted through numerous boreholes found on the bank of the aquifer, from the lower catchment through Rooibank to Dorop South (Bäumle et al. 2011).

Sampling and Analyses

Due to lack of water resources database and sources ownership in the Cuvelai basin, random sampling was applied based on water availability and accessibility. Whereas, in the Kuiseb basin, the borehole database for NamWater was used for sampling. In total, 52 samples were collected and analysed for stable isotopes; of which a total of 48 samples were taken through elements analysis. The Kuiseb samples consisted of two samples of fog water, 21 samples of underground water (boreholes), two sea water samples and a sample of spring water. About 75% of sampled water bodies in the Cuvelai-Etosha Basin were mainly shallow wells consisting of a mixture of different water, whereas, the rest of the samples were collected from the water canal that brings in water from the Calueque dam, Ruacana waterfall, artificial spring and Etaka, the paleo-channel from Cunene River into the central Cuvelai (Amakali 2003).

Physical parameters of the sampled water bodies were measured onsite using a HACH DR/800 Series Portable Multi-parameter Meter and HQ40d Portable pH Meter.

Fog water was harvested using the Standard Fog Collector (SFC) from the Gobabeb Research and Training Centre (GRTC).

Samples were first filtered using 0.45 micron syringe filters and desalinated using a cryogenic vacuum distillation before isotope ratios could be measured. Isotope ratios of Hydrogen and Oxygen were measured using a Cavity Ring-Down Spectroscopy (CRDS) method, Picarro L2120-i, Santa Clara, USA model. Isotope ratios were determined using the VSMOW standard equation:

$$\delta = \left(\frac{Isotope\ ratios\ of\ the\ sample}{Isotope\ ratios\ of\ VSMOW\ standard\ water} - 1 \right) X\ 1000$$

The ratios were conventionally expressed in delta notation "$\delta^{18}O$ and $\delta^{2}H$" of their relative abundance as deviations in ‰ from the Vienna Standard Mean Ocean Water.

Samples for trace elements were analyzed with U.S EPA Method 200.8 using the NexION 300D/300D ICP-MS at North-West University in South Africa. The samples were kept cool but not frozen until analysis. Samples were filtered and treated with nitric acid (HNO_3) and calibration with HNO3 was performed in-between samples.

Results

Isotope Composition

The isotope ratios of different water bodies were grouped per type of water body and plotted together with the Global Meteoric Water Line (GMWL) as shown in Figure 2. Isotope ratios in the Kuiseb Basin ranged from -6.4 ‰ to 0.4‰ for $\delta^{18}O$ and -43.8 ‰ to -13.5 ‰ for $\delta^{2}H$ for Kuiseb boreholes and -6.4 ‰ to 0.4 ‰ for $\delta^{18}O$ and -43.8 ‰ to -13.5 ‰ for $\delta^{2}H$ and -3.0 ‰ to 0.1 ‰ for $\delta^{18}O$ and -36.5 ‰ to -0.7 ‰ for $\delta^{2}H$ for Walvis Bay fog samples. The only spring water sample obtained from the Kuiseb Basin recorded isotope ratios of 1.9 ‰ and -8.1 ‰ for $\delta^{18}O$ and $\delta^{2}H$ respectively. The overall minimum deuterium excess value of -22.999 ‰ was recorded for the entire basin. The Kuiseb boreholes' and fog samples plotted along the GMWL and LMWL "Precipitation (Turewicz 2013)", while, the spring sample plotted away from the GMWL.

The isotope ratios of open water bodies of the Cuvelai-Etosha Basin ranged from -3.9 ‰ to 30.8 ‰ for $\delta^{18}O$ and -32.5 ‰ to 138.2 ‰ for $\delta^{2}H$ with deuterium excess in the range of -108 ‰ to 1.2323 ‰. Most samples from open water bodies of the Cuvelai-Etosha Basin plotted away from the GMWL, along the evaporation line. The overall maximum deuterium excess value of 1.2323 ‰ for the Cuvelai-Etosha Basin was recorded in Etaka (paleo-channel from Kunene River). While, the overall minimum deuterium excess value of -108.35 ‰ was recorded in the modified spring. Similar to the Kuiseb Basin samples, the correlation matrix did not indicate any correlations between altitude and deuterium excess.

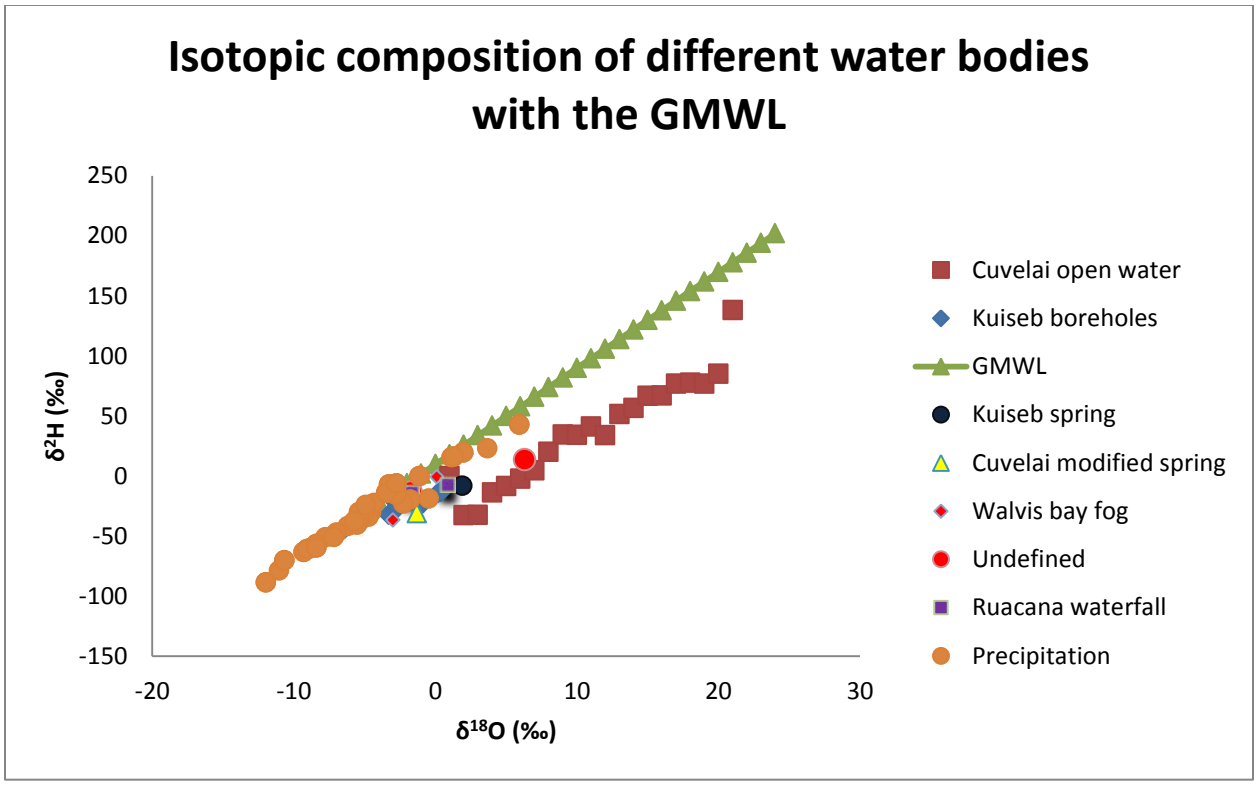


Figure 2 Isotopic composition of different water bodies plotted with the GMWL

Trace elemental and isotopic composition

Maximum concentrations of 4.533 $\delta^{18}O$ µg/L and 2.689 µg/L for Manganese (Mn) and Molybdenum (Mo) were recorded in the Cuvelai-Etosha Basin (Figure 3).

Trace elements with significant correlations to $\delta^{18}O$ in the Kuiseb Basin recorded the highest concentrations of 210 µg/L and 45.613 µg/L for Lithium (Li) and Strontium (Sr) respectively (Table 1).

The observed correlations in the Cuvelai-Etosha between $\delta^{18}O$ and trace elements indicated a positive non-linear relationship with scatter plots in which the $\delta^{18}O$ composition increased with an increase in the concentration of Manganese (Mn) and Molybdenum (Mo) (Figure 3).

Discussion

Physical Parameters of the Water Samples

^{2}H and ^{18}O ratios are defined by the fraction of $H_2{}^{18}O$ remaining in water after evaporation and condensation (Araguas-Araguas, Froehlich and Rozanski 2000), hence, an increase in salinity, TDS and turbidity could potentially reduce the rate at which heavy isotopes evaporate. It should be noted that, the presence of dissolved salt or salinity decreases the chemical potential and spontaneous transformation of liquid into vapour state, thus, reducing the evaporation rate (Kokya and Kokya 2006), which is significantly linked to variations in the isotopic composition.This could be the case with Cuvelai-Etosha samples that recorded the highest salinity.

It was also noted in Shanyengana, Seely and Sanderson (2004) that an increase in TDS concentration as linked to seasonal variations, consequently increases the chemical content of groundwater. A similar study on environmental tracers emphasized that the chemical and physical fractionation in water could cause a shift in isotope ratios, considering that trace elements normally occur at low concentration levels (Elliot, 2014).

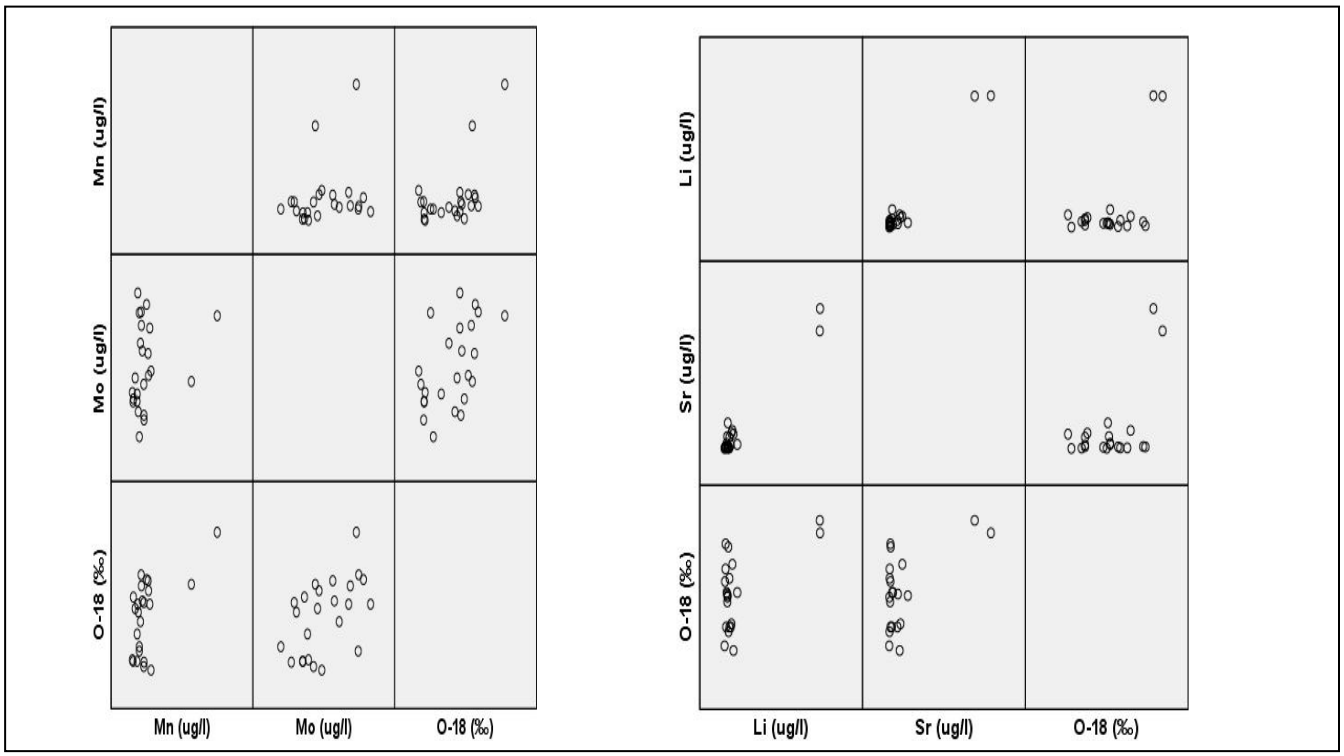
Table 1 Significant correlations observed between isotope ratios and trace elements in the (a) Cuvelai- Etosha Basin and (b) Kuiseb Basin

	Mn (µg/l)	Mo (µg/l)	O-18 (‰)	d (‰)	d-excess (‰)
Mn (µg/l)	1 26	.447* .022 26	.554** .005 24	.603** .002 24	-.492* .015 24
Mo (µg/l)	.447* .022 26	1 26	.522** .009 24	.493* .014 24	-.541** .006 24
O-18 (‰)	.554** .005 24	.522** .009 24	1 24	.951** .000 24	-.980** .000 24
d (‰)	.603** .002 24	.493* .014 24	.951** .000 24	1 24	-.911** .000 24
d-excess (‰)	-.492* .015 24	-.541** .006 24	-.980** .000 24	-.911** .000 24	1 24

	Li (µg/l)	Sr (µg/l)	O-18 (‰)	d (‰)	d-excess (‰)
Li (µg/l)	1 22	.979** .000 22	.575** .006 21	.496* .022 21	-.368 .101 21
Sr (µg/l)	.979** .000 22	1 22	.559** .008 21	.487* .025 21	-.333 .140 21
O-18 (‰)	.575** .006 21	.559** .008 21	1 24	.904** .000 24	-.865** .000 24
d (‰)	.496* .022 21	.487* .025 21	.904** .000 24	1 24	-.691** .000 24
d-excess (‰)	-.368 .101 21	-.333 .140 21	-.865** .000 24	-.691** .000 24	1 24

**. Significant at the 0.01 level 2-tailed

Figure 3 Elemental Concentrations and isotopes in the (a)left: Cuvelai-Etosha and (b)right: Kuiseb Basin



Stable isotope ratios and the GMWL

With exception to the Kuiseb spring which followed the trend of open water bodies, isotope ratios of groundwater samples plotted in the negative range, along meteoric water lines. This trend is indicative of direct recharge from precipitation and water that has been subjected to little or no evaporation beyond the evaporation-influenced zone (Schilling 2015).

It was also noted that the spring water sample that recorded the second utmost ratios to seawater recorded the overall minimum deuterium excess in the Kuiseb Basin. This is the only sample obtained from an open water body inland and subjected to a certain degree of evaporation as reflected by its low deuterium access of -22.999 ‰. The fact that seawater samples, Walvis Bay fog and the spring samples plotted away from the borehole samples, indicate evaporation effects on these samples that is also reflected in their enrichment with heavy isotopes. Yeh, Lin, Lee, Hsu and Wu (2014) also noted that surface water sources recharged by underground water discharges tend to exhibit isotopic composition similar to that of open water bodies. Hence, the variations observed in groundwater from wells, boreholes and that of the Kuiseb spring that is plotting along with open water bodies of the Cuvelai Basin (Figure 2).

The Walvis Bay fog water sample recorded isotope ratios greater than that of groundwater (Kuiseb boreholes) that is recharged by flash floods of the Indian Ocean origin occasional rainfall (Ploethner 1998) but depleted in isotope ratios compared to the seawater samples. Both Walvis Bay fog and the seawater obtained from the Walvis Bay shore originate from the Atlantic Ocean (Shanyengana, Henschel, Seely and Sanderson 2002), but the seawater samples (liquid state) were more enriched in heavy isotopes compared to the atmospheric water samples (volatile state) which ware depleted in heavy isotopes. Similar to this study, observation in Gat et al. (2001), noted that meteoric water was depleted in heavy isotopes compared to seawater. This was attributed to the fact that oceans have larger isotope fractionation during evaporation than the reverse fractionation during the condensation process to precipitation (Gat et al. 2001). In addition to large isotope fractionation, Aggarwal, Froehlich and Kulkarni (n.d) noted that precipitation undergoes significant evaporation during its fall and this could also be a contributing factor to the variations.

Overall, the open water bodies of the Cuvelai-Etosha Basin recorded the lowest deuterium excess of -108.35 ‰ reflecting their evaporated water and the resultant enrichment in heavy isotopes compared to the Kuiseb boreholes which recorded the minimum deuterium excess of -22.999 ‰ and isotope ratios in the negative range. The trend followed by the isotope ratios of the Cuvelai open water bodies is similar to that of evaporated water (Hamutoko et al. 2015).

Variations in Isotope Ratios

The isotope ratios of -3.9 ‰ to 30.8 ‰ for $\delta^{18}O$ and -32.5 ‰ to 138.2 ‰ for $\delta^{2}H$ measured in this study are higher than the ratios (-9.4‰ to 13.6‰ and -63.1‰ to 45‰ for $\delta^{18}O$ and $\delta^{2}H$ respectively) obtained in a similar study conducted by Hamutoko et al. (2015) in the Cuvelai Basin. The same trend "plotting towards the evaporation line" was observed in the way the Cuvelai groundwater ratios of Hamutoko et al. (2015) plotted with the GMWL.

Although no precipitation samples were analyzed for this study, existing precipitation isotope database for the Cuvelai-Etosha Basin (Turewicz 2013) indicated an increase from the range of -10.67 ‰ to -1.12 ‰ for $\delta^{18}O$ and -70.12 ‰ to -0.4 ‰ for $\delta^{2}H$ in 2008 to -11.98 ‰ to 5.94 ‰ for $\delta^{18}O$ and -88.60 ‰ to 42.80 ‰ for $\delta^{2}H$ in the year 2013/2014 (Turewicz 2013). The enrichment of precipitation in 2013/2014 could be attributed to the resultant temperature increase of the drought year (2013).

Conclusion

Open water bodies of the Cuvelai-Etosha Basin were enriched in heavy isotopes and plotted along the evaporation line, reflecting the high evaporation of the basin. Compared to open water bodies, the Kuiseb boreholes were depleted in heavy isotopes and plotted along the meteoric water lines, indicating direct recharge from rainfall and minimum, if any, evaporation effects.

Comparison of the available isotope data from different period indicated an increase in heavy isotope ratios of open water bodies, groundwater and precipitation. Correlations with R-values slightly above 0.5 indicated positive relationships in which

the $\delta^{18}O$ and $\delta^{2}H$ increased with concentrations of certain elements.

The altitude and amount effects in precipitation remain inconclusive. The study could not conclude on the seasonal variations or lack of thereof. Thus, recommends for the isotope measurements of similar studies to be inclusive of all seasons of the year.

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