

THE DISTRIBUTION OF DEUTERIUM AND OXYGEN 18 IN SURFACE WATER AND PRECIPITATION IN THE CUVELAI, ETOSHA BASIN

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1. Introduction

The Cuvelai Etosha Basin (CEB) is located in the north-central part of Namibia, stretching across four regions, namely Oshana, Omusati, Oshikoto and Ohangwena. The CEB is further divided into four basins, namely; Olushandja, Lishana, Nipele and Tsumeb. The CEB is characterised by an interconnected system of shallow water courses locally called “Oshanas”. The water in the basin originates from local rainfall (precipitation), run-off in ephemeral rivers (surface water) and aquifers (underground water storage) (Mendelsohn, 2002).

In general, the sourcing of water for water supply in Namibia is a challenging undertaking. This can be attributed to the low rainfall and high evaporation experienced in Namibia. Astonishingly, vast populations of people live in areas far from major water sources, which are; ground water reserves, perennial rivers and dams (Mendelsohn, 2002). It is imperative therefore, to improve access to safe water. Consequently, numerous investigations have been undertaken in order to improve groundwater management in various areas in Namibia.

1.1 Background

The CEB has in the recent past become a major topic of discussion and investigation owing to the salinity of the water in aquifers in the area. The focus of this study is to scrutinize the isotopic distribution of the stable isotopes ^{18}O and ^2H in precipitation and surface waters in the CEB. Understanding the spatial distribution of water isotopes (^{18}O and ^2H) also called “water isotope tracers” is important because water isotope tracers can be traced from reservoir to reservoir as they normally preserve their isotopic signature very well. Studies of water isotope tracers are used to determine the geospatial origin of water, geological or biological material this can be applied in the CEB. Accurate mapping of the distribution of ^{18}O and ^2H in surface water and

precipitation is critical, because the isotopic signal underlying isotopic hydrology studies is the spatial variation in stable isotopes in precipitation and environmental water. An increasing number of hydrological, forensic and ecological applications also rely on water isotope tracers. Furthermore, comparing the results obtained from the CEB with various results obtained from different locations in southern Africa is important as it gives a local as well as a regional view on the distribution of isotopic composition in precipitation.

2. Problem Statement

The assertion of the problem with regard to the area of study (the Cuvelai Etosha Basin) is that the distribution of the stable isotopes ^{18}O and ^2H in precipitation and surface-water is undetermined. The influence of the factors that control the distribution of the isotopic composition in precipitation and surface-water in the CEB has not been investigated. Finally, also undetermined is the relation of isotopic composition in precipitation and surface-water in the CEB to the “bigger southern African picture” with the equator regarded as the northern reference.

2.1 Objective of the Study

This study is aimed at understanding the geospatial distribution of ^{18}O and ^2H in precipitation and surface-water in the CEB by the following:

- ❖ Determining the LMWL of the CEB and comparing it to with the GMWL. Observing the relationships between the LMWL and GMWL slopes and giving reasons for deviation from the global-trend, inconsistencies or both.
- ❖ Understanding how the factors that control isotopic composition of ^{18}O and ^2H in precipitation and surface-waters influence the CEB and also determine which factors dominate and are therefore a significant subject of discussion.
- ❖ Comparing isotopic composition results obtained from selected (IAEA/WMO) run meteorological stations in southern African countries and discussing their relationships in order to have regional picture of the distribution of isotopic compositions of ^{18}O and ^2H in precipitation in selected locations south of the Equator.

2.2 Hypothesis of the Study

Based on the discussed factors that influence the isotopic composition of precipitation and surface-water. It is appropriate to hypothesize that, the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of precipitation should decrease from east to west as most of southern African precipitation originates from the Indian Ocean. Therefore, the depletion in ^{18}O and ^2H in precipitation is expected resulting in more negative values from east to west. A corresponding assumption to the statement above is the depletion in the ^{18}O and ^2H content of precipitation from north to south (from the Equator to

the south-most part of Africa) as a result of the latitude effect. Furthermore, a variation in the slopes is expected from east to west and from north to south due to the assumed variation in isotopic composition distribution. With regard to the CEB another factor that is expected to contribute to the variation in the distribution of isotopic composition is the influence of precipitation from the western coast, the Atlantic Ocean.

2.3 Significance of the Study

A study on the distribution ^{18}O and ^2H in precipitation and surface-water is relevant as, precipitation is the ultimate source of ground-water in essentially all systems. “Water isotope tracers” such as ^{18}O and ^2H are used to determine the geospatial origin of water, geological or biological material. Knowledge of the factors that control the isotopic composition before and after recharge allows the use of ^{18}O and ^2H as tracers of water sources and processes. This therefore makes the use ^{18}O and ^2H relevant in the study of precipitation and surface-water in the Cuvelai Etosha Basin (CEB).

3. Literature Review

3.1 The Cuvelai-Etосha Basin (CEB)

The CEB generally situated in the central northern part of Namibia as illustrated in figure 3. It extends into the south Angola. The CEB is relatively the most densely populated territory in Namibia accommodating about 50 % of the country's population and is economically one of the fastest growing areas in the country. Sufficient water supply is therefore critical. In the past the local populace in the CEB depended on surface water during the rainy season and hand dug wells during dry periods. The rapid growth in population has led to the water sources being inadequate. Presently an expensive pipeline system conveying water from the Kunene River and the Calueque Dam (located in Angola) supplies drinking water for most of the CEB populace. The most important water source in the CEB is groundwater and it is located in a complex system of stratified aquifers containing fresh to saline water. The quantity and quality of the groundwater resources are not yet known. Therefore in 2007 the project 'Groundwater for the North of Namibia' was started to improve groundwater management in the CEB. Bittner (2006) stated that the Federal Institute of Geosciences and Natural Resources of Germany (BGR) implemented the 6-year project within the framework of German-Namibian Technical Cooperation. In order to understand the groundwater potential in the catchment area, the aim of the project is to provide hydrogeological base information.

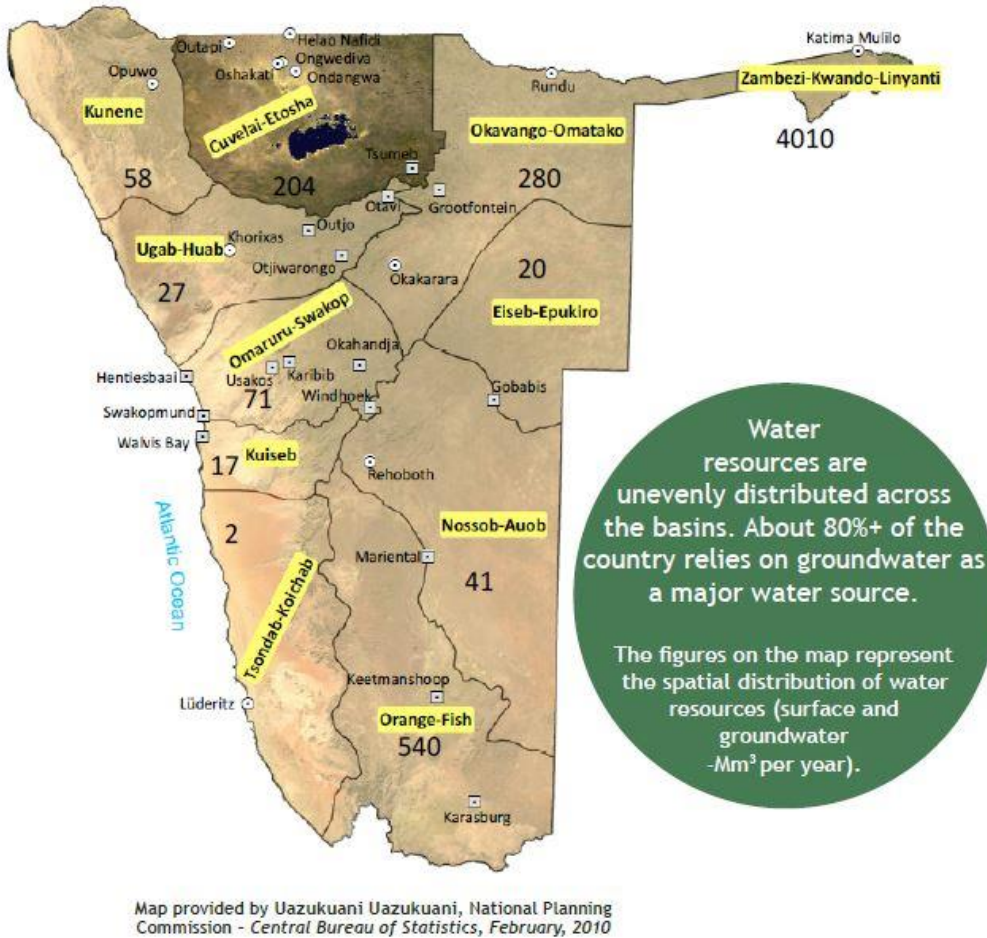


Figure 1: Represents the map of Namibia and also indicates the location of the CEB (IWRM, 2010)

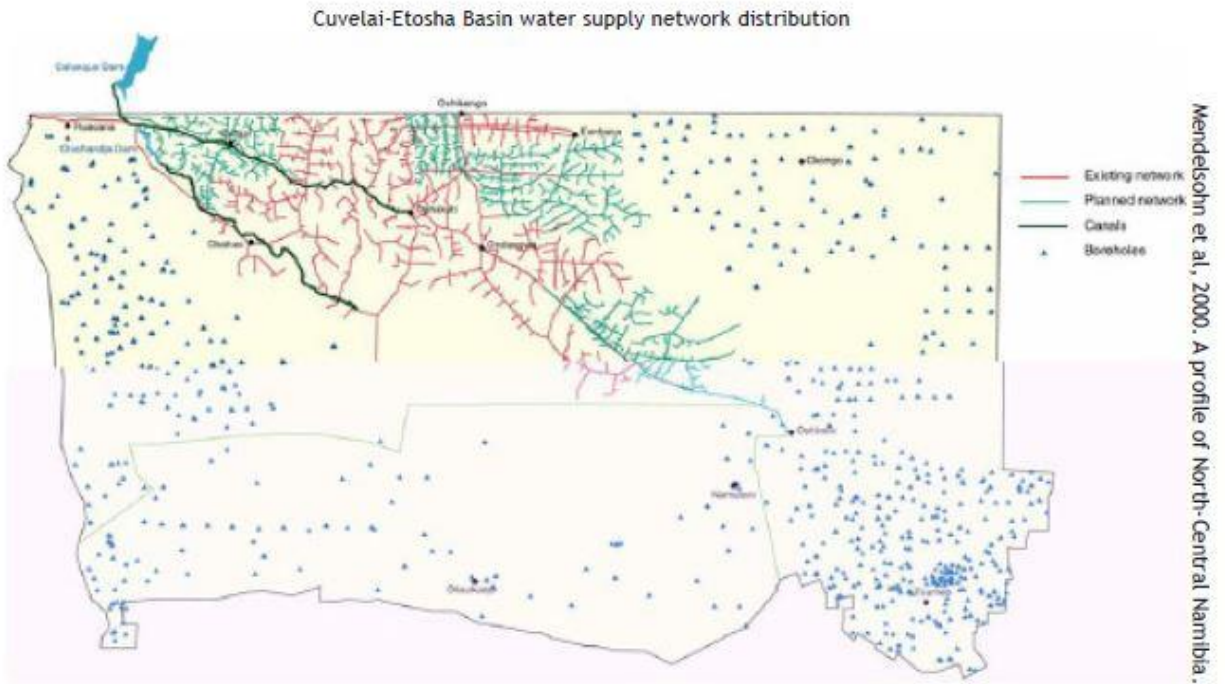


Figure 2: Represents the CEB water supply distribution network (Mendelsohn et al, 2000)

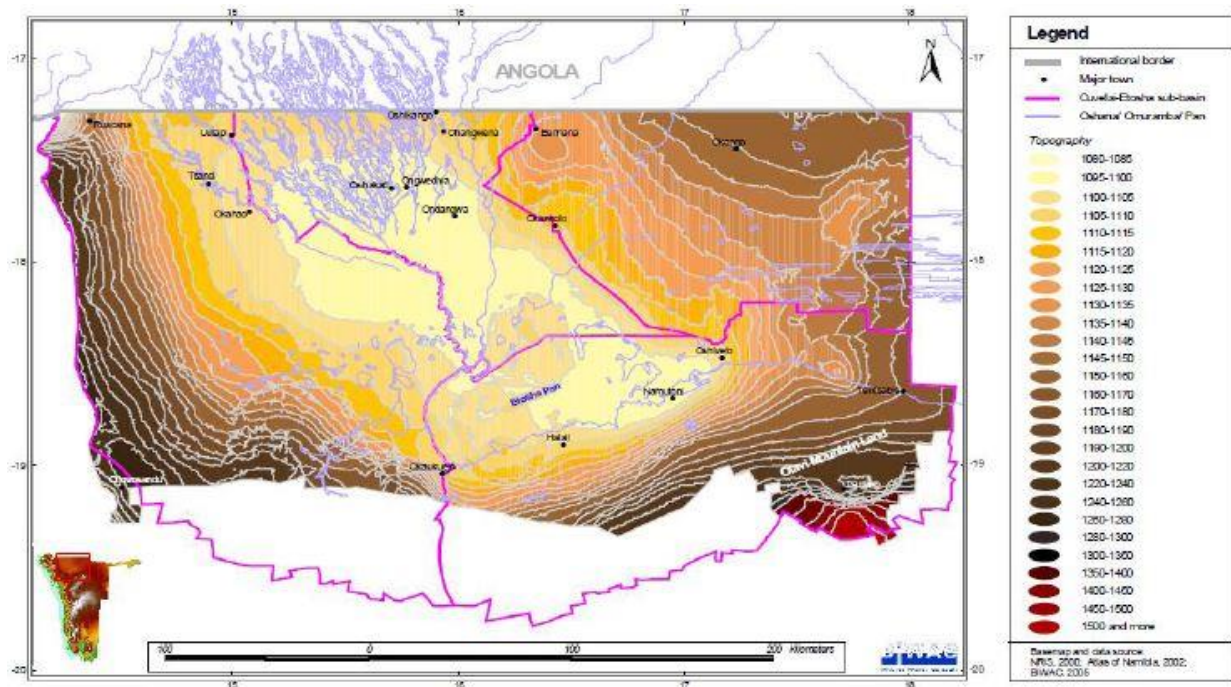


Figure 3: Illustrates the topography of north-central Namibia where the Cuvelai Etosha Basin. (CEB) (Bittner, 2006)

3.2 History of the use of stable isotopes to determine isotopic composition of fresh waters worldwide precipitation

Shortly after world-war II in the late 1940's significant developments in mass spectrometry techniques made accurate measurements of the natural abundances of ^{18}O and ^2H in meteoric waters possible (Rozanski et al., 1993). Craig (1961) made the first attempt to sum up the available information on the isotopic composition of fresh waters worldwide (precipitation included).

In that very year the International Atomic Energy Agency (IAEA) in collaboration with the World Meteoric Organization (WMO) commenced a worldwide survey aimed at systematically collecting isotope content data of precipitation (Rozanski et al., 1993). Measurements of the stable isotopes of water ^{18}O , ^{16}O , ^2H and ^1H is an important tool isotope hydrogeology, as they can be used as tracers of the origin of groundwater recharge. Out of nine isotopically different water molecules, only three occur in nature in easily detectable concentrations: H_2^{16}O , H_2^{18}O and $^1\text{H}^2\text{H}^{16}\text{O}$ (Mook, 2001). Oxygen has three stable isotopes whose natural abundances are as follows: ^{16}O (99.63%), ^{17}O (0.0375%) and ^{18}O (0.1995). Hydrogen on the other hand has two stable isotopes: protium (^1H) and deuterium (^2H , D). Deuterium comprises 0.0184-0.0082% (Kendall et al, 1995).

3.3 Isotopic fractionation: the driving force for the distribution in isotopic composition of precipitation

Considering the abundances stated it is logical to assume that a large proportion of water is composed of ^{16}O and ^1H and small proportion of water molecules incorporate ^{18}O and ^2H in their molecular structure. The heavier isotopes of water have a slightly lower vapour pressure than the lighter isotopes, therefore, they move much slower than the in the liquid, meaning they evaporate more slowly but condense more readily. When a thermodynamic phase change occurs such as, gas to liquid or vice-versa the result is a fractionation.

Isotopic fractionation is an important phenomenon that is defined by the following principles: a reservoir of liquid water under evaporation will become isotopically heavier as lighter isotopes evaporate more readily while a reservoir of water vapour will become isotopically lighter as the heavier isotopes condense preferentially to the lighter isotopes.

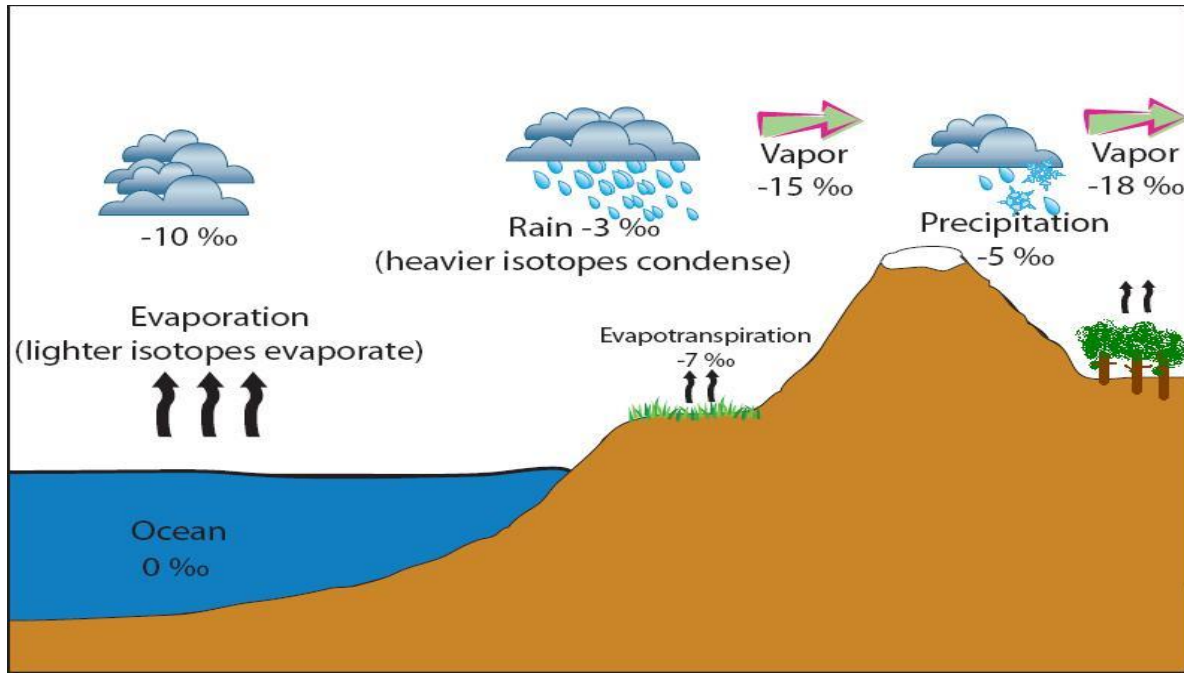


Figure 4: Illustrates the isotopic fractionation process
(source: http://serc.carleton.edu/microbelife/research_methods/enviro_n_sampling/stableisotopes.html).

Ratios of $^{18}\text{O} / ^{16}\text{O}$ and $^2\text{H} / ^1\text{H}$ in waters are reported in ‰ (per mill) relative to Vienna Standard Mean Ocean Water (VSMOW). The delta notation is normally used to report the measured isotope variations, is defined by the following equation;

$$\delta = \left[\frac{R_{\text{Sample}}}{R_{\text{Standard}}} - 1 \right] \times 1000 [\text{‰}] \quad (\text{Equation 1})$$

Where R_{Sample} and R_{Standard} stand for the isotope ratio of the sample and the standard respectively (Rozanski et al., 1993)

Dansgaard (1964), observed based on the assessments of early data compiled by the IAEA/WMO network that a number of environmental parameters characterizing the sampling site, such as, the latitude, altitude, distance from the coast, the amount of precipitation and the surface air temperature have an influence on the distribution of the heavy isotopes ^{18}O and ^2H in meteoric waters. Dansgaard's discoveries were later substantiated by Yurtserver and Gat (1981), Gonfiantini (1981) and Gofiantini (1985). This led to the understanding that the above listed empirical relationships (so called "effects") can in fact be considered as the measure of rainout of

moisture from a given air mass on the way from the source region to the site of precipitation (Rozanski et al., 1993).

Most of the information the follows was taken from Kendall et al (1995).

Craig (1961) observed an important relationship between $\delta^{18}\text{O}$ and $\delta^2\text{H}$ ($\delta \text{ D}$) values of precipitation. This was that $\delta^{18}\text{O}$ and $\delta^2\text{H}$ ($\delta \text{ D}$) values of precipitation that has not evaporated are linearly associated by

$$\delta^2\text{H} = 8 \delta^{18}\text{O} + 10 \quad \text{Equation (2)}$$

“When $\delta^2\text{H}$ is plotted as a function of $\delta^{18}\text{O}$ for water found in continental precipitation, the above experimental linear relationship is observed, described by (equation 2)” (Mayo, Muller & Ralston, as cited in Fetter, 2001). Equation (2) is known as the Global Meteoric water line (GMWL).

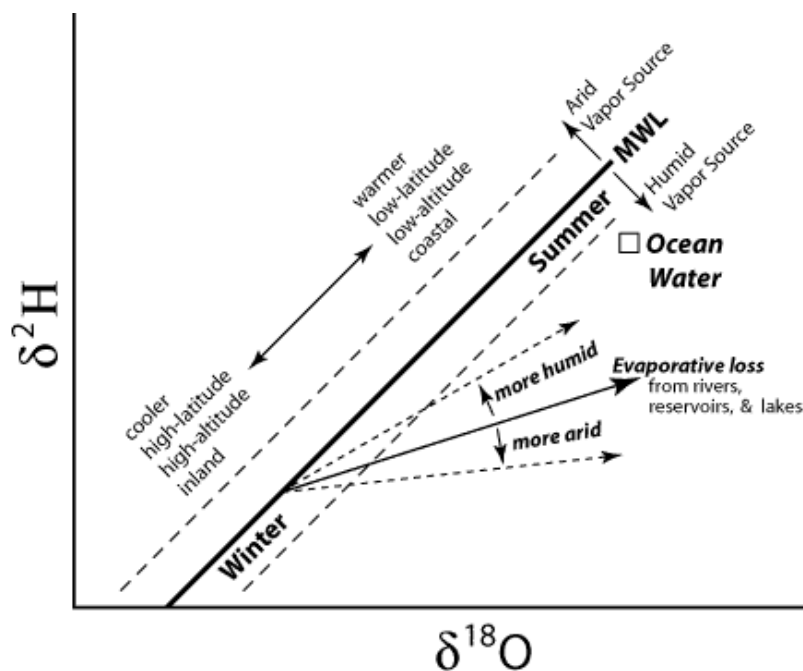


Figure 5: A schematic guide used to illustrate the Global Meteoric Water Line the, the evaporation line and all the necessary information that can be deduced from such plots (figure kindly provided by Paul Koeniger, lecture notes Hydrogeology II, 2013).

The variations of the plots along the GMWL are dependent on the temperature and latitude of the sampled site. Figure 5 therefore summarizes all the important information that can be concluded

based on $\delta^2\text{H}$ vs. $\delta^{18}\text{O}$ cross plots. According to Craig (1961) precipitation that falls in areas with lower temperatures or at higher latitudes tends to have lower $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values as illustrated in figure (5), oceanic water will certainly fall below the meteoric water line as it is isotopically enriched. The GMWL has a linear regression value (correlation coefficient) $r^2 > 0.95$. Kendall et al (1995) asserted that a high correlation coefficient reflects the fact that ^{18}O and ^2H in water molecules are closely related. This is the reason why isotopic ratios and fractionations of the two isotopes are discussed collectively.

Similar to the GMWL is the Local Meteoric Water Line (LMWL), which is derived the same way the GMWL is derived; the only exception is that the LMWL represents precipitation from a single site or local sites. “The slope and intercept of any "Local Meteoric Water Line" (LMWL), which is the line derived from precipitation collected from a single site or set of "local" sites, can be significantly different from the GMWL. In general, most of these local lines have slopes of 8 \pm 0.5, but slopes in the range of 5 and 9 are not uncommon (Kendall et al 1995)”.

Craig (1961) stated that “deviations from the meteoric water line can be interpreted as being caused by precipitation that occurred during a warmer or colder climate than the present.” Kendall et al (1995) substantiated Craig’s findings with regard to the processes that cause waters to plot off the GMWL. Water that has undergone evaporation or mixed with evaporated water generally plots below the MWL at the location of original un-evaporated composition of water. Their slopes are commonly in the range 2 to 5.

Other processes that cause alterations to the isotopic signature of precipitation are: geothermal exchange, as it increases the ^{18}O content of waters and decreases the ^{18}O content of rocks as the waters and rocks attempt to reach a new state of isotopic equilibrium at the elevated temperature (Mayo, Muller & Ralston, as cited in Fetter, 2001). This exchange results in a change in $\delta^{18}\text{O}$ values, but the $\delta^2\text{H}$ values of geothermal waters remain unchanged. Low temperature diagenetic reactions involving silicate hydrolysis can sometimes cause increases in the $\delta^{18}\text{O}$ and δD values of waters.

Most water vapour from which precipitation is derived originates from the evaporation of low latitude oceans. The resulting precipitation from the water vapour is more enriched in ^{18}O and ^2H than the water vapour from which it is derived due to the phenomenon of isotopic fractionation.

Progressive fractionation results in the vapour becoming progressively lighter and lighter as the clouds travel across the continent.

3.4 Effects controlling distribution of isotopic compositions

According to Dansgaard (1964) the distribution of isotopic compositions on a regional scale is controlled by the following:

- ❖ *Latitude effect:* The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values decrease with increasing latitude due to the increasing degree of "rain-out". Water vapour generally becomes lighter as it is transported to higher latitudes.
- ❖ *Amount effect:* The greater the amount of rainfall, the lower the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of the rainfall; this effect is not seen in snow. This effect is dominant in tropical areas.
- ❖ *Altitude effect:* On the windward side of a mountain, the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of precipitation decrease with increasing altitude.
- ❖ *Continental effect:* The ratios decrease inland from the coast. Due to progressive isotopic fractionation and rain-out
- ❖ *Seasonal effect:* since fractionation is temperature dependent, precipitation is isotopically depleted in ^{18}O and ^2H during winter and more enriched during summer

3.5 The mechanisms responsible for the continental and altitude effects

Fundamentally, the same mechanisms are responsible for both the continental and altitude effects gradual removal of moisture from the air mass by condensation initiated by isotopic fractionation as the air mass moves inland or as they experience orographic uplift. This suggests that the general assumption that the ocean is a major source of water vapour might not always be satisfied as large water bodies exist in the interior of continents and the locally re-evaporated water from these water bodies plays an important role in the atmosphere water balance (Salati et al; Sonntag et al; Ingraham and Taylor, as cited in Rozanski, 1993).

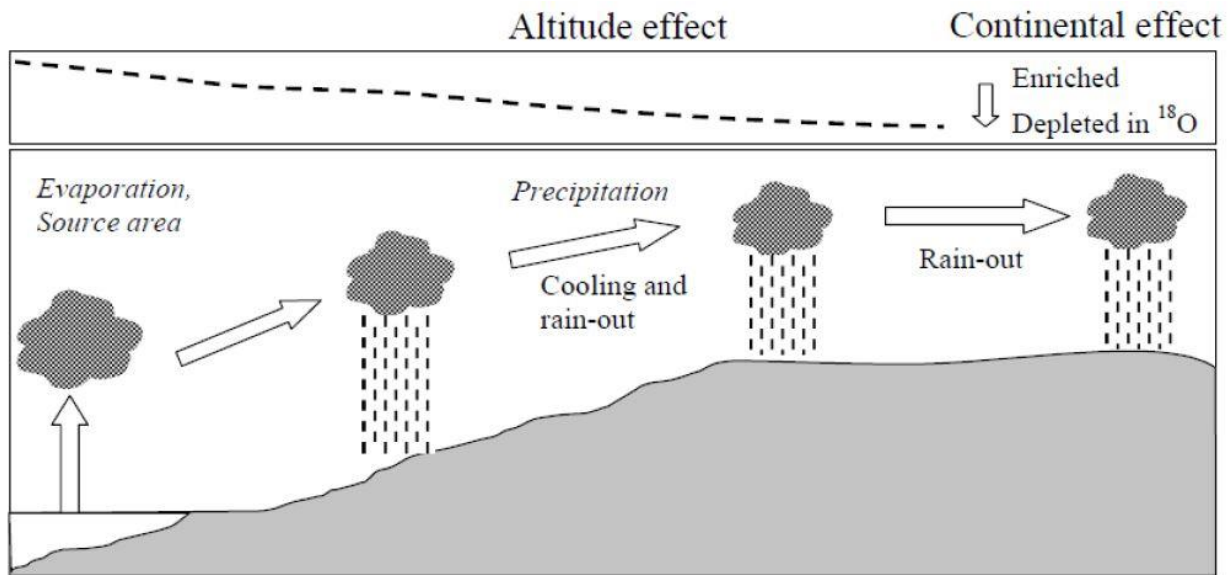


Figure 6: Illustration of the altitude and continental (Kuells, 2000)

The phrase “amount effect” was first coined by Dansgaard (1964), following his observation on the apparent correlation between the amount of monthly precipitation and its isotopic composition. Since southern Africa is a part of this study, figure (7) below illustrates the distribution of precipitation across southern Africa.

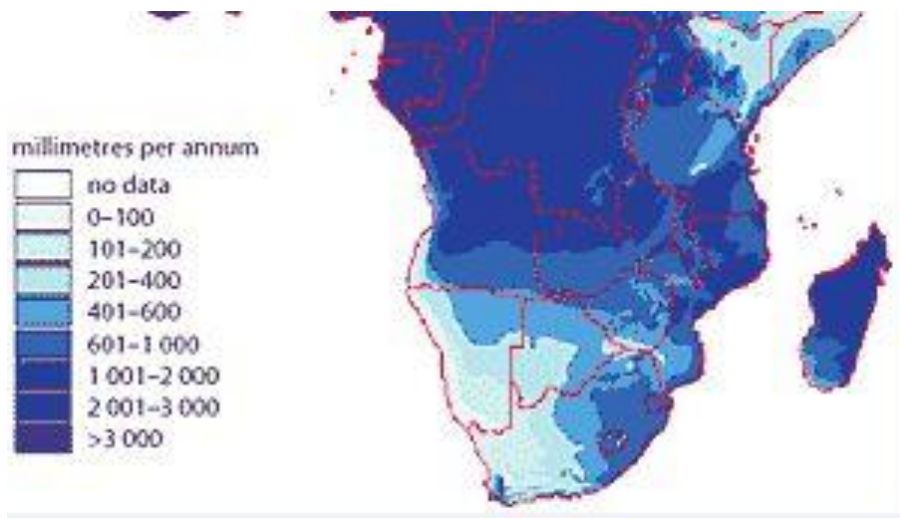


Figure 7: Represents the annual distribution of precipitation south of the Equator showing a decrease from north to south illustrating the latitude and amount effects as a controlling factor of isotopic composition precipitation, and also a decrease of precipitation from east to west, as the Indian ocean is the dominant source of precipitation in southern Africa especially on the eastern side while the Atlantic ocean dominates influence on the western coast. (accessed at <http://www.fao.org/nr/water/aquastat/index.stm>, data based on Leemans and Cramer, 1991).

Gat and Tzur (1967) observed that at a given location, the seasonal variations in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of precipitation and the weighted average annual $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of precipitations remain relatively constant from year to year. This is due to the fact that the annual range and sequence of climatic conditions such as; temperatures, vapour sources, direction of air mass movement remain fairly constant annually. Generally consistent with the “seasonal effect”, rain in summer is isotopically heavier than in winter. This alteration in isotopic signature is predominantly caused by seasonal temperature variations but is also affected by seasonal variations in moisture sources and storm tracks. Shallow groundwater $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values reflect or maintain the local average precipitation isotopic signature but are subsequently altered by selective recharge and fractionation processes that may adjust the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of the precipitation before it extends its influence into the saturated zone (as cited in Kendall, 1995).

3.6 Precipitation and subsurface infiltration

According to Stichler (1987), some of the processes responsible for the modification of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of the precipitation prior to or as it infiltrates the subsurface are the following:

- ✓ Evaporation of rain during infiltration
- ✓ Selective recharge
- ✓ Interception of precipitation by the tree canopy
- ✓ Exchange of infiltrating water with atmospheric vapour

In the case of snow, various post-positional processes such as melting and subsequent infiltration of the surface layers and evaporation may alter the content of the snowpack which often leads to melt-water δ values becoming increasingly enriched.

3.7 Meteoric water in the saturated zone of the subsurface

After meteoric water (water derived from precipitation; rain or snow) infiltrates the subsurface, it traverses the zone of aeration and subsequently enters the saturated zone. The δ values of the subsurface water are altered by mixing with waters that have dissimilar isotopic contents. The homogenizing effects of recharge and dispersive processes produce ground water with δ values

that approach uniformity in time and space, therefore the δ values approximate a damped reflection of the precipitation over a period of years.

“Stichler’s study also revealed that although an individual storm may be large and isotopically very different from the old water in the catchment, the amount of precipitation that infiltrates will likely be small compared to the amount of old water in storage. Although there may be significant storm-to-storm and seasonal variations in precipitation $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values, base flow δ values remain relatively uniform in most streams in humid, temperate areas (Kendall et al, 1995).”

3.8 Stable isotopes in precipitation in relation to catchment areas

According to Turner et al (1987), seasonal variations in precipitation δ values in small catchments may be reflected by temporal and spatial variability in ground water and base flow δ values. These variations are however, less extreme and usually delayed relative to the temporal variations that occur in precipitation. These temporal variations can be utilized for water residence time calculations.

Sklash et al (1976) asserted that isotope hydrologists use the potential difference between the uniform old water and variable new water to determine the contribution of old and new water to a stream during periods of high run off. When storm-to-storm and intra-storm variations in the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of precipitation are superimposed on the seasonal cycles in precipitation δ values, the variations may be as large as the seasonal variations.

4. Research Methodology

The research methodology of this project was composed of three main parts

1. Desk study (on the topic)
2. Field work (sample collecting)
3. Analytical methods (a spectro-analyzer was used to analyze for ^{18}O and ^2H content, followed by chloride content analysis using an ion selective electrode)

4.1 Desk study

A desktop study was conducted in order to have a clear understanding and overview of what the topic entails, to spot the knowledge gaps and more importantly in order to follow the stipulated guidelines set by the IAEA for sample collection and analytical methods used in the determination of oxygen-18 and deuterium content of meteoric water; in order to plan for the field work to be done. Isotope precipitation data obtained from IAEA/GNIP/WMO stations in other parts of southern Africa were also analyzed in order to make comparisons and infer from them the likely expectations of the distribution of isotopic compositions across southern Africa.

4.2 Field work (sample collection)

Sampling of the meteoric waters (precipitation) was conducted in the Namibian northern flood plains that form part of the Cuvelai Etosha Basin (CEB). The sampling procedure involved rinsing the sampling vial with the water, twice; then filled vial to the brim, tightly closing it and labeling it. GPS measurements of the sampling point as well as the turbidity, electric conductivity and temperature of the water were taken and recorded on the spot in addition to a brief description of the landscape and vegetation surrounding the sampling point.

The sampling plan involved making two major traverses, one oriented N-S and the other E-W. This was in order to fit the hypothesis that precipitation generally becomes isotopically lighter from east to west (as precipitation comes in from the Indian Ocean) and becomes isotopically lighter from north to south away from the Intercontinental Convergence Zone (ITCZ), in this study the equator is the northern reference.

The sampling was conducted at an approximate ± 5 km sampling interval though some samples were taken in closer proximity to one another and others further apart depending on the distance that had to be covered and the accessibility of sampling spots. 50 samples were collected and stored for laboratory analysis.

4.3 Analytical methods

Stable isotopic composition of water and dissolved substances in water have a relatively long application history in water and groundwater resource studies. Until recently the analyses of the stable isotopes have been dominated by IRMS while since a few years laser spectrometers have become a more common analytic tool. Laser spectrometers for stable isotope analyses are offered by several companies now on a commercial basis (e.g., Picarro, Los Gatos and Thermo Scientific). Especially for the analyses of the ratios of stable isotopes of water ($^2\text{H}/^1\text{H}$ and $^{18}\text{O}/^{16}\text{O}$), the laser spectrometers are very cost effective regarding investment and maintenance costs. In addition they are applicable for field studies, relative easy to run and results are obtained in short time periods, e.g. the Los Gatos LGR DLT-100 at the University of Namibia can analyze up to 30 samples for both isotopic ratios within 24 hours.

The principle for the determination of the isotope ratios is based on characteristic absorptions lines that are shown by gas molecules in the near infrared. The peak height can then be used for the concentration determination with a defined wave length and under controlled environmental conditions (pressure and temperature). Specific techniques, e.g. cavity ring-down, increase the sensitivity of the measurement in such a way that they can also be used for isotopic analyses.

The collected samples were then analyzed for their ^{18}O and ^2H content in the hydrogeology lab at University of Namibia. The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values were determined using a laser spectrometer (Los Gatos). The results were then recorded in a spreadsheet for data and interpretation of the results.

Isotope composition determination.

An auto sampler injects a few μl of sample from 10 ml bottles into a vaporizer. The water vapour is carried in a stream of nitrogen under defined temperature and pressure conditions to the absorption measurement in the analyzer (laser chamber).



Figure 8: Laser Spectroanalyzer at the Geology Department, University of Nmaibia.



Figure 9: Selective ion electrode

The samples were then analyzed for the chloride content using an ion selective electrode. The chloride content analysis was then performed on each of the 50 samples. This was done by immersing and rinsing the electrode in a small amount of each surface water sample. 25ml of the water sampled was transferred into a beaker. Subsequently, an ionic strength adjustment powder was added to the water sample in the beaker. The beaker contents were then stirred using the electrode until the powder had dissolved and the selective ion electrode device attained the chloride content value of the sample. The values obtained were then recorded. The beaker was then rinsed and the process repeated for all the samples.

5. Data analysis and interpretation of results

5.1 Results

The table that follows shows results of the preliminary analysis of the data used in this study and from which interpretation of the results is derived.

Table 1 shows data preliminary analysis of data used in the study of the CEB

Sample ID	Longitude	Latitude	EC (μs/cm)	Temp(° C)	δ ² H(‰)	δ ¹⁸ O (‰)	Cl content (mg/l)
NM-1	15.46775	-17.6626	3020	21.2	67.3	16.4	699
NM-2	15.47497	-17.6901	394	20.4	34.1	9.81	30.9
NM-3	15.48495	-17.7085	937	22.3	66.6	17.01	95.8
NM-4	15.49138	-17.7215	382	20.1	4.4	3.65	44.4
NM-5	15.49376	-17.7365	396	20.4	4.9	2.86	72.5
NM-6	15.48639	-17.7457	874	22	51.3	12.24	230
NM-7	15.47884	-17.7834	2190	24.2	74.7	15.46	583
NM-8	15.47417	-17.7879	431	21.2	44.8	10.01	87.3
NM-9	15.49218	-17.7295	1494	21.9	62.2	14.23	527
NM-10	15.49202	-17.7288	4900	25.8	97.8	21.21	1864
NM-11	15.47676	-17.649	241	25.6	41.5	10.5	31.8
NM-12	15.46371	-17.6557	350	25.7	39.6	10.25	56.3
NM-13	15.4534	-17.6498	315	24.6	38	10.57	60.4
NM-14	15.4259	-17.6072	1227	25.3	29.8	9.48	390
NM-15	15.41153	-17.5986	467	24.3	32.5	8.89	49.2
NM-16	15.39962	-17.5839	4330	23.8	59.3	12.35	1841
NM-17	15.37527	-17.5541	1515	23.4	23.4	6.81	447
NM-18	15.36589	-17.5148	2040	24.2	10.3	4.17	720
NM-19	15.33562	-17.4539	214	24.7	-2.7	0.94	27.6
NM-20	15.35455	-17.4268	159.4	26	32.4	8.76	34.5
NM-21	15.36674	-17.3974	108.6	26.6	29.5	8.2	5.68
NM-22	15.4578	-17.463	368	26.4	60.2	14.24	28.5
NM-23	15.40075	-17.4577	235	25.5	18	6.02	31.4
NM-24	15.2788	-17.4441	206	27.3	22.8	6.84	21.2
NM-25	15.19127	-17.4543	35.3	27.1	104.8	21.02	2.27
NM-26	15.17559	-17.4576	121.6	25	49.3	11.95	36.8
NM-27	15.10488	-17.4643	645	26.4	63.3	14.6	136
NM-28	15.05863	-17.4858	115.6	25.3	35.9	9	12.7
NM-29	15.0041	-17.5008	275	18.7	-5.4	0.76	56.4
NM-30	14.95855	-17.4935	67	18.9	-6.9	0.84	4.75

NM-31	14.86303	-17.4627	129	19.6	47.1	12.13	16
NM-32	14.8302	-17.4286	140	20.6	5.9	4.25	12.9
NM-33	14.74762	-17.4389	782	22.7	101.5	22.75	234
NM-34	14.64187	-17.4319	136.1	24	-2.1	0.56	6.53
NM-35	14.59672	-17.425	214	23.7	26	7.62	14.2
NM-36	14.21693	-17.4066	570	24.1	-24.4	-3.9	4.8
NM-37	14.68192	-17.4368	82.7	26.1	41.6	12.53	9.06
NM-38	14.94936	-17.5383	98	22.7	9.8	4.38	12.5
NM-39	14.97408	-17.5521	104.3	24.4	13.1	4.73	12
NM-40	15.00686	-17.5533	396	24.9	43.4	10.85	96.4
NM-41	15.19943	-18.4265	170	27.1	76.1	21.04	50.4
NM-42	15.1952	-18.3963	168.8	27.8	42.6	12.69	16.3
NM-43	15.15417	-18.0162	215	25.8	19.8	6.9	32.2
NM-44	16.2595	-18.0871	173.9	19.2	14.8	5.88	15.7
NM-45	16.09205	-17.9674	270	23.2	32.3	10.25	29.5
NM-46	15.72733	-17.7875	246	23.7	36.4	9.5	19.6
NM-47	15.3919	-17.9333	1222	26.3	10.1	4.21	371
NM-48	15.31382	-17.8013	3890	28.2	82.8	17.66	1119
NM-49	15.26395	-17.7745	415	27.1	44.2	11.24	117
NM-50	15.27037	-17.6396	255	23.6	23.3	6.63	51.1

The information in table1 is important as it covers most aspects of this study. Therefore the graphs that follow (figure11 and 12) are based on the information derived from table 1.

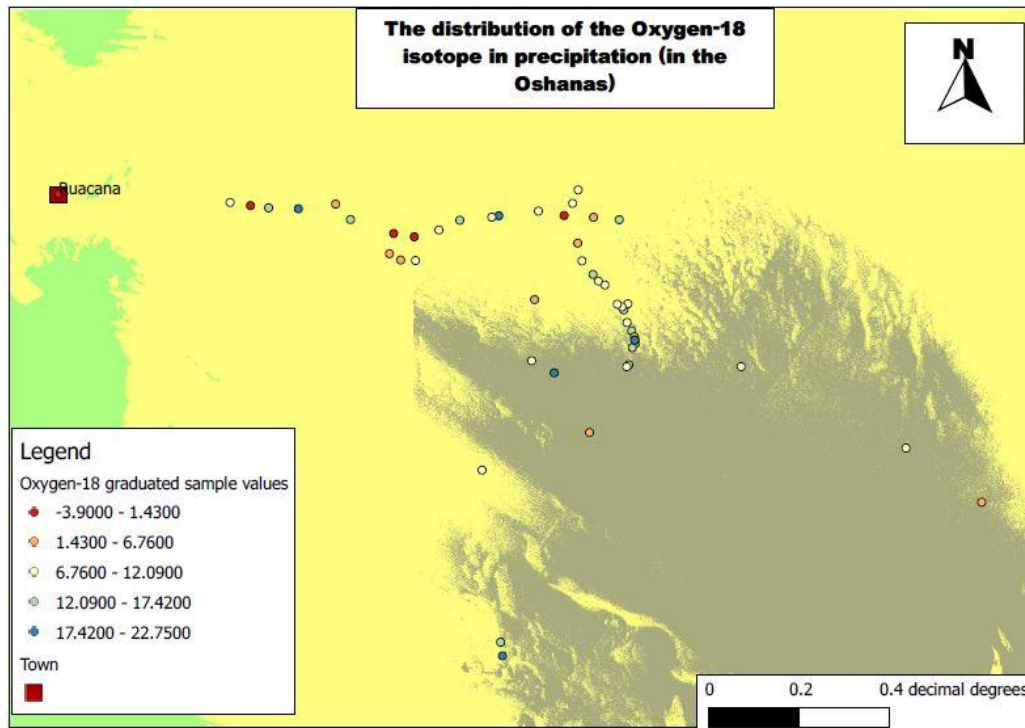


Figure (10) Map showing the distribution of $\delta^{18}\text{O}$ in surface waters in the CEB (Q-gis)

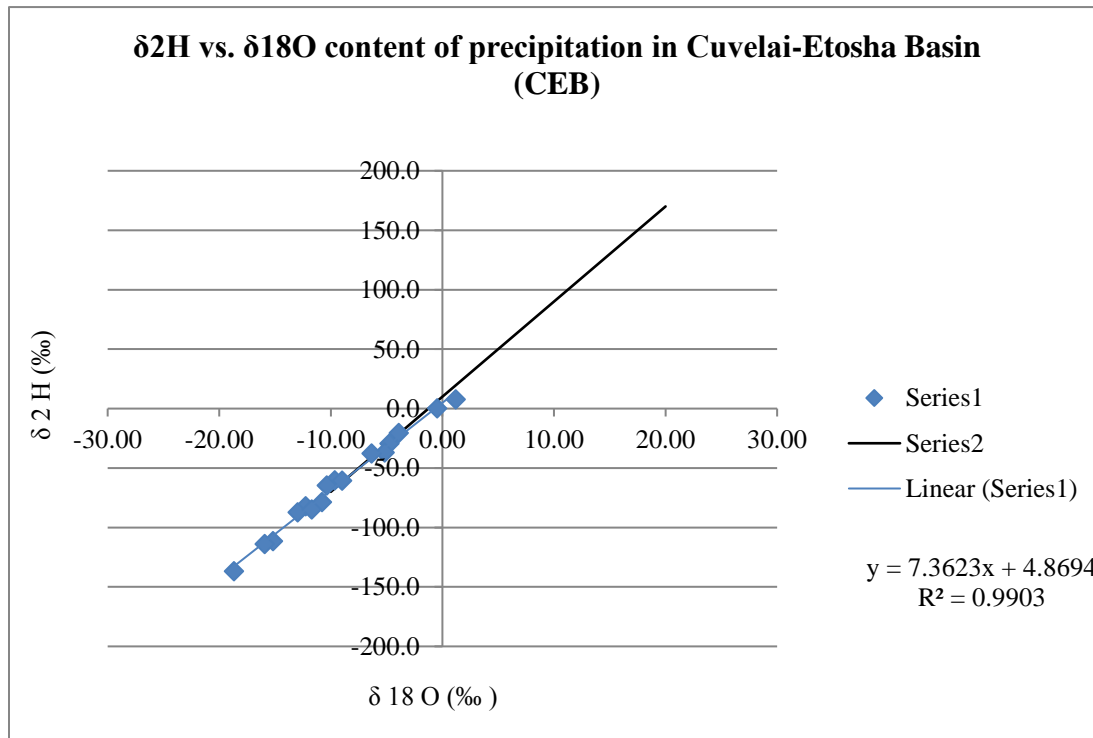


Figure (11): Illustrates a plot of $\delta^2\text{H}$ vs. $\delta^{18}\text{O}$ from which the Local Meteoric Water Line (LMWL) for the Cuvelai Etosha Basin (CEB).

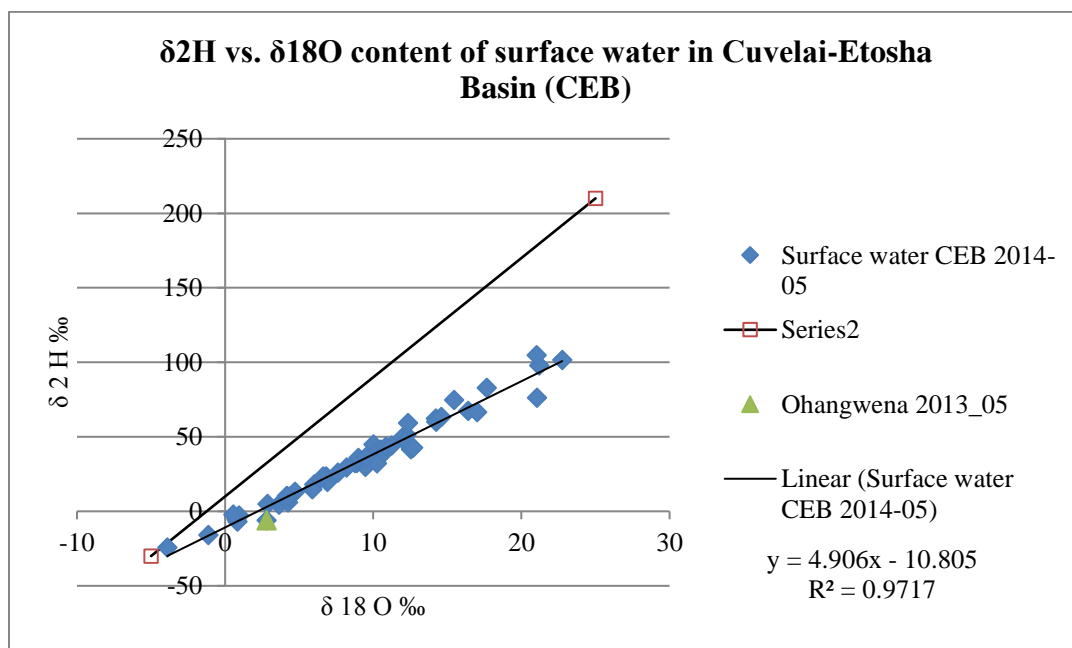


Figure (12): Illustrates the plot of $\delta^2\text{H}$ vs. $\delta^{18}\text{O}$ of the surface water which indicates the evaporation line for the Cuvelai Etosha Basin (CEB).

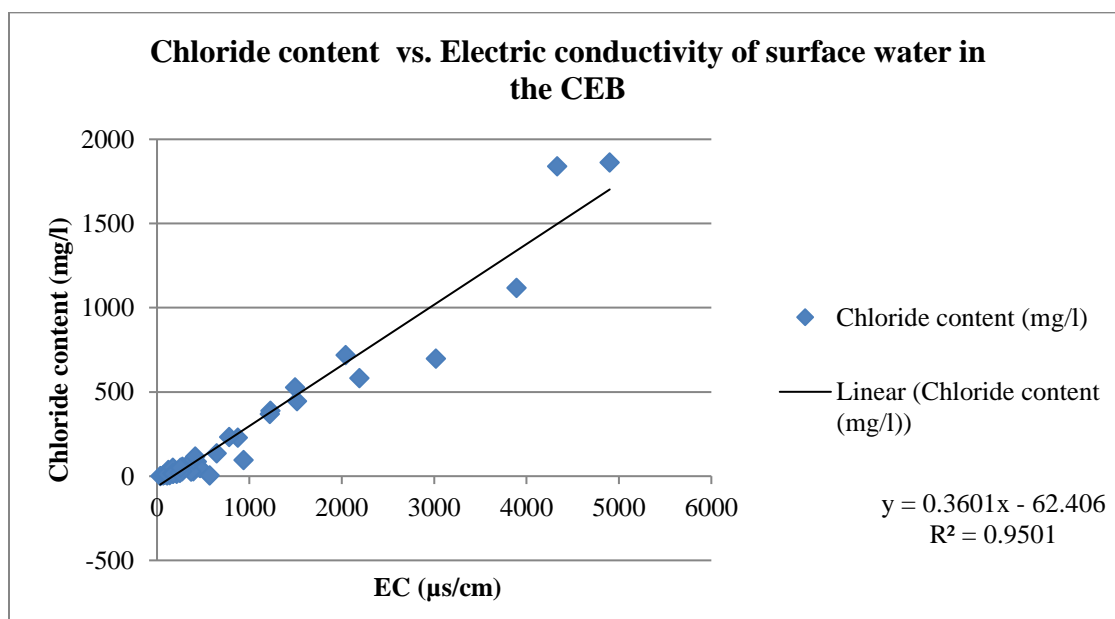


Figure (13) show a graph of the chloride content plotted against the electric conductivity and shows the direct proportionality and intimate relationship between the two parameters.

The schematic below shows the mean isotopic composition of precipitation of Windhoek from 1961 to 2001.

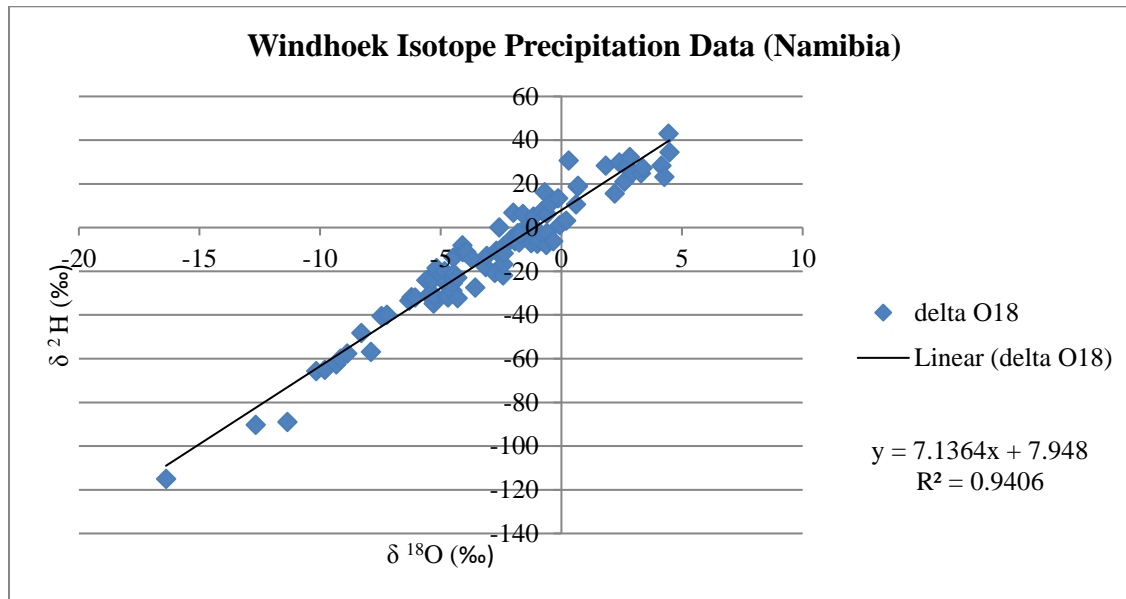


Figure 14: Shows a $\delta^2\text{H}$ vs. $\delta^{18}\text{O}$ plot for Windhoek (precipitation data) for the period between 1961 and 2001.

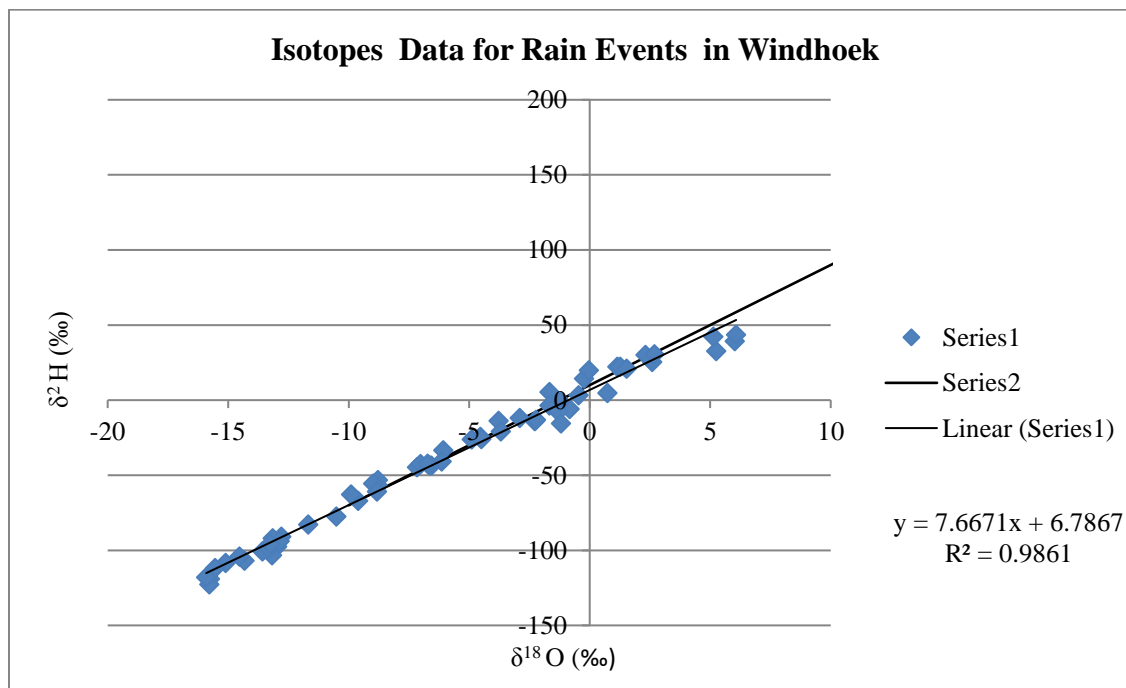


Figure 15: Shows a $\delta^2\text{H}$ vs. $\delta^{18}\text{O}$ plot for Windhoek rain events for the past two years.

The preceding results depict the local Namibian picture of the variation in isotopic composition of precipitation and surface waters. A look at the “bigger southern African picture” is advantageous as it clearly shows the spatial variation and distribution of isotopic composition in precipitation, variation in LMWL from location to location in relation to, the latitude, the source of precipitation, the local environmental and climatic conditions. And consequently substantiates the theories on the factors that control the isotopic composition of precipitation. Table 2 contains results from selected locations south of the Equator.

Table 2: Represents the different locations south of the Equator used to investigate some factors that control the isotopic composition of precipitation such as the latitude and altitude as well as the resultant LMWL slope and correlation factor indicating the “bigger southern African picture”. (Source)

IAEA/WMO station	Country	Latitude	Longitude	Altitude	LMWL (slope)	R ² value)
Rukungiri	Uganda	-0.84	29.94	1595	7.77	0.98
Muguga	Kenya	-1.22	36.63	2070	7.92	0.96
Kinshasa (Binza)	DRC	-4.37	15.25	438	7.93	0.97
Dar- es Salaam	Tanzania	-6.88	39.2	55	7.18	0.89
Ndola	Zambia	-13	28.65	1331	6.85	0.86
Menongue	Angola	-14.67	17.7	1348	6.6	0.93
Harare	Zimbabwe	-17.83	31.02	1471	7.8	0.96
Windhoek	Namibia	-22.94	17.15	1685	6.63	0.65
Cape town	South Africa	-33.97	18.6	44	6.01	0.92

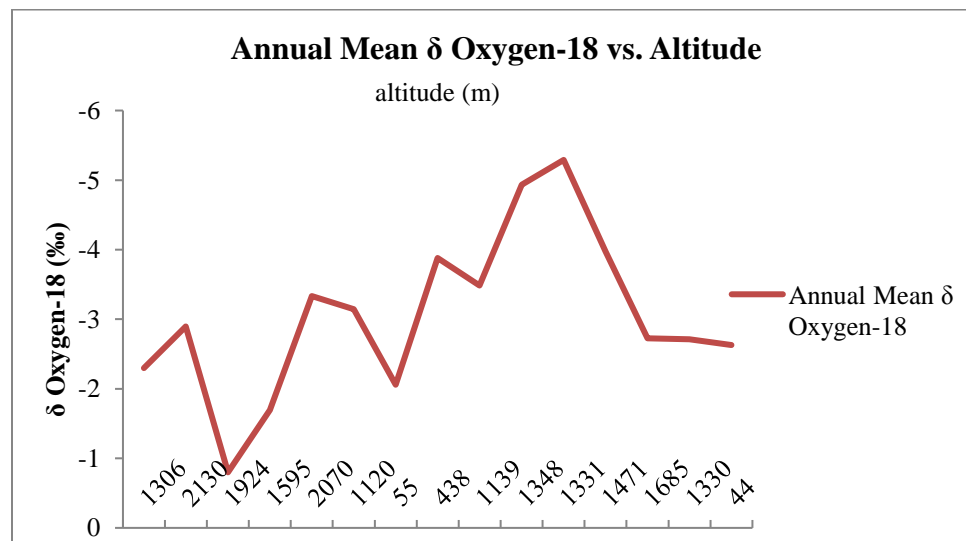


Figure 16: represents $\delta^{18}\text{O}$ values for IAEA stations plotted against the altitude of the station's location.

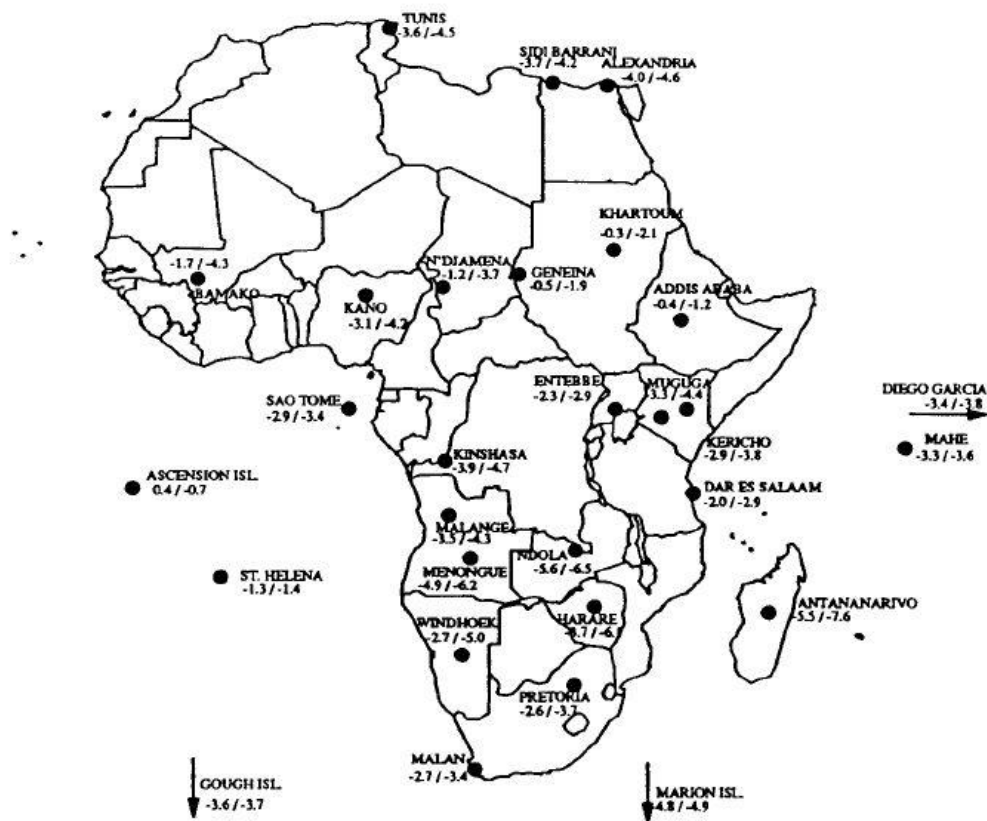


Figure 17: shows the geographic distribution of the IAEA network stations across Africa. The stations are identified by name. For each station the long term arithmetic mean (first number) and the weighted mean (second number) of $\delta^{18}\text{O}$ values are indicated (Rozanski, 1993)

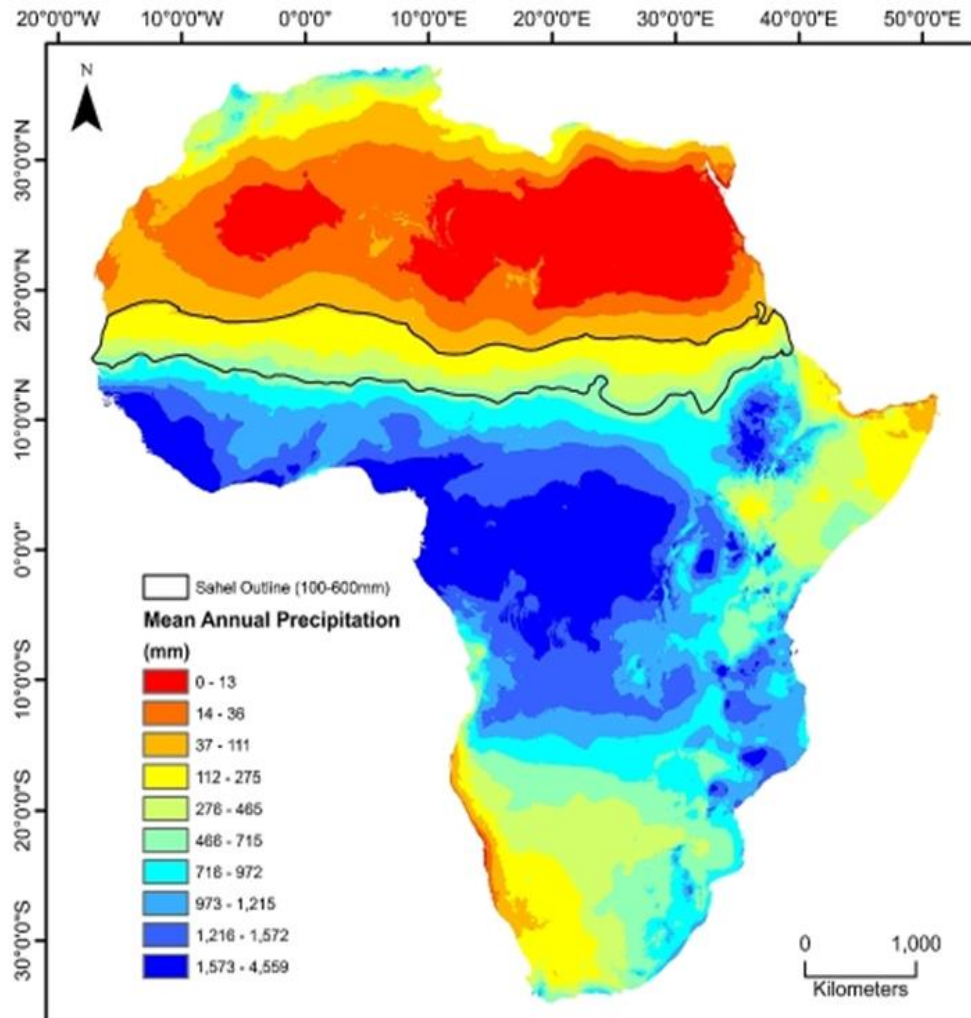


Figure 18: A schematic that shows distribution of annual mean precipitation on the continent of Africa
(Source: <http://www.nateko.lu.se>)

6. Discussion

The map in figure (10) illustrates the $\delta^{18}\text{O}$ distribution of surface waters in the CEB sampled area. It is evident from the map that $\delta^{18}\text{O}$ values are random and show no particular ^{18}O isotopic distribution pattern which is shown by the contrast in the $\delta^{18}\text{O}$ isotopic signatures of the sampled waters. Based on this observation it can be deduced that the sampled waters may have undergone differential evaporation and / or possible mixing with locally or regionally evaporated water depending on the interconnectivity of the part of basin sampled. This assumption is because some of the surface water bodies lie in total isolation, some isolated water bodies undergo mixing during flooding and still others are part of regionally extensive systems. These assumptions or conclusions are consistent with the findings of Craig, as cited in Kendall et al. (1995).

With reference to figure (11) the slope of LMWL of the Cuvelai-Etosha Basin (CEB) study area is 7.36 and the consequent linear regression value obtained, R^2 is 0.99. In general, most local lines have slopes of 8 ± 0.5 , but slopes in the range of 5 and 9 are not uncommon. High correlation coefficient (R^2) values > 0.95 suggests that the oxygen and hydrogen stable isotopes in water molecules are intimately related, it is therefore unquestionably the reason the ^{18}O and ^2H isotopic ratios and fractionations are frequently studied together according to Craig, as cited in Kendall et al. (1995). This therefore possibly indicates that the precipitation originated from the same source and the water has not undergone considerable mixing. An R^2 of 0.99 could also indicate consistency in the source of precipitation.

Figure (12) illustrates a plot of $\delta^2\text{H}$ vs. $\delta^{18}\text{O}$ of the surface water which indicates the evaporation line for the (CEB). The evaporation line has a slope of 4.91 and R^2 value of 0.97 as initially stated, the high correlation coefficient indicates the close relationship between ^{18}O and ^2H . Water that has undergone evaporation or mixed with evaporated water generally plots below the MWL at the location of original un-evaporated composition of water typically have slopes in the range 2 to 5, which is also consistent with Craig's findings substantiated in Kendall et al (1995) and exemplified in figure (5).

Figure (13) is a schematic illustrating the importance of electrical conductivity and chloride content analysis of surface water. Since electrical conductivity is the ability of a material to let current flow through it when an electric current is applied, it is linked to the quantity of salts dissolved in the water (Bernard, 2003). The two parameters are directly proportional and therefore, have a linear relationship and as indicated in figure (13) the graph has a high correlation coefficient (R^2) value of 0.9501 indicating an intimate relationship between the two parameters. They can in fact be considered as a measure of evaporation that the meteoric water has experienced. With lower values indicating considerably low evaporation and high values signifying significant evaporation of meteoric or surface water.

A comparison of the results obtained for Windhoek (central Namibia) figure (14) with those obtained in the CEB (north central Namibia) figure (11) with an additional reference to figure (7) which indicates the amounts of precipitation across southern Africa. It is quite evident that in CEB, the “latitude effect”, “precipitation amount effect” and seasonality are play the most dominant role in influencing the distribution of isotopic composition of the meteoric precipitation. The CEB receives more precipitation annually, the CEB has a regular source of precipitation while the source of precipitation received in Windhoek has various sources, it is located at a lower latitude and Windhoek is considerably drier than the CEB. The variation in sources is observed in when LMWL’s of the CEB and Windhoek are compared. Windhoek has a lower correlation coefficient (R^2) value of 0.94 indicating a slightly distant ^{18}O and ^2H isotopic relationship as compared to the (R^2) value of 0.99 for the CEB. The LMWL slope for Windhoek is 7.14 compared to 7.36 which is possibly due to variation in temperatures, vapour sources, evaporation rates and direction of air mass movement.

A comparison between figure (14) and figure (15) which represent results from Windhoek on a long term and a relatively shorter term, respectively. Figure (15) has a slope of 7.67 while figure (14) has a slope of 7.14. Though no conclusions can be drawn from the two year period for figure (15) due to the relatively short time of study, the variations could probably be as a result of climate change, the way in which the samples were taken over a long period compared to shorter period or maybe in line with Stichler’s (1987) which revealed that although an individual storm may be large and isotopically very different from the old water in the catchment and there

may be significant storm-to-storm and seasonal variations in precipitation $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values, base flow δ values remain relatively uniform in most streams in humid, temperate areas.

Taking into consideration the “bigger southern African picture” several observations were made. In view of the annual precipitation information illustrated in figure (18) and figure (7) combined with the information in table 2. It is apparent that on a regional scale, the distribution of isotopic compositions is dominantly controlled by two factors, namely, the “latitude effect” and the “amount effect”. The altitude effect is not really observed to have any dominant influence on the distribution of isotopic compositions of ^{18}O and ^2H in precipitation figure (16) substantiates this. The influence of these effects on the isotopic composition of meteoric water is consistent with the assertions made by Dansgaard, (Dansgaard, 1964)

The a diminution in the precipitation is observed from east to west, with the least precipitation observed in the south-west part of Africa, a decline in precipitation is similarly observed in from north to south. Signifying the influence of the latitude effect and the amount effect on the distribution of isotopic compositions of ^{18}O and ^2H in precipitation.

Another observation made is that as one moves down south from the Equator there is an observed decrease in the LMWL slopes. This is demonstrated in table 2 from Muguga to Cape Town, the LMWL slope values decrease from 7.92 to 6.01 respectively. This could possibly be as a result of difference in sources of precipitation and/or mixing of air masses carry precipitation with different isotopic signatures and the path of fractionation of the air mass from source to the site of precipitation.

On the western coast the lower correlation coefficient values could be attributed to the interference or the influence of precipitation from the Atlantic Ocean as southern African precipitation is dominantly sourced from the eastern coast- the Indian Ocean.

The results obtained are consistent with the assumptions stated in the hypothesis of the study and are coherent with previously published work on the topic.

7. Conclusion

In conclusion, the determination of the LMWL of the CEB and the linear regression analysis (correlation coefficient determination) enabled the understanding of how evaporation of precipitation and surface waters differs from one location to the next due to difference in topography, vegetative cover, variations in temperature and vapour sources, path fractionations, evaporation rates and direction of air mass movement. LMWL's were not constant but varied with respect to location and environmental conditions. It was also resolved that correlation coefficients can be used to determine the intimate relation between ^{18}O and ^2H in precipitation which consequently leads to the determination of the source (single source or variable sources).

It was apparent that there was no clear pattern observed in the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values obtained, variation in the values at each sampling site meant that the sampled waters had experienced differential evaporation or experienced considerable mixing with evaporated waters from local or regional sources. This was consequently shown by the contrast in the $\delta^{18}\text{O}$ isotopic signatures of the sampled waters.

Electrical conductivity and chloride content analysis of the meteoric water was very important as it is used to determine the measure of evaporation that the meteoric water has experienced and also substantiating the evidence of how much evaporation the waters has undergone.

Evidently from the results obtained that in the CEB, the “latitude effect”, “precipitation amount effect” and seasonality are play the most dominant role in influencing the distribution of isotopic composition of the meteoric water with higher isotopic values encountered in warmer or drier periods.

It was obvious based the study on a regional scale that; the distribution of isotopic compositions south of the Equator is predominantly controlled by “latitude effect” and the “amount of precipitation effect” while the altitude effect was not really observed to have any dominant influence on the distribution of isotopic compositions of ^{18}O and ^2H in precipitation.

The observed lower correlation coefficient values from north (Equator) to the south of the African continent could be attributed to the influence of precipitation from the Atlantic Ocean as southern African precipitation mainly originates from the Indian Ocean.

References

1. Bernard, J. (2003). The principles of geophysical methods for groundwater investigations. Retrieved September 1, 2014, from www.heritagegeophysics.com/papers/Groundwater_n_Geophysics.pdf
2. Bittner, A. (2006). Desk Study Report: Cuvelai-Etosha Groundwater Investigation. Bittner
3. Water Consult CC, Windhoek, Namibia
4. Craig, H. (1961). Isotopic variations in meteoric waters. *Science* 133: 1702-1703
5. Dansgaard, W. (1964). Stable isotopes in precipitation. - *Tellus* 16: 436-468.
6. Fetter, C.W. (2001). *Applied Hydrogeology*, 4th edition. Pearson prentice hall
7. Gat, J.R., and Tzur, Y. (1967). "Modification of the isotopic composition of rainwater by processes which occur before groundwater recharge". *Isotope Hydrology*, Proc. Symp. Vienna 1966, IAEA, Vienna, 49-60
8. Gonfiantini, R. (1982). On the Isotopic Composition of Precipitation. *Rendiconti Soc. It. Miner. Petr.*, 38 pp 1175-1187
9. Gonfiantini, R. (1985). On the Isotopic Composition of Precipitation in Tropical Stations, *Acta Amazonica*, 15, pp 121-139.
10. Ingraham, N.L., and Taylor, B.E. (1986). Hydrogen Isotope Study of Large-Scale Meteoric Water Transport in Northern California And Nevada, *J. Hydrol.*, 85 pp 183-197.
11. Integrated Water Resource Management (Cuvelai-Etosha River Basin) booklet (2010).
12. Kendall, C., Snyder, D. & Caldwell, E. (1995). Resources on Isotopes.
13. Kuells, C. (2000). Groundwater of the North-Western Kalahari, Namibia, Estimation of Recharge and Quantification of the Flow System. - Doctorate Thesis, Julius-Maximilian University of Würzburg.
14. Leemans, R. and Cramer, W. (1991). The IIASA database for mean monthly values of temperature, precipitation and cloudiness on a global terrestrial grid. Research Report RR-91-18. November 1991. International Institute of Applied Systems Analysis, Laxenburg, Austria. 61 p.

15. Mayo, A.L., Muller, A.B. & Ralston. (1985). Hydrogeology of the Meade Thrust Allochthon, Southeastern Idaho, U.S.A., and its relevance to stratigraphic and structural groundwater flow control. *Journal of hydrology* 76:27-61
16. Mendelsohn, J., Jarvis, A., Roberts, C. & Robertson, T. (2002). Atlas of Namibia. - 200 p.; David Philip Publishers/Capetown.
17. Mook, W.G. (2000). UNESCO/IAEA Series on Environmental Isotopes in the Hydrological Cycle, Principles and Applications. – No. 39 Vol. 1 UNESCO, Paris, 2000
18. Rozanski, K., Araguás-Araguás, L., & Gonfiantini, R. (1993). Isotopic Patterns in Modern Global Precipitation. - Geophysical Monograph Series, VOL. 78
19. Salati, E., Dall'Olio, A., Matsui, E. & Gat, J.R. (1979). An Isotopic Study: Recycling Of Water in the Amazon Basin. *Water Resour. Res* 15, pp 1250-1258.
20. Sklash, M.G., Farvolden, R.N., and Fritz, P., (1976). "A conceptual model of watershed response to rainfall, developed through the use of oxygen-18 as a natural tracer". *Can. J. Earth Sci.*, 13: 271-283.
21. Sonntag, C., Rozanski, K., Munnich, K.O. & Jacob, H. (1983). Variations Of Deuterium and Oxygen-18 in Continental Precipitation and Groundwater and their Causes, in the Global Water Budget. pp 107-124. edited by A. Street et al., Reidel Publishing Company.
22. Stichler, W. (1987). "Snowcover and snowmelt process studies by means of environmental isotopes", In: H.G. Jones and W.J. Orville-Thomas (Eds.), *Seasonal Snowcovers: Physics, Chemistry, Hydrology* D. Reidel Publishers, pp. 673-726.
23. Turewicz, V. (2013). Stable Isotopes in Waters in Namibia – B.Sc. Geosciences Thesis, University of Cologne.
24. Turner, J.V., Macpherson, D.K., and Stokes, R.A., (1987). "The mechanisms of catchment flow processes using natural variations in deuterium and oxygen-18." In: A.J. Peck and D.R. Williamson (Eds.), *Hydrology and Salinity in the Collie River Basin, Western Australia*. *J. Hydrol.*, 94: 143-162.
25. Yurtserver, Y. & Gat, J.R. (1981). Atmospheric waters in Stable Isotope Hydrology; Deuterium and Oxygen-18 in the Water Cycle, edited by Gat J.R and Gonfiantini, Technical Report Series, No. 210, pp 103-142, International Atomic Energy Agency, Vienna.

