

**GROUNDWATER RECHARGE OF PERCHED AQUIFERS IN THE CUVELAI-
ETOSHA BASIN, NAMIBIA**

A DISSERTATION SUBMITTED IN FULFILMENT OF THE REQUIREMENTS FOR THE
DEGREE

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BY

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Abstract

The United Nation predicted that by 2025, 1.8 billion people will be living in countries with absolute water scarcity and two-thirds of the world population could be under stress condition. In semi-arid regions, most communities depend on groundwater as the source of drinking water and thus with changes in global climatic conditions and increase in population, groundwater resources are facing challenges of both over-exploitation and contamination. Therefore, there is an urgent need to improve the understanding of existing groundwater resources in terms of aquifer distributions and interactions and process that control the groundwater dynamics, recharge and chemistry groundwater for an effective strategy to reduce the pressure on the hydrologic system.

The **main aim** of this PhD is to contribute to knowledge about shallow groundwater in semi-arid environments by estimating groundwater recharge of perched aquifers in the Cuvelai-Etосha Basin (CEB). Four specific objectives were examined in this study; first, the study characterizes the groundwater chemistry and isotopic composition of oxygen ($\delta^{18}\text{O}$) and hydrogen ($\delta^2\text{H}$) in order to understand mechanisms of groundwater dynamics and quality of groundwater in perched aquifers, secondly, it analyses and understand the spatial and temporal variations of hydrochemical data and isotopic compositions of hand-dug wells in the CEB, with particular focus on water origin and recharge processes, thirdly, the study evaluates the relationship between the shallow (perched) aquifer and the deeper seated aquifers and finally develops a conceptual model for the perched aquifers.

Methods employed in this research are based on isotopic and hydrochemical data to understand groundwater recharge mechanisms. Integrated isotopic and hydrochemical tracers along with standard hydrological data are used to understand complex dry land hydrological processes on different spatial and temporal scales. Different spatial and temporal scales are particularly important for arid environments due to high heterogeneity that are associated with these environments. Therefore in this study, water samples were collected from rain collectors, hand-dug wells and boreholes and analysed for major ions and stable isotopes (^{18}O and ^2H) for three years (2014-2017) in a total of 12 sampling campaigns. Chemical analyses were performed at the Analytical Laboratory Services in Windhoek, Namibia and at the hydrochemistry laboratory of BGR in Hanover, Germany using Titration, Ion Chromatography and ICP-OES. The reliability of

the analyses was checked by an ion charge balance error on all samples. Stable isotopes were measured at the University of Namibia (UNAM) and BGR laboratories using an off-axis integrated cavity output spectroscope (OA-ICOS, Los Gatos DLT-100) and a cavity ring down spectrometer (CRDS, model L2120-i, Picarro Inc.) respectively.

Results show that groundwater chemistry of perched aquifers is controlled mainly by strong evaporation, dissolution of carbonate minerals (calcite and dolomite) and evaporitic minerals (gypsum and halite) and silicate weathering and cation exchange. Stable isotope composition suggests that deep groundwater is recharged by high intensity/large rainfall events, whereas the shallow wells can be recharged by less intense/small rainfall events. Water in deep wells reflect mixture of water influenced by evaporation during or before infiltration and water that infiltrated through fast preferential pathways whereas shallow wells are strongly influenced by evaporation. The mean parent isotopic composition for shallow wells in the ephemeral river is -7.8 for $\delta^{18}\text{O}$ and -51.8 for $\delta^2\text{H}$, for deep wells in the pans and depressions is -8.7 and -58.2 for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ as well as -8.6 and -57.5 for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ for wells in Omusati region. Hydrochemical and isotopic data reflect spatial variability between samples from Omusati and Ohangwena regions. The spatial heterogeneity as shown by TDS can be attributed to lithological, climatic and anthropogenic factors. Furthermore, temporal variations indicate the timing of the groundwater recharge. Results also imply interaction between perched aquifer and regional aquifer in the pans and depressions while in the ephemeral river no relation could be established. High recharge rates are estimated for the pans and depressions (7.3 % to 25.5%) in comparison to the ephemeral river (7.9% to 17.8%).

Therefore, it is **recommended** that groundwater management practices should be designed taking into account differences in perched aquifer characteristics. For example designing abstraction infrastructures which include treatment for natural contaminants i.e. fluoride and TDS. On the other hand contaminants from anthropogenic sources in the wells can be reduced or prevented by introducing protection zones. Education on basic water usage and protection will also be of an advantage. Furthermore, it could be shown that it is indeed essential to unravel the hydrogeological complexities of heterogeneous perched aquifers using isotopic and hydrochemical tracers at different spatial and temporal scales and thus more research is needed in this regard.

List of Publication(s)/Conference(s) proceedings

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List of Abbreviations and/or Acronyms

BGR	Federal Institute for Geosciences and Natural Resources
BMBF	Federal Ministry for Economic Cooperation and Development
CBE	Charge Balance Error
CEB	Cuvelai-Etosha Basin
CMB	Chloride mass balance method
DO	Otavi Dolomite Aquifer
EC	Electric Conductivity
EU	European Union
GMWL	Global Meteoric Water Line
IC	Ion Chromatography
ICP-OES	Inductively Coupled Plasma - Optical Emission Spectroscopy
IWRM	Integrated Water Resource Management
KEL	Etosha Limestone Aquifer
KOH	Ohangwena Aquifer
KOH-0	Ohangwena Aquifer
KOH-I	Ohangwena 1 Aquifer
KOH-II	Ohangwena 2 Aquifer
KOM	Omusati Multi-zoned Aquifer
KOS	Oshana Multi-layered Aquifer
KOV	Oshivelo Multi-layered Aquifer
LMWL	Local Meteoric Water Line
m a.s.l.	Meters above sea level

m b.g.l.	meters below groundwater level
NAMWATER	Namibian water cooperation
NCRST	National Commission of Research Science and Technology
NTU	Nephelometric Turbidity Units
PIAHS	Publications International Association of Hydrological Sciences
SADC	Southern African Development Community
SASSCAL	Southern African Science and Service Centre for Climate Change Adaptive Land Management and Land use
SDG	Sustainable Millennium Development Goals
SI	Saturation index
T	Temperature
TDS	Total Dissolved Solids
TOC	Total organic compounds
UNAM	University of Namibia
UNCCD	United Nations Convention to Combat Desertification
UNEP	United Nation Environment Programme
V-SMOW	Vienna Standard Mean Ocean Water
WFD	Water Framework Directive
WHO	World health organization

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Dedication

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Tate Fillemon, when I didn't get admission into medical school, he told me not worry because I will be a Dr one day, little did I know that this is what he meant. Thank you for believing in me.

DECLARATIONS

I, Josefina Tulimevava Hamutoko, hereby declare that this study is my own work and is a true reflection of my research, and that this work, or any part thereof has not been submitted for a degree at any other institution.

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CO-AUTHORS ROLES

The author of this thesis have prepared all the three manuscripts with contributions from the following co-authors.

- Wanke, H. is main supervisor and therefore the scientific backbone of this work. She was involved in planning the project, field work, analysed the stable isotopes at University of Namibia and editing of manuscript.
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1 Introduction

1.1 Background of the study

Water is unanimously one of the most essential natural resources, if not the most valuable of all. The United Nations stated that “Water is complex because it is linked to almost everything in the world. But, complexity should not hinder understanding: Water is a precondition for human existence and for the sustainability of the planet” (UN-Water, 2017). In the first paragraph of the European Union (EU) Water Framework Directive (WFD) established by the European Parliament and the Council of the 23rd of October 2000; it is also emphasised that, “Water is not a commercial product like any other, but rather, a heritage which must be protected, defended and treated as such” (EC, 2000). Therefore, water is life. The absence or scarcity of water makes normal life difficult if not impossible, and thus its importance cannot be stressed enough. However, the amount of fresh water on earth is limited, according to United Nation Environment Programme (UNEP), (2014) about 90% of the world's readily available freshwater resources occur as groundwater, and 1.5 billion people depend upon it for their drinking water. It is especially vital for most communities in semi-arid regions (Foster et al., 2000; JMP, 2008; MacDonald and Edmunds, 2014). Groundwater is not only exploited for meeting basic human needs, but it is also crucial for economic development and to sustain the environment. Yet, the quality and quantity of available fresh water is constantly under pressure; the quantity is compromised by over-exploitation and climatic conditions while quality is threatened mainly by human activities.

Many parts of the world, especially in developing countries, people still face major problems with regards to clean water supplies and sanitation. UN-Water (2014a) report stated that, “One in nine

people worldwide doesn't have access to improved sources of drinking water and one in three lacks improved sanitation". Therefore, the United Nations had set the reduction by 50% of the size of the global population without access to sustainable and safe drinking water and basic sanitation by 2015 as one of their Sustainable Millennium Development Goals (SDG #6).

Another crisis faced by the world is water scarcity, it is estimated that by 2025, 1.8 billion people will be living in countries with absolute water scarcity and two-thirds of the world population could be living in regions under water stress conditions (UN-Water, 2014b). Water scarcity can be defined in terms of availability due to physical shortage, or scarcity as a result of lack of access due to the failure of institutions to ensure a regular supply or due to a lack of adequate infrastructure (UN-Water, 2017). Figure 1.1 shows global physical and economic water scarcity. In the last century, the use of water has been growing universally at more than twice the rate of population increase, and it is increasing the number of regions that are reaching the limit at which water services can be sustainably delivered, especially in arid regions (UN-Water, 2017).

Africa still faces major water issues, among other economic and developmental problems. Water issues in Africa include growing water scarcity, inadequate water resources development and management that results into depletion of water resources through human activities (UNECA, 2014). Water is anticipated to play a major role in alleviating numerous socio-economic development problems. Thus, an African Water Vision for 2025 was developed by the UN: for equitable and sustainable use and management of water resources towards poverty alleviation, socio-economic development, regional cooperation, and the environment (UNECA, 2014). The success of this vision is determined by several factors: for example, fundamental changes in

policies, effective strategies and legal frameworks, and cooperation between regions and countries within the continent and finally, a new way of thinking about water (UNECA, 2014). Thus, there is an urgent need to create awareness and consensus about the vision within all African nations.

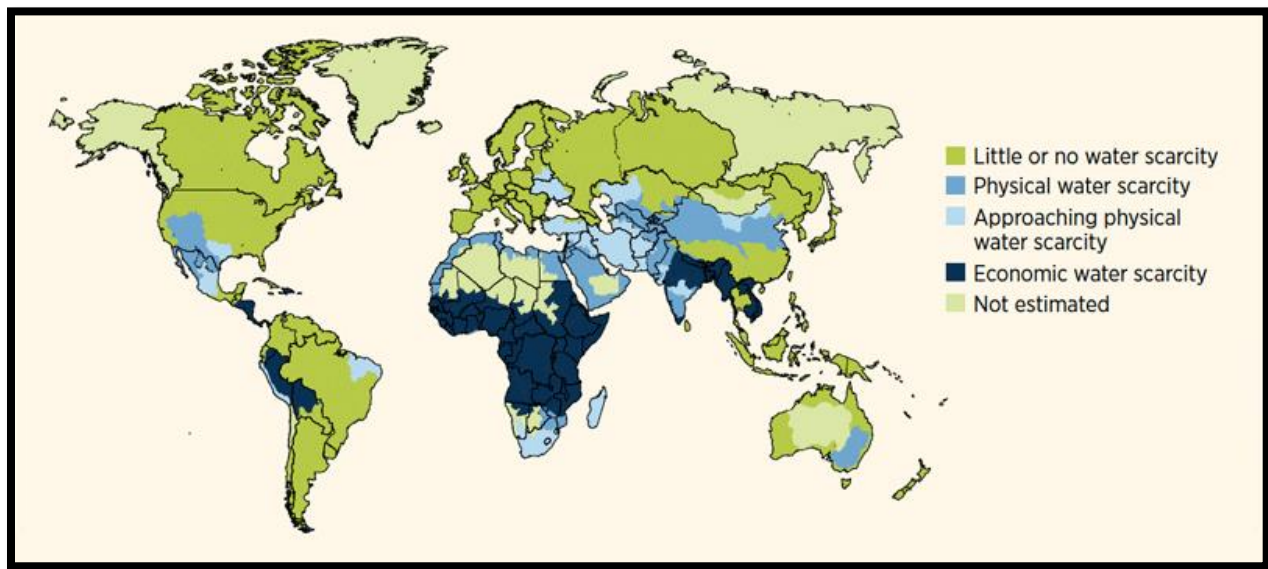


Figure 1-1: Global physical and economic water scarcity. Map source: (UN-Water, 2017)

In the Southern African Development Community (SADC), more than 98 Million people do not have access to safe drinking water (SADC, 2011). Access to water and sanitation are recognized by the United Nations as human rights, reflecting the fundamental nature of these basics in every person's life. The United Nations has defined access to safe drinking water as follows (Un-water, 2017):

- “Safe”: The water required for each personal or domestic use must be safe, therefore free from micro-organisms, harmful chemical substances, and radiological hazards that

constitute a threat to a person's health. Measures of drinking-water safety are usually defined by national and/or local standards for drinking-water quality.

- “Acceptable”: Water should be of an acceptable colour, odour and taste for each personal or domestic use. All water facilities and services must be culturally appropriate and sensitive to gender, lifecycle and privacy requirements.
- “Physically accessible”: Everyone has the right to a water and sanitation service that is physically accessible, within or in the immediate vicinity of the household, educational institution, workplace or health institution.

Namibia, the most arid country in sub-Saharan Africa, faces major water problems. Water scarcity and erratic rainfall patterns, insufficient sanitation, lack of a dedicated water law and the failure to implement already existing policies and plans are some of the key issues related to water resources management in Namibia (SADC, 2015). Water scarcity in Namibia has become a reality with serious threats, such that water bulk supply to all Namibians has become untenable. The headlines in the daily newspapers are awash with reports of issues pertaining to the drought affecting Namibians, signalling the fact that water shortages have become a part of normal life. The water crises are not only a result of the current drought, but a combination of factors that play a major role. These factors include increase in population, impact of climate change and variability, inadequate infrastructure, overexploitation and environmental degradation (Pietersen and Beekman, 2006). The rapid increase in population has resulted in high water demand. The growing population require a water infrastructure that grows or is developed according to the increase in population. This is currently not the case, the infrastructure lags behind significantly. Moreover,

the impact of climate change, which has resulted in fewer rain days across the rainy season. United Nations Convention to Combat Desertification (UNCCD) (2007) highlighted that with the current climate change predictions, water scarcity in some arid and semi-arid places will displace between 24 million and 700 million people by 2030.

In SADC, 70 % of the rural population depend on groundwater as source of water supply, whereas in Namibia 60% of the population depend on groundwater. Groundwater is preferred in certain municipalities as a source of drinking water because it is generally good quality in its natural state when compared to surface water. However, for semi-arid countries like Namibia, where surface water is scarce, groundwater is the commonly available water. Therefore, over-exploitation of groundwater resources may threaten the livelihood of the population living in such areas. Consequently, a comprehensive understanding of the groundwater system through integrated hydrogeological investigations are obligatory for effective planning, management and utilisation of the groundwater resources and to address water supply sustainability and water quality (Conrad et al., 2004).

One of the most important parameters that directly impacts the physical characteristics and behaviour of groundwater, is the amount of groundwater recharge occurring in an area. Generally, recharge pattern is principally influenced by the distribution of landscape, soil, vegetation, and the climate. Klock (2001) points out that understanding groundwater recharge mechanisms and quantifying its amounts reliably is very crucial for sustainable groundwater management. However, the scarcity of data still limits our understanding of recharge and groundwater flow in Africa. Moreover, the episodic nature of recharge caused by extreme events like flooding makes

reliable recharge estimates difficult. An example is taken from the Cuvelai-Etосha Basin (CEB) in northern Namibia, which has a complex hydrogeological setting that is representative for semi-arid regions. It is characterised by a thick unsaturated zone composed of the Kalahari sands and extreme climatic conditions, i.e. very low precipitation and high evaporation rates ranging between 250 and 600 mm/a and 2000 - 3000 mm/a respectively and thus has low recharge values which are very difficult to calculate (Allison and Hughes, 1983; De Vries et al., 2000; Skrzypek et al., 2015; Stadler et al., 2010). Knowledge of groundwater processes in the CEB will aid in understanding the hydrogeological conditions in comparable environments elsewhere, including other parts of Africa, Australia and the western United States.

1.2 Problem statement

Even though there has been an increase in water supply from deep boreholes that feed a pipeline system connecting to most parts of the CEB, most rural communities in the basin still use hand-dug wells as their source of domestic water supply. Yet, the quality and quantity of the perched aquifer which is accessed by hand-dug wells is not monitored nor has its sustainability been assessed, its groundwater recharge mechanisms are not assessed, nor are the recharge rates estimated. The perched aquifers have a relatively shallow water table (from 0 to 30 m), and thus, they are more vulnerable to changes in both land use and climate in comparison to the deeper aquifers, yet their spatial and temporal variations in water quality and quantity are not known. The relation of the perched aquifers to the regional aquifers is also not known. For sustainable groundwater management, processes governing water quality and quantity must therefore be assessed.

1.3 Aim and Objectives of the study

The overall aim of the study is to understand groundwater recharge mechanisms and the groundwater quality of the perched aquifers in the Cuvelai-Etosha basin (CEB). To achieve this, the following objectives should be met:

1. Characterise groundwater chemistry and isotopic composition to understand groundwater dynamics, recharge processes and how these influence the quality of the groundwater.
2. Analyse spatial and temporal variations in water quality and quantity of perched aquifers and explaining how the processes that lead to these variations.
3. Define the relationship between the perched aquifer (KOH-0) and the upper regional aquifer (Ohangwena 1 (KOH-1)).
4. Develop a conceptual model of recharge mechanisms in the Cuvelai-Etosha Basin (CEB) and quantify recharge rates.

1.4 Significance of the study

The research develops, enhances knowledge and understanding of shallow perched aquifers in the Cuvelai-Etosha Basin with regards to its quality and quantity. In terms of water quality, the knowledge will help to improve access to safe drinking water as stipulated in the Namibia vision 2030 (GRN, 2004), NDP4 (GRN, 2009) and Millennium Development Goals #6 that state, “everyone should have access to safe drinking water”. A baseline database was also developed for water quality and geochemistry of perched aquifers. In terms of water quantity, the research generated knowledge that helped in understanding the processes that control groundwater recharge

of perched aquifers. This information will help in the management of these water resources. Lastly, the Namibia Water Resources Management Act 24 of 2004 encourages research for water resources management and sustainable development. The methodologies applied here will help in understanding other perched/shallow aquifers in Namibia, e.g. in Kunene Region, Erongo Region and Zambezi Region as well as in other countries with a similar hydrological setting.

1.5 Limitation and delimitation of the study

Groundwater studies requires long term observation periods, ideal 30 years, however such data (dataset) does not exist for this area and in fact does not exist anywhere in Namibia, so therefore lack of data over a long observation period was a major limiting factor in estimation of groundwater recharge rate. The CEB is a very complex catchment with variable precipitation. The rivers are a combination of seasonal and ephemeral and even perennial in the headwaters, therefore the collected data points cannot be regionalised to the whole basin. As such the study should be seen as an example and should not be used to make conclusions for the entire basin.

1.6 Thesis structure/scope

This thesis is structured into 6 chapters. Chapter 1 begins with the background of the research, the research problem and objectives. The significance of the study is also elucidated followed by the limitations. Chapter 2 gives a literature review on the principles of groundwater recharge and an overview of different methods that are used to estimate it.

In Chapter 3, hydrogeochemical composition and isotopic signature of perched aquifers in the Ohangwena region were characterised. The original paper was published in the journal *Isotopes in*

Environmental and Health Studies under the doi.org/10.1080/10256016.2016.1273913. In Chapter 4, comparisons between the Ohangwena and Omusati regions were made, with special focus on the spatio-temporal changes of hydrochemical composition and isotopic signatures of groundwater in hand-dug wells. A manuscript from this chapter was submitted to Publications International Association of Hydrological Sciences (PIAHS) and is currently under-review.

Chapter 5 focuses on recharge mechanisms and hydrogeochemical evolution as well as the relation of perched aquifers to the deep regional aquifer. The original manuscript will be submitted to reputable journal in hydrogeology field. Chapter 6 concludes the thesis by outlining the main research findings from the three chapters and recommendations are given in chapter 7. Furthermore, the outlook for further research on groundwater recharge in the CEB is then outlined.

This thesis mainly depended on hydrochemistry and isotopes. The sampling points, procedure and analytical process for both chapters are therefore the same and are described in details in the first manuscript to avoid repetition. What is different about the chapters is mainly how hydrochemistry and stable isotopes were used answer different research questions hence, the data analysis as well as the timeframe of the sampling. The project was planned in a progressive manner. Firstly, groundwater chemistry and isotopic composition was characterised and groundwater quality was determined using results from the first seven sampling campaigns (November 2013, March, June, and September in 2014 and in March, June and August in 2015). After characterisation groundwater chemistry and isotopic composition, they were analysed how they change with time and space in manuscript two focusing on determined elements of concern as well as on parameters

such as chloride that help in understanding groundwater recharge. In manuscript two, Omusati and Ohangwena regions were compared and it had longer time series data from eleven sampling campaigns (November 2013, March, June, and September in 2014 and in March, June, August and November in 2015, March, June, October in 2016). In the last manuscript hydrochemistry and isotopic composition of perched aquifer were compared to the regional aquifer. Hydrochemistry and stable isotopes data for the regional aquifer was collected from literature and within the field work of this thesis.

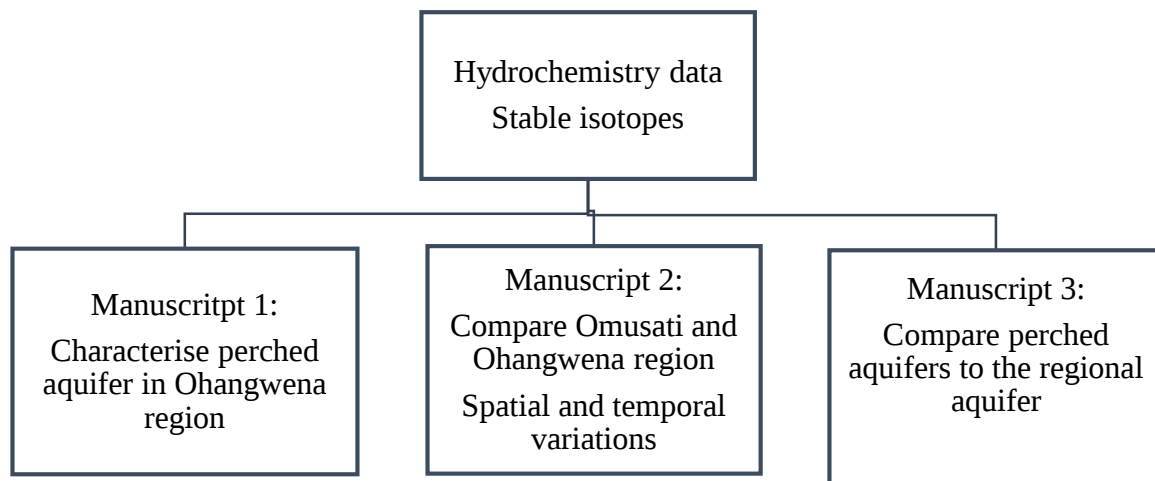


Figure 1-2: A chart showing how hydrochemistry and stable isotope data was used for three manuscripts in this thesis.

2 Literature review

2.1 Groundwater recharge

Groundwater recharge, is defined as the water that reaches an aquifer from any direction either by downward, upward or lateral flow (Rushton and Ward, 1979; Scanlon et al., 2002). Freeze and Cherry (1979) have defined groundwater recharge as the “entry into the saturated zone of water made available at the water-table surface, together with the associated flow away from the water table within the saturated zone”. It is a very important parameter for proper water management but it is neither easy nor straightforward to quantify because it cannot be measured directly. Furthermore, it has been proven to be more challenging for semi-arid to arid environments where potential evapotranspiration excessively exceeds precipitation, vegetation cover is limited and unsaturated zones are thick which result in lower groundwater recharge than for humid climates (Allison & Hughes, 1983; Skrzypek et al., 2015; Stadler, et al., 2010).

Külls (2000) states that groundwater recharge studies are more adequate, if concepts of recharge mechanisms and their relative importance in the climatic realm are differentiated and assessed at the beginning. The uncertainties associated with the recharge mechanisms also make it difficult to predict long-term effects of climate change, meteorological variability, and effect of land-use changes on groundwater resources (Yamoah, 2013). Therefore groundwater recharge studies should start by defining recharge mechanisms.

Recharge mechanisms are often classified as direct and indirect recharge. Direct (also known as diffuse) recharge is recharge that results from rainfall infiltration and from the balance of vertical flow in the soil column, without lateral surface runoff participation. On the other hand, indirect

(localised) recharge only occurs after generation and concentration of surface runoff; water travels laterally at (or near) the land surface and then collects in streams or topographic depressions before it infiltrates (Healy, 2010; Hiscock, 2005; Simmers, 1987). Indirect recharge is known to be increasing significantly with aridity. It must be noted that some classifications confine the term localized recharge to recharge from small depressions, joints, or rivulets and use the term indirect recharge for recharge beneath mappable features such as rivers and lakes (Lerner et al., 1990 in Scanlon et al., 2002). In this study, the former definition is used. Figure 2.1 Shows the main processes that control recharge in arid and semi-arid regions.

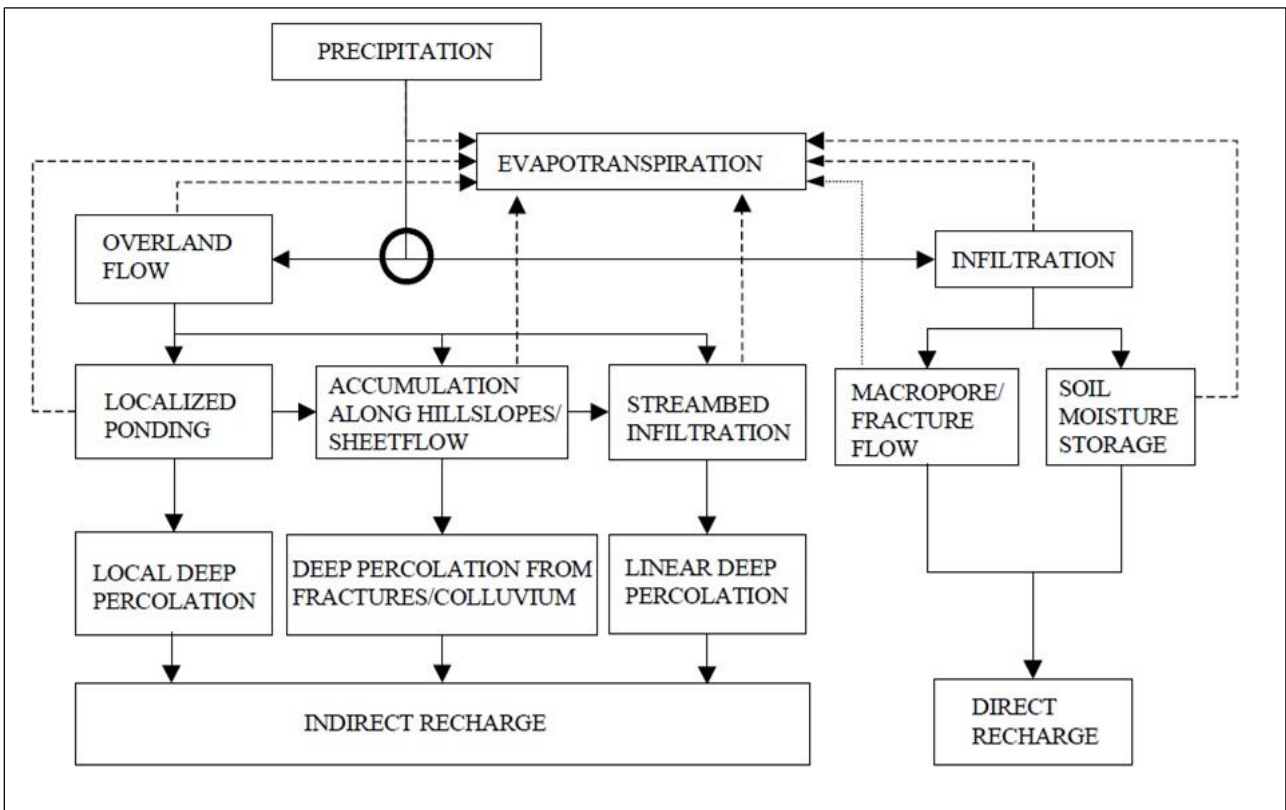


Figure 2-1: Flow chart of hydrological processes controlling direct and indirect recharge in arid and semi-arid environments (after Külls, 2000)

The difference between matrix and macropore recharge is another significant subject that relates to groundwater recharge mechanisms. Matrix or interstitial recharge refers to infiltration that occurs through intergranular pore spaces of the sediment or rock whereas within macropore recharge, recharge occurs through higher permeability zones such as deep desiccation cracks, animal burrows, root tubes, pipes, fissures, and fractures (Maliva & Missimer, 2012). Rapid percolation through macropores is normally referred to as preferential flow paths and it results in higher recharge rates when compared to matrix recharge. Therefore, both direct and indirect recharge often travel through preferential pathways, rather than exclusively through the soil matrix. Here are some of the key components that control the rate of infiltration and recharge in semi-arid regions (Maliva & Missimer, 2012; Scanlon et al., 2002; Xu & Beekman, 2003):

- Rainfall (intensity, duration, timing and magnitude of rainfall events).
- Climate (exposure and amount of solar radiation and evapotranspiration).
- The presence and abundance of macro pores present at land surface that are capable of accepting infiltration.
- The degree to which the macro pores are connected to underlying aquifers.
- Land use/ land cover (the condition of the land surface, including roughness, vegetative cover, moisture content and irrigation practices).
- Topography (slope, aspect).
- Composition and hydraulic properties of soils (porosity, texture, hydraulic conductivity, thickness, heterogeneity, soil moisture).
- Hydraulic conductivity of the aquifer.

2.2 Methods to Estimate of Groundwater Recharge

Many methods have been developed for quantifying the groundwater recharge, but it is often difficult to choose the appropriate method for a specific area. A wide range of factors are therefore normally considered when choosing the method to estimate groundwater recharge. These methods have been reviewed (Healy, 2010; Scanlon et al., 2002; Seiler and Gat, 2007; Simmers, 1997, 1987). Groundwater recharge is estimated for various reasons for example for water resource management (Cartwright and Morgenstern, 2012; Chenini and Ben Mammou, 2010; Mair et al., 2013) and for understanding transport of contaminants in the aquifer system (Amer et al., 2012; Osenbrück et al., 2009). For that reason, one of the most important factors in choosing the appropriate method to quantify recharge is the goal of study (Scanlon et al, 2002). Secondly, space and time scales are also very critical for all the recharge studies (Obuobie et al., 2012) and should be considered when choosing the appropriate method. Another factor influencing the choice of method is the physical characteristics of an area, i.e. geomorphology, hydrology and geology of the site as well as the climate. The difference in recharge sources and rates between arid and humid settings illustrates how significant climate is in controlling recharge. Generally, humid regions are characterised by shallow water tables, high precipitation amounts, high recharge rates and diffuse recharge is dominant. However, in arid regions, the water table is rather deep, precipitation and recharge rates are low and focused recharge becomes dominant (Scanlon et al., 2002).

Most of the techniques are based on the water budget equation:

$$P + Q_{in} = ET + Q_{out} + \Delta S \dots\dots\dots (2.1)$$

Where P is precipitation; Q_{in} and Q_{out} are water inflow and outflow, respectively; ET is evapotranspiration; and ΔS is the change in water storage (Scanlon et al., 2002).

Using methods related to water budget has an advantage of flexibility; each variable in the equation can be measured or estimated and they can be applied over a wide range of space and time scales (Scanlon et al., 2002). On the other hand, the accuracy of the water budget components determines the accuracy of the recharge estimates. “If the recharge amount is in the order of magnitude of the uncertainty of precipitation and evaporation, the calculated recharge will have an uncertainty as large as its value which is inadequate for meaningful sustainable water resource planning” (Klock, 2001).

In semi-arid and arid regions, recharge is usually estimated with techniques related to the unsaturated zone. To present date the following methods have been used to estimate groundwater recharge (Gundogdu and Hasan, 2000; Scanlon et al., 2002):

- **Water-table fluctuation method**

This method is based on the principle that rises in groundwater levels in unconfined aquifers are due to recharge water arriving at the water table. Recharge is calculated as

$$R = \frac{S_y dh}{dt} \dots\dots\dots (2.2)$$

Where S_y is specific yield, h is water-table height, and t is time. Crosbie et al. (2005) applied this method to estimate recharge of 49.3% of annual rainfall in the Tomago sand beds near Newcastle, Australia and concluded that gross recharge estimates are very sensitive to time step size and specific yield.

- **Precipitation vs. water level relation method**

This method estimate recharge based on the statistical relation between precipitation and water levels in areas that are unaffected by heavy pumping. Cai and Ofterdinger (2016) analysed of groundwater-level response to rainfall and estimated annual recharge in fractured hard rock aquifers in Ireland and found recharge rates between 4-19% of the annual rainfall.

- **Physical methods (lysimeters)**

“Lysimeters consist of containers filled with disturbed or undisturbed soil, with or without vegetation that are hydrologically isolated from the surrounding soil, for purposes of measuring the components of the water balance. All lysimeters are designed to allow collection and measurement of drain- age. Precipitation and water storage are measured separately in drainage lysimeters”, (Scanlon et al., 2002).

- **Chemical and isotopic methods and**

Chemical or isotopic tracers are applied as a pulse at the soil surface or at some depth within the soil profile to estimate recharge. These will be discussed in details in section 2.2.1.

- **Numerical models**

Numerical models are used to estimate recharge rates over different spatial and temporal scales and generally they provide recharge estimates as a residual term in the water-budget equation. Tubau et al. (2017) quantified recharge rates in urban environments of Barcelona and concludes that it is important to estimate areal recharge. The reliability of the recharge estimates depends on the accuracy of the input parameters i.e. hydraulic conductivity.

All these methods are normally subjected to large errors and huge range of uncertainty and as a result different methods are applied to verify one another. In this study chemical and isotopic methods will be used to identify recharge processes while chloride mass balance will be used to quantify the recharge rate. These methods were chosen because they were used successfully by Klock, 2001; Külls, 2000; Wanke et al., 2008; Macdonald & Edmunds, 2014 and Kanduč, et al., 2014 to estimate recharge in areas with similar settings (i.e. climate, vegetation, hydrogeology, etc.). Furthermore, the study area has limited hydrological data which is needed for the applicability of most methods discussed above. Lack of data is discussed in Külls (2000) as one of the primary problems not only in estimating groundwater recharge but in the overall management of water resources in the world's semi-arid and arid regions.

2.2.1 Groundwater investigations using hydrogeochemical and isotopic methods

The use of hydrogeochemical and isotope tracers has been increasing in all parts of the world with different climatic conditions, they're used to better understand groundwater recharge processes, quantify the spatial and temporal variations in groundwater recharge, and as well as for understanding aquifer interactions (Cartwright & Morgenstern, 2012; Conrad et al., 2004; Okkonen & Kløve, 2012; Vanderzalm et al., 2011; West et al., 2014). Advantages of using hydrogeochemical and isotopic methods over physical methods (e.g. lysimeters) in semi-arid regions have been discussed in details by Allison et al. (1994), Lapworth et al. (2013) and Stadler et al. (2010). Hydrological data in remote areas and semi-arid climates in most developing countries is scarce, thus these methods become significantly essential. Additionally, hydrogeochemical and isotopic methods can be used at both local and regional scales to provide significant information on groundwater recharge patterns. Different spatial and temporal scales are

particularly important for arid environments, due to the high spatial heterogeneity and strong inter and intra-annual variations of climatic conditions that are associated with these environments.

Hydrogeochemical data traces the evolution of the recharging water from its source to current groundwater state, while signatures of stable isotopes of water (i.e. $\delta^{18}\text{O}$ and $\delta^2\text{H}$) serve as a powerful tracer of hydrological processes in both the unsaturated and saturated zone by providing an integral fingerprint of water origin, flow path and transport processes (Afrifa et al., 2017; Volkmann and Weiler, 2013). The isotopic signatures distinguish different recharge sources both at local and regional scale with temporal scales between seasonal and hundreds of years, but it is difficult to quantify recharge rates (Scanlon et al., 2002). Furthermore, stable isotopic tracers can give an idea of the roles of the intervening surficial material in modulating vertical infiltration and percolation of rainwater into the saturated zone, and also constrain the recharge estimates in the light of the prevailing climatic conditions (Cartwright and Morgenstern, 2012).

In Mexico, Ledesma-Ruiz and Mahlknecht (2017) used major ions to show that water-rock interaction and cation exchange are the main processes that modify the groundwater chemistry using major ions in Tecate. Liu et al. (2015) used hydrochemistry and stable isotopes in the Subei Lake Basin, China to identify the origin and geochemical evolution of groundwater, and concluded that the dissolution of carbonate minerals is the main geochemical process. Vanderzalm et al. (2011) showed that the alluvial basins in arid central Australia have multiple recharge sources that varied spatially with the proximity of the recharge source to the aquifer. Demlie et al. (2008) characterized the groundwater flow, occurrence, and major ion chemistry in a complex fractured volcanic aquifer system in central Ethiopia while Kpegli et al. (2015) demonstrated that

geochemical processes are influenced by recent recharge and mixing of aquifers using stable isotopes in the Kandi Basin of Benin.

Generally, groundwater hydrochemistry is dependent mainly on the degree of evaporation, chemical composition and mineralogy of the rocks through which the infiltrating water passes through (Fetter, 1994; Freeze and Cherry, 1979). The mineralization, which can be indicated by the amount of total dissolved solids usually increases with distance from a recharge zone; as a result of water-rock interactions and the dissolution of aquifer minerals (Appelo and Postma, 2005; Hiscock, 2009). Ionic ratios are commonly used to determine the main processes that led to the formation of the groundwater chemistry. For example, Na^+/Cl^- , $\text{Ca}^{2+}/\text{HCO}_3^-$, $\text{Ca}^{2+}/\text{SO}_4^{2-}$ are commonly used to show dissolution of halite, calcite/dolomite and gypsum/anhydrite, respectively. Some water types are defined by certain cation ratios. Consequently, such waters are recognisable from Piper diagram plot, and the common water types of rain water, recharge water after soil passage, recharge water from fast infiltration and dolomitic waters are indicated in Fig 2.2 (Klock, 2001). Furthermore, in the anion field the mentioned water types are characterised by a very dominant HCO_3^- component.

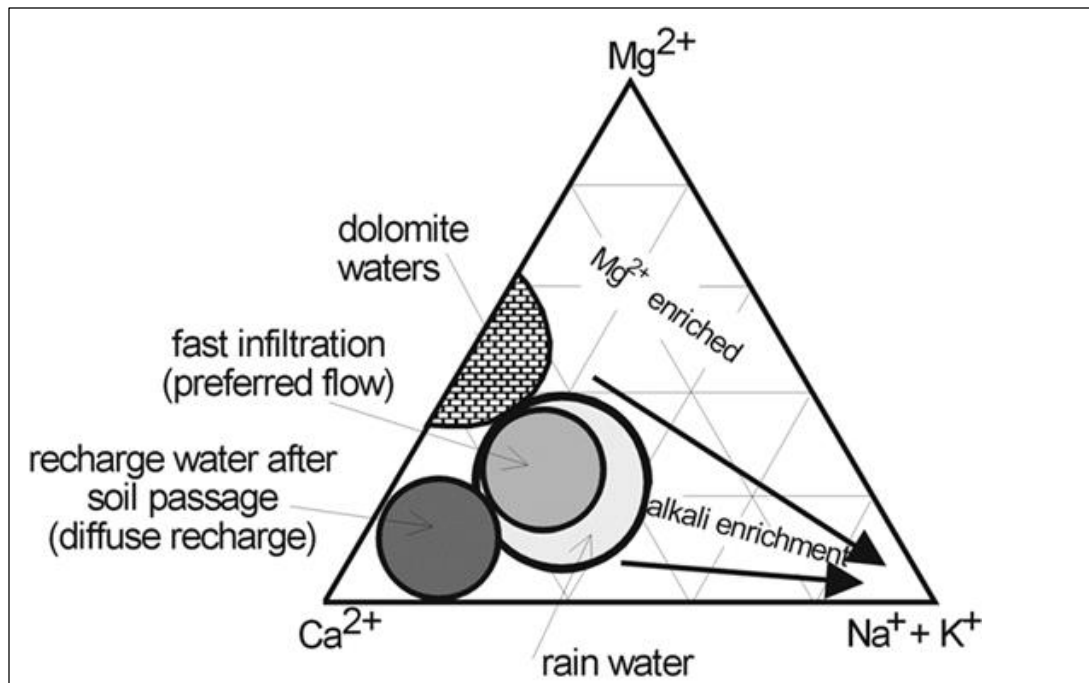


Figure 2-2: Appearance of cation compositions for some typical waters. Grey values are increasing with electric conductivity (Klock, 2001).

2.2.2 Chloride mass balance method (CMB)

CMB is a well-established method for quantifying direct recharge in arid and semi-arid regions. It is one of the most commonly used methods that estimates recharge in both saturated and unsaturated zones, it has been based on mass conservation since its inception in 1969 by Eriksson and Khunakasem (1969). According to Edmunds et al. (1988) recharge rates in areas without geogenic chloride sources can be estimated using a simple mass balance for a given groundwater volume:

$$FN + FD = FS + FM \dots\dots\dots (2.3)$$

Where FN, FD, FS and FM are mean mass input by wet deposition (precipitation), mean mass input by dry deposition, mean mass output by seepage water, and mean mass output by adsorption

and transformation into the mineral phase respectively. The FM term is considered negligible according to Allison & Hughes (1978) and Gieske et al. (1995) who illustrated that chloride is a conservative tracer. (Gieske, 1992) assumed that the dry input is negligible for the Kalahari because it is relatively small compared to the wet deposition (varies between 0.4 and 1.1 mg/l). Yet, Wanke et al., (2014) discussed that dry deposition contributes 20 to 50 % to the total deposition of chloride and thus for areas without geogenic chloride sources equation (2.4) should include the dry deposition factor. The rate of groundwater recharge is inversely proportional to the degree which chloride concentration is raised from that of rainfall (Harrington et al., 2002). The use of CMB requires the following assumptions to be met (Harrington et al., 2002):

1. There is no source of chloride in the groundwater other than that from precipitation and concentration occurs by evapotranspiration prior to recharge.
2. Chloride is conservative in the system; it is not involved in any geochemical reaction.
3. Steady-state conditions are maintained with respect to long-term precipitation and chloride concentration in that precipitation.
4. There is no surface runoff in the catchment or it can be estimated with reasonable precision.

The groundwater recharge rate is estimated using the equation:

$$R = (P * Cl_p) * DDF / Cl_{gw} \quad (2.4)$$

where R recharge in mm/a, P is mean annual rainfall in mm/a, Cl_p mean concentration chloride in precipitation in mg/l, Cl_{gw} is chloride concentration in groundwater in mg/l and DDF is dry deposition factor and is assumed to be between 1.2 and 2. This method is relatively cheap and can be carried out at a local scale while the temporal scale ranges between years and hundreds of years

but in cases where there are other sources of chloride in the soil e.g. salts rather than the one contained from rainwater, the results could be false (Kinzelbach et al., 2002). Its accuracy therefore depends on the input function from both precipitation and dry deposition, but this data is not readily available for many developing countries.

2.3 Definition and occurrence of perched aquifers

This study pays particular attention to the perched aquifers. A perched aquifer is defined as an isolated and unconfined water body that occurs above the regional water table, and which is typically controlled by stratigraphy or structures as shown in Fig. 2.3 (Davis and Dewiest, 1966; Fetter, 1994; Freeze and Cherry, 1979). They result from formation of an impermeable layer which acts as hydrological barrier and thus water is collected above it (Melly et al., 2017). Generally perched aquifers are present in all terrestrial environments, but they are easily distinguished in environments where the regional water table is regularly very deep. In the CEB, the perched aquifers are widely distributed underneath pans and depressions. This coincides with De Vries et al., (2000) who stated that, in the Kalahari “perched water bodies are found locally in the Kalahari Beds in areas with large pans, they are related to episodic flooding and rapid infiltration through fractured duricrust deposits.” Pans are geomorphological features that appear as shallow sub-circular to sub-elliptical isolated depressions; they are predominantly associated with crescent dunes which can rise to a height of 30 to 40 m above the pan floor (Lancaster, 1978). Depressions have similar physical properties as pans, but lack crescent dunes in their proximity. Burrough et al., (2012) and Nash and McLaren (2003) argued that even though pans have similar morphology with some landforms that occur in temperate regions, e.g. karst depressions or permanent lake

systems, they are characteristic for dry land because of the set of processes that are involved in their formation. Bowler (1986) suggested that pans can serve as either a discharge or recharge point, depending on the present hydrologic dynamics and their soil hydraulic properties. Moreover, their ground surface may be covered or partly covered by grass, bare clay and/or calcrete with a few shrubs, mainly acacia species, while the dunes are covered by thick forest.

In general, perched aquifers are more vulnerable to contamination and changes in both land use and climatic conditions, as a result of their shallow depth to the water table (Cruz and Andrade, 2015). As such, perched water may present an important subsurface pathway for facilitating, or a barrier for inhibiting contaminant transport from the ground surface to the regional aquifer, and complicating contamination problems in several ways (Oostrom et al., 2013). Rains et al. (2006) highlighted that perched layers/aquifers reduce the recharge rates to the regional aquifers as they redirect subsurface water flow along horizontal flow paths.

Perched aquifers in the CEB are encountered in such special situations. Although perched aquifers have long been recognised, they are infrequently studied (Oostrom et al., 2013; Rains et al., 2006). So far, studies in the literature focus on the formations of perched water tables for example (Dippenaar, 2014; Melly et al., 2017), investigations of perched water as contamination pathways (Carroll et al., 2012; Oostrom et al., 2013) as well as potential artificial recharge sites (Flint et al., 2012; Flint and Ellett, 2004). However, to this point, it is not known if attempts were taken for investigation of the perched aquifers and regional aquifers water interaction at the necessary spatial and temporal scale.

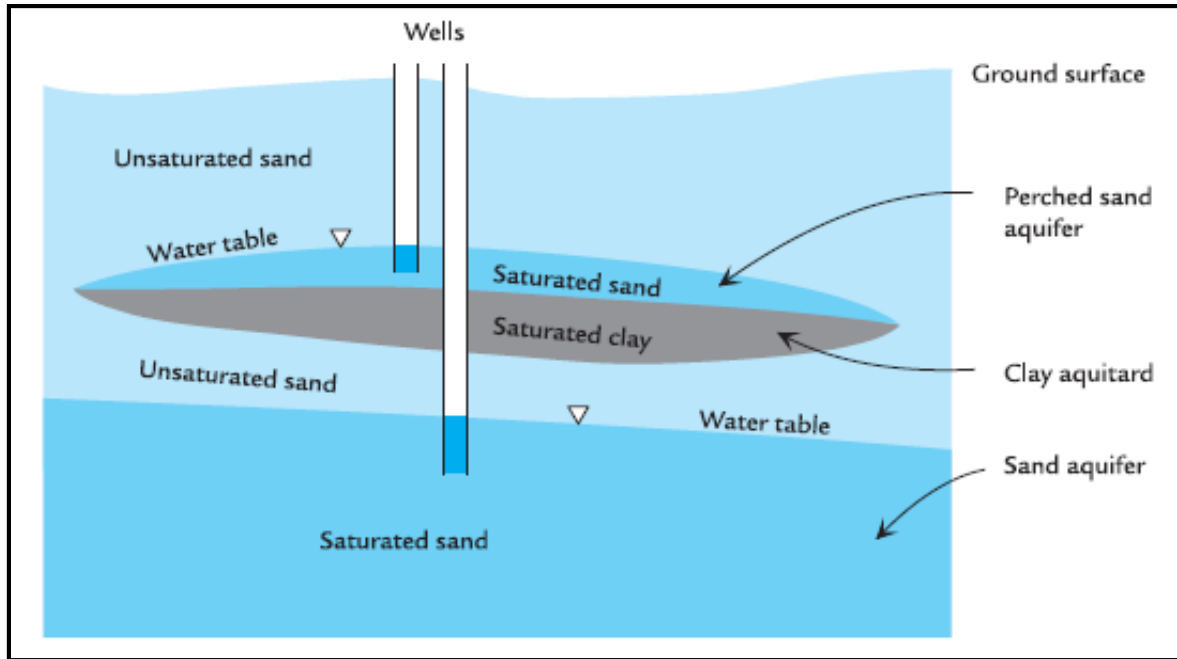


Figure 2-3: Schematic cross-section of a perched aquifer (Fitts, 2002)

2.4 Previous studies in the study area

The Cuvelai-Etosha Basin is part of the intra-continental Owambo Basin which is an extensive sedimentary basin that is part of the much larger Kalahari Basin, covering parts of Angola, Namibia, Zambia, Botswana and South Africa (Miller, 1997). Therefore, groundwater recharge in Cuvelai Basin is comparable to the other parts of the larger Kalahari Basin. Several studies on groundwater recharge have been carried out in the Kalahari Basin both in Namibia and Botswana as summarised in Abiye, 2016 and Xu and Beekman, 2003. Table 2.1 summarizes the existing literature on the Kalahari Basin complete with recharge estimates. One of their main conclusions is that chloride mass balance, saturated volume fluctuation and water table fluctuations methods are the most reliable methods for groundwater recharge estimation in the region. And also that

recent groundwater recharge takes place in most locations, although rates are low, varying between 0.1 and 2.6 % of mean annual rainfall. High recharge rates and preferred flow paths are indicated in places like pans, areas with shallow calcrete, and areas with less sand cover (Külls et al., 2000). However, even though these areas have comparable hydrological characteristics, when they are investigated at local scales, some differences exist and therefore, the results cannot simply be projected to the whole study area. Furthermore, they paid attention to the regional deep aquifers rather than the perched aquifers.

David (2013) estimated groundwater recharge in the perched aquifer using chloride mass balance and soil water balance methods in the CEB. Recharge rates ranged from 19 mm/a in areas with thick sand to 59.8 mm/a in depressions. However, a clear explanation of processes that contribute to recharge in the area was not clearly documented. Hence, there is a need for understanding the processes that control recharge in the area and then eventually they will determine the appropriate method to adequately quantify recharge rates in the area. Additionally, previous studies (Nakwafila, 2011; Hamutoko, 2013; Wanke, et al., 2014) show that water in hand-dug wells does not meet the requirements for drinking water standards because of the presence of fluoride, nitrate, sulphate, salt content (TDS) and bacterium such as *E. coli*. This was attributed to inappropriate well design which allows all the dirt including livestock's dropping to be washed into the wells with surface water, and also the transport of dry faeces as wind-blown dusts and transport into the aquifer by infiltration. Consequently an investigation in a well design for improvement of water quality still needs to be done.

There has been ongoing research on groundwater in the CEB, most of it is carried out under the project “Groundwater of the North” by the BGR, which is technical cooperation framework between Namibia and Germany. The aim of the project is to provide well founded information concerning the groundwater resources in the Cuvelai-Etosha Basin as a basis for Integrated Water Resource Management (IWRM) (Lohe & Houben, 2014). However, they have focused mainly on exploration and exploitation of the deep aquifer (Ohangwena II). Therefore, there is quite a substantial amount of data for the deep aquifers which could be used to understand the relationship between the shallow and deep aquifers. Thus this study focuses mainly in collecting new data for the perched (shallow) aquifers and comparing it to the available data.

Lohe et al., (2013) and Ananias (2015) evaluated borehole lithology logs and the results suggested that perched aquifers in the CEB are connected in some areas to the regional aquifer Ohangwena KOH-1. Both studies focused on the aquifer properties using the hydraulic parameters such transmissivity and thickness of the aquifers. However, recharge and geochemical evolution processes are still not understood and therefore this study will use hydrochemistry and isotope geochemistry to understand these processes. Lohe et al. (2013), delineated the area where perched aquifers are dominant based on the thickness of the aquifer (Fig. 2.3.).

Table 2-1: Mean annual rainfall and recharge in some parts of Southern Africa. RF: Rainfall, CMB: Chloride Mass Balance, SVF: saturated volume fluctuation, WTF: water table fluctuation, GWM: Groundwater modelling, EARTH: extended model for aquifer recharge and moisture transport through unsaturated hard rock, BF: Base flow separation, K: hydraulic conductivity, T transmissivity, S: storativity, η : total porosity edited and updated from Abiye (2016)

Recharge Method	Mean Annual Rainfall (mm)	Recharge (mm/yr)	Percentage of annual rainfall (%)	Locality	Reference
BF	830-1480	14-371	1.7-25	Malawi and Zimbabwe	Wright, 1992
	551-896	0-80	0-8.9		
CMB	460	4.5	1	Eastern Cape, South Africa	Sami and Hughes, 1996
CMB	350-450	1-5	0.3-1.1	Kalahari, Botswana	de Vries et al., 2000
SVF	200-600	9.5-16.1	2.9-4.9	Karoo, South Africa	Van Tonder and Kirchner, 1990
CMB, GWM	550	25	4.5	Zambesi Basin, Zimbabwe	Larsen et al., 2002
CMB	500	1.5-8.3	1	Northern Sandveld, South Africa	Conrad et al., 2004
SVF	500	0.8-4.3	0.5		
EARTH	500	1.1-8.5	1%		
Water Balance	400	0.1-38	9.5	TMG/ Karoo	Sun, 2005
	600-800	<5	0.6		
	>800	10-20	1.9		
CMB	190	0.22-1.14	0.8	Namaqualand, South Africa	Adams et al., 2003

SVF	190	0.2-4.4	2.3	Namaqualand, South Africa	Adams et al., 2003
CRD	190	0.1- 3.06	1.6	Namaqualand, South Africa	Adams et al., 2003
CMB	299-714 1842	30 137	5.9 7.4	Table Mountain Group Aquifer	Xu et al., 2007
River base flow analysis groundwater hydrochemical analysis and GWM	Semi-arid	82, 11, 39, 27, 8, 9, 12, 7, and 3	2-5	Victoria province, Zimbabwe	Houston, 1988
Tracer, WTF, Darcian flow net computations, GWM	Semi-arid	15-20		Southern Zimbabwe	Sibanda et al., 2009
CMB	555	19-62	7.3	Nyamandhlova, Zimbabwe	Sibanda et al., 2009
WTF	555	2-50	4.7		
Darcyan Flow Net	555	16-28	4		
¹⁴ C	555	22-25	4.2		
GWM	555	11-26	3.3		

Table 2-2: The summary of groundwater recharge estimation in various locations in Namibia (adopted and updated from Andjamba (2016)). GW = Groundwater, *CMB = Chloride Mass Balance, *WBM = Water Balanced Model

Method	Mean Annual Rainfall (mm/a)	Annual Recharge (mm/a)	Location	Author (s)
CMB	100-200	0.41-24.43	Namib Naukluft	Kambinda, (2014)
CMB	400-600	1-224	Ohangwena	Hamutoko et al., (2016)
CMB		4-27	Stampriet	Stone Edmund (2013)
CMB (Saline GW) Otavi dolomite		>5 50	Oshivero	Herczeg (2004)
CBM Satellite image Hydrochemical data		0.2-100 0.88-4.53 1.39	Kalahari	Klock (2001)
CMB GW flow model	400-500	0.8-7	Kalahari (Unsaturated)	Mainardy, 1999
CMB (GW) (Soil)	400	0.6-10 0.3-10.3	Kalahari	Wrabel, 1999
peak displacement technique & water stable isotopes	400-500	0 and 29	Cuvelai-Etosha Basin, Namibia	Beyer et al., 2016, 2015
Soil water balance using unsaturated zone water stable isotopes	400-500	4 and 5	Cuvelai-Etosha Basin, Namibia	Gaj et al., 2015
CMB	250 - 500	1- >100	Perched aquifers in Namibia	Wanke et., 2014
Group Aquifer	400-500	19 -59.8	Cuvelai-Etosha Basin, Namibia	David, 2013

Physical Water Balance Model (MODBIL)				
MODBIL	409	8	NE Namibia/NW Botswana	Wanke et al., 2008
Numerical modelling	150-300	2.25	SE Kalahari, Stampriet	Peck, 2009
CMB	175-240	7-46	Stampriet, Namibia	Stone and Edmunds, 2012
CMB	370	1.5-15	NW Kalahari, Namibia	Külls, 2000
CMB	450	16-24		
Soil Moisture Balance	450	0.4-9.6		

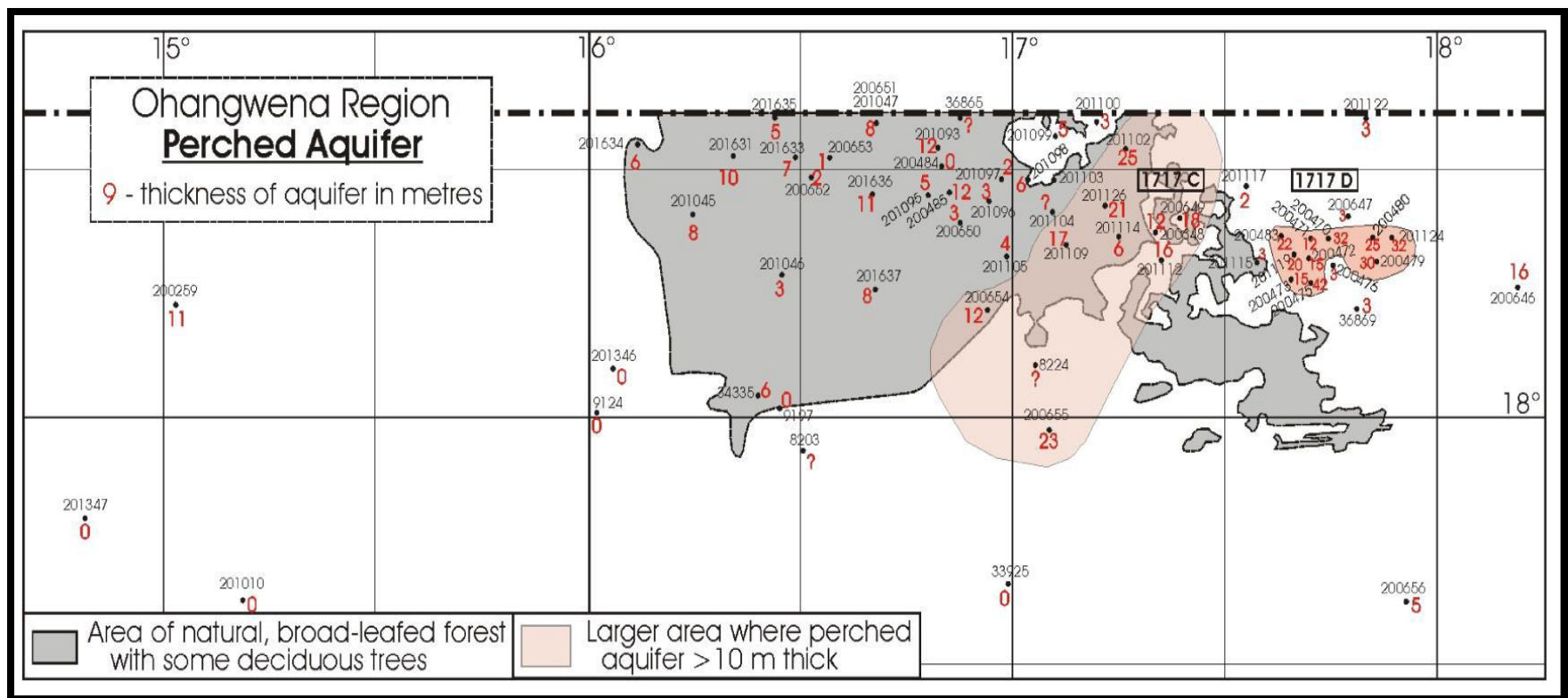


Figure 2-4: Thickness of perched aquifer in the Ohangwena region based on texture (Lohe et al., 2013)

3 Hydrogeochemical and isotope study of perched aquifers in the Cuvelai-Etosha Basin, Namibia

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3.1 Abstract

A hydrogeochemical and stable isotopic study (^2H and ^{18}O) was carried out in the Cuvelai-Etosha Basin in order to characterise available groundwater and to identify possible recharge mechanisms for the perched aquifers. Data was collected during 7 field campaigns between 2013 and 2015 from a total of 24 shallow and deep groundwater wells. In the investigated groundwater, bicarbonate is the dominating anion in both well types, whereas cation varies between calcium ion and magnesium ions in deep wells, and sodium and potassium in shallow wells. Groundwater chemistry is controlled by dissolution of carbonate minerals, silicate weathering and ion exchange. Stable isotope composition suggests that deep groundwater is recharged by high intensity/large rainfall events, whereas the shallow wells can even be recharged by less intense/small rainfall events. Water in deep wells reflect a mixture of water influenced by evaporation during or before infiltration and water that infiltrated through fast preferential pathways whereas shallow wells are strongly influenced by evaporation. The findings of this research contribute to improving understanding of hydrogeochemistry, recharge paths and temporal variations of perched aquifers.

3.2 Introduction

Groundwater is the main water source for most communities in semi-arid regions (Foster et al., 2000; Macdonald and Edmunds, 2014). For effective planning, management and utilisation of the groundwater resources addressing water supply sustainability and water quality, a comprehensive understanding of the groundwater system through integrated hydrogeological investigations are obligatory (Conrad et al., 2004). The Cuvelai-Etosa Basin (CEB) located in northern central Namibia (Figure 1) is home to approximately 40% of the Namibian population; more than 80% of this population live in rural areas where they depend on groundwater for drinking water and livestock watering (Mendelsohn et al., 2013). Groundwater in this region occurs in both deep and perched aquifers. Fetter (1994) and Freeze & Cherry (1979) defined perched aquifers as bodies of groundwater (a saturated zone) that is unconfined and open to the overlying unsaturated zone but is separated from an underlying main body of groundwater by an unsaturated zone. In other words, perched aquifers occur as discontinuous small water bodies trapped by impermeable layers within the unsaturated zone. In the CEB, these perched aquifers are tapped by traditional hand-dug wells, which are owned and managed by individual families, and thus, each village might have more than 10 wells in one well-field. Normally these hand-dug wells are unprotected and not covered and therefore contaminants including animal faeces are washed from the surface and migrate to the wells, making the wells highly vulnerable to pollution (Nakwafila, 2011). Consequently, having several open wells not only promotes over-exploitation of groundwater resources on a local scale, but also increases the risk of groundwater contamination. High population densities, rapidly growing population and lack of infrastructure in rural areas add further pressure on the limited groundwater resources.

In recent years, the German Federal Institute for Geosciences and Natural Resources (BGR) has carried out extensive research on groundwater in the study area; however their focus concentrates on the exploration and utilisation of deep aquifers (Lindenmaier et al., 2014). For the perched aquifers it was found that the water quality in these wells is inappropriate for human consumption due to high amounts of fluoride, nitrate, sulphate and total dissolved solids (Hamutoko, 2013). Additionally, perched aquifers are susceptible to contamination not only because of their shallow water level, but also because of improper well designs (Hamutoko et al., 2016). Recharge rates estimated in the study area are higher than 100 mm per year in some areas (Wanke et al., 2014), which was described as exceptional for specific sites and hence cannot be up scaled to the CEB (David, 2013). Beyer et al., (2016, 2015) estimated recharge rates of 0 and 29 mm/a using a peak displacement technique for two subsequent years. Gaj et al., (2016) calculated a soil water balance using unsaturated zone water stable isotopes and estimated recharge rates between 4 and 5 mm/a. It was further shown that transpiration is responsible for most of the depletion in soil water storage (Gaj et al., 2016). However, hydrochemical processes and recharge mechanisms of perched aquifers are not yet understood and to the author's knowledge have not been investigated thoroughly. Consequently, little is known about the perched aquifer in the CEB, though its temporal and spatial evolution can be related to direct infiltration of rainfall (Lindenmaier et al., 2014).

Tracer methods and isotope tracers in particular have been extensively used in hydrogeology. For determining groundwater age often radioactive isotopes are applied (e.g., tritium, or carbon-14), whereas stable isotopes (e.g., carbon-13, nitrogen-15) are powerful parameters to decipher biogeochemical processes or problems concerning pollution of groundwater. Methods based on

stable isotopes and hydrochemical techniques have been used in hydrogeological studies around the globe to provide substantial information about groundwater origin (Acheampong and Hess, 2000; Asmael et al., 2015), recharge mechanisms (Al-Gamal, 2011; Cartwright and Morgenstern, 2012), biogeochemical processes in groundwater (Kanduč et al., 2014), water flow directions (Cartwright et al., 2012; Marques et al., 2013), residence time distributions of groundwater (Bouchaou et al., 2008), salinization of aquifers (Ghabayen et al., 2006; Hamed and Dhahri, 2013), intermixing of aquifers (Cartwright et al., 2010), the nature of the aquifer through which the water has circulated (Demlie et al., 2008; Khalil et al., 2015), as well as anthropogenic influences affecting the groundwater system (Jiang et al., 2009).

Generally, understanding of geochemical processes and recharge mechanisms often lead to an understanding of groundwater quality and quantity and can potentially initiate valuable predictions such as presented in Chang and Wang (2010). This study focused on the perched aquifers in the CEB, which are of crucial importance for local communities, but the hydrogeology and hydrology are poorly understood. The aim of this study is to characterize the groundwater chemistry and isotopic composition of oxygen ($\delta^{18}\text{O}$) and hydrogen ($\delta^2\text{H}$) to understand the mechanisms of groundwater dynamics and quality of groundwater. A particular focus is given on the origin of groundwater in perched aquifers and a potential evaluation of recharge processes.

3.3 Study site

The CEB is the Namibian part of the Cuvelai catchment (Fig 3.1), which is a vast sedimentary basin extending from the southern Angola highlands into northern central Namibia covering 165,000 km² (Lindenmaier et al., 2012; Mendelsohn et al., 2013). Perennial tributaries within the Cuvelai catchment are limited to the Angolan part, whereas tributaries (locally known as Iishana) in Namibia are generally ephemeral (Christelis and Struckmeier, 2001). The topographic gradient is extremely low, with elevation ranging between 1,092 and 1,110 meters above sea level (m a.s.l.) (Christelis and Struckmeier, 2001). All drainage is directed towards the saline Etosha pan which is the lowest point in the basin.

The majority of the population in the basin lives in rural areas and uses groundwater wells that tap both shallow and deep aquifers. The CEB climate is characterized as semi-arid with low annual rainfall ranging from 250 mm/a in the west and up to 550 mm/a in the east (Mendelsohn et al., 2013). Mean annual temperatures range from 17°C in June and July to 25°C from October until December (Mendelsohn et al., 2013). The mean potential evaporation rate can be as high as 3,000 mm/a, which is five times higher than the precipitation (Christelis and Struckmeier, 2001). The rainy season lasts from November to April; however the amount and distribution of rain are quite variable (Bittner, 2006). The CEB is divided into four major sub-basins called Iishana, Niipele, Olushandja, and Tsumeb. In this study core sites were chosen in the Niipele Sub-basin, in the proximity of Okongo town (Fig. 3.1).

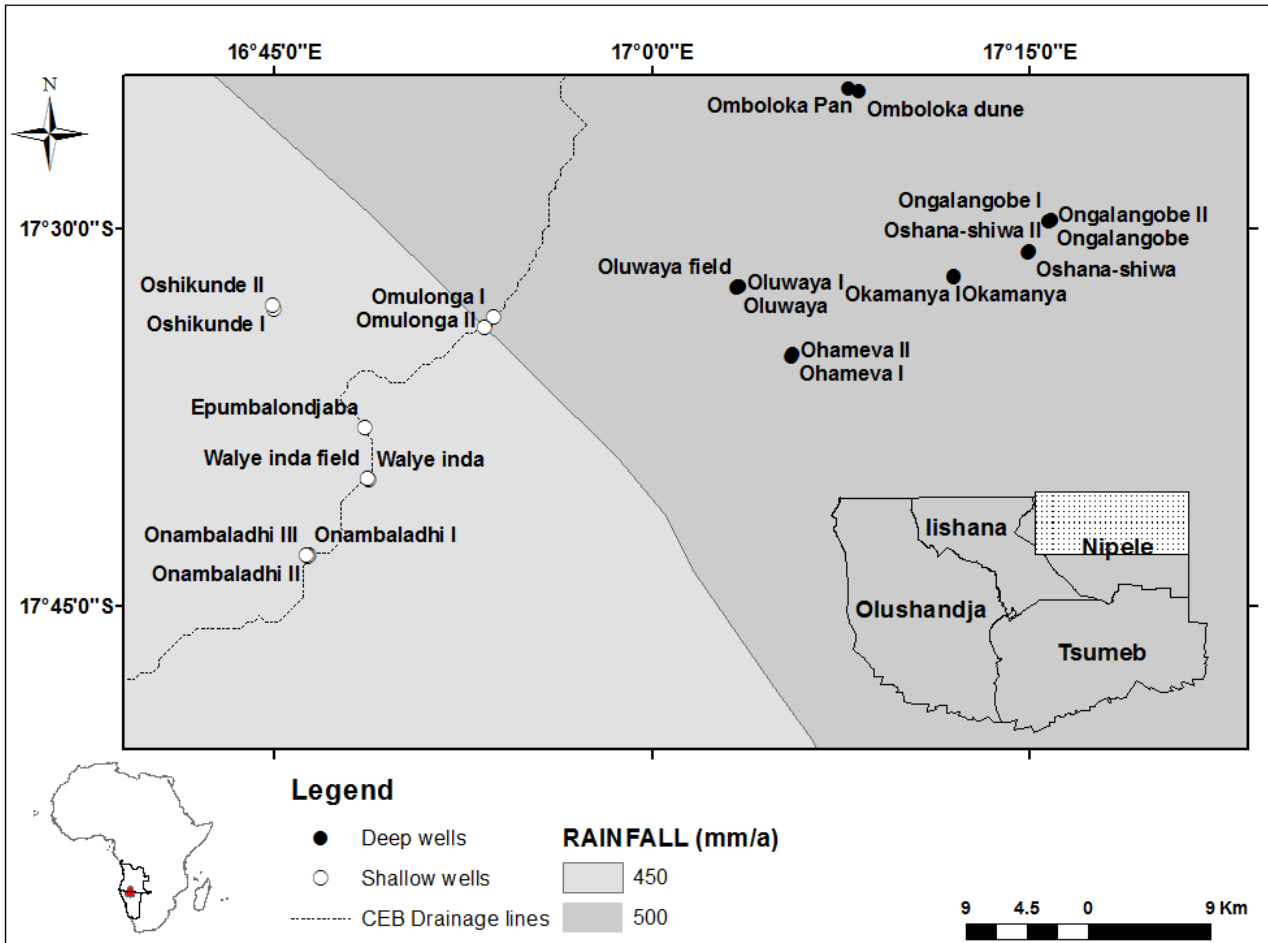


Figure 3-1: Location of the study area. The study area cover a precipitation gradient from 450 to 500 mm/a, and most shallow wells are located along the old river (water doesn't flow on the surface anymore)

The hydrogeological system in the study area is called Ohangwena Multi-Layered Aquifer System. This system is made up of three major hydrogeological units that are contained within the unconsolidated to semi-consolidated sediments of the Andoni and Olukonda Formations (Lindenmaier et al., 2014; Miller et al., 2010):

- (i) The upper aquifer is the discontinuous shallow perched aquifer (KOH-0) characterised by well-sorted, fine to medium grained sands with minor silt. It occurs within the unsaturated

zone as small water body trapped by an impermeable base above the regional water table.

The thickness of the aquifer ranges between 1 and 40 m.

- (ii) The subsequent aquifer is the regional Ohangwena I aquifer (KOH-I). It is characterised by fine-grained sands with varying silt and clay contents. The aquifer lies between 60 and 160 metres below ground level (m b.g.l.).
- (iii) The deep-seated aquifer is the recently discovered Ohangwena II aquifer (KOH-II), occurring at the depth of 250 to 350 m b.g.l. and is made up of well sorted, fine-grained sands, mixed with calcretes, silicretes and dolocretes.

This study pays particular attention to the perched aquifers. In the CEB, the perched aquifers are widely present underneath pans and depressions. Pans are geomorphological features that appear as shallow sub-circular to sub-elliptical isolated depressions; they are predominantly associated with crescent dunes which can rise to a height of 30 to 40 m above the pan floor (Lancaster, 1978). Depressions have similar physical properties with pans, but lack crescent dunes in their proximity. Burrough et al. (2012) & Nash and McLaren (2003) argued that even though pans have similar morphology with some landforms that occur in temperate regions e.g., karst depressions or permanent lake systems, they are characteristic for dry land because of the set of processes that are involved in their formation. (Bowler, 1986) suggested that pans can serve as either discharge or recharge point, depending on the present hydrologic dynamics and their soil hydraulic properties. Moreover, their ground surface may be covered or partly covered by grass, bare clay and/or calcrete with few shrubs mainly from the acacia species, while the dunes are covered by thick forest.

These perched aquifers are tapped mainly by two types of hand-dug wells (Fig. 3.2); the shallow wells, locally known as “Omifima” (funnel-shaped hand-dug wells) and the deep wells known as “Eendungu” (cylindrical-shaped hand-dug wells). The shallow hand-dug wells have a water table ranging from the topographic surface to a maximum depth of 5 m b.g.l. In contrast, the deep hand-dug wells have depth to water level ranging between 5 and 30 m b.g.l. The deep wells are equipped with a rope and a bucket is used to abstract water from the aquifer. Whereas the deep wells are mainly found in areas where a distinct impermeable caliche layer close to the soil surface is present, the shallow wells are mainly concentrated in areas with deep sheet sands. The terms “shallow wells” and “deep wells” will be used in the subsequent sections for differentiating the type of wells in this paper.

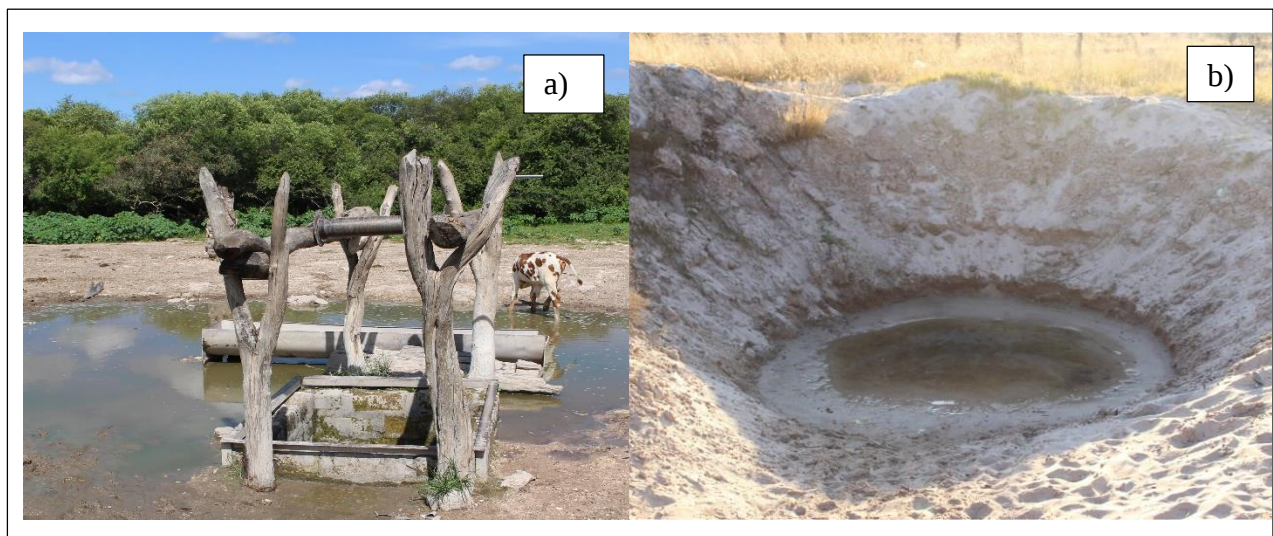


Figure 3-2: Examples of hand-dug wells. a) Deep wells locally known as “Eendungu” (cylindrical-shaped hand-dug wells) and b) shallow wells locally known as “Omifima” (funnel-shaped hand-dug wells)

3.4 Sampling and methods

Water samples were collected from 24 hand-dug wells, of which 10 are shallow and 14 are deep wells. Seven sampling campaigns were carried out with the first in November 2013, followed by

campaigns in March, June, and September in 2014 and in March, June and August in 2015. Some wells were not sampled at all times because they were not in use and dry during the particular field campaign; thus sampling would have been unrepresentative. The rainy season data were collected during March, June campaigns denote after rainy season data. In addition, samples collected in August/September represent the dry season. Samples from November comprise dry/beginning of rainy season data.

In the field the physical parameters pH, electrical conductivity (EC), redox potential (Redox), oxygen content (O₂) and temperature (T) were measured with Hach field portable instruments (HQ 11d pH meter, HQ 14d conductivity meter, HQ 40d multi-meter) (Fig. 3.3). The water level was measured with an electrical contact gauge. Three samples were taken at each well: a 100 ml polypropylene bottle for cations, a 500 ml polypropylene bottle for anions and a 50 ml glass bottle for stable isotopes. The glass bottle for stable isotopes was carefully sealed to prevent evaporation during transport. The cation samples were filtered through 0.45 µm filters and subsequently preserved with nitric acid whereas, anion samples were kept cool using a cooler box and refrigerator until analysed in the laboratory. Rain samples were collected as monthly cumulative rain samples at collectors in Okongo and Eenhana. Occasionally event samples were collected for isotope analysis.

Chemical analyses were performed at the Analytical Laboratory Services in Windhoek, Namibia and at the hydrochemistry laboratory of BGR in Hanover, Germany. The methods used at each laboratory are summarized in Table 3.1. The reliability of the analyses was checked by an ion charge balance error on all 98 samples. A total of 51 samples were within 5% error while the rest were above; however, it was observed that mainly samples from the shallow wells were having

high errors as a result of high total organic compounds (TOC) in samples. TOC was measured for numerous samples and explains the relative high ion charge balance error. TOC reflect anion behaviour but is not considered as anion during measurements which results in lower anion concentrations in comparison to cation concentrations. Therefore, all samples were used to characterise water types despite some having a charge balance error above 5%.



Figure 3-3: Measuring on-site parameters in the field

Stable isotopes were measured at the University of Namibia (UNAM) and BGR laboratories using an off-axis integrated cavity output spectroscope (OA-ICOS, Los Gatos DLT-100) and a cavity ring down spectrometer (CRDS, model L2120-i, Picarro Inc.) respectively. All values are given as δ -values in per mil (‰) against the international standard Vienna Standard Mean Ocean Water (V-SMOW, normalized to V-SMOW/SLAP scale) as defined by equation (1),

$$\delta = \left[\left(\frac{R_{SA}}{R_{ST}} \right) - 1 \right] \times 1000 \quad (3.1)$$

Where R_{SA} (-) denotes the isotope ratio of $^2\text{H}/\text{H}$ or $^{18}\text{O}/^{16}\text{O}$ of the sample and R_{ST} (-) of the standard respectively. Analytical errors of a quality check sample measured within each run are better than 0.20‰ for $\delta^{18}\text{O}$ and 0.8‰ for $\delta^2\text{H}$ measurements.

Table 3-1: Analytical methods used for analyses of major ions at the laboratories

Group	Elements	Analytical Laboratory Services	Federal Institute for Geosciences and Natural Resources (BGR)
Anions	HCO_3^- , CO_3^{2-} , alkalinity	Titration	Titration
	F^- , NO_2^- , Br^- , Cl^- , NO_3^- , SO_4^{2-}	NO_2 & NO_3 – Photometric Cl – Argentometric F – Ion Selective Electrode SO_4 – Turbidimetric Br – Iodometric	Ion Chromatography
Cations	NH_4^+ , Na^+ , Mg^{2+} , Ca^{2+} , K^+ , Ag^+ , Al^{3+} , Ba^{2+} , Be^{2+} , As^{3+} , Fe^{2+} , Zn^{2+} , etc.	Photometric Plasma Emission Spectroscopy	Photometric ICP-OES

3.5 Results and discussion

3.5.1 Physio-chemical parameters

The physical and chemical parameters of 98 groundwater samples that were measured in the field are summarized in Table 2. The temperature of the collected groundwater samples ranges between 15 and 36 °C with lowest temperatures recorded during mornings in winter while summer afternoons displayed the highest temperatures. The average temperature is 25°C, which is close to the mean annual air temperature of the study area. Low temperatures during mornings in winter and high temperatures during summer afternoons reflect a direct relationship between groundwater

and air temperature. The EC indicate that the deep wells are highly mineralised in comparison to shallow wells with EC ranging from 489 to 1,199 $\mu\text{S}/\text{cm}$ and 52 to 296 $\mu\text{S}/\text{cm}$ respectively (Table 3.2). The total dissolved solids (TDS) were calculated from EC thus, it shows the same trend as EC, higher in deep wells than in shallow wells. No temporal variation could be established; each well has similar values in all the campaigns (Fig. 3.4). The mean pH is 7.1 for shallow wells and 7.6 for deep wells; however, they both range from slightly acidic to slightly basic. Values for both TDS and pH are within drinking water threshold of the world health organization (WHO) guideline (WHO, 2008).

The shallow wells are highly turbid with values ranging from 27 to 255 Nephelometric Turbidity Units (NTU) indicating the presence of many un-dissolved particles in the water. Deep wells have lower turbidity ranging between 1 and 20 NTU (Table 3.2). According to the Namibian water cooperation guidelines (NAMWATER) (NamWater, 2011), turbidity should not be higher than 10 NTU in drinking water, and all the shallow wells have turbidity values above 10 NTU and thus classifying them as not suitable for human consumption.

Table 3-2: Minimum, mean and maximum values for the physio-chemical parameters at all the sampling sites

Parameters	Shallow wells (n=43)			Deep wells (n=55)		
	Min	Max	Mean	Min	Max	Mean
Water level (m)	0.0	5.0	2.0	5.6	28.6	13.5
Temperature ($^{\circ}\text{C}$)	15.0	36.0	25.0	22.0	27.0	25.0
O ₂ (mg/l)	4.2	20.0	8.2	1.3	6.9	4.3
Redox potential (mV)	29.0	177.0	104.0	22.0	230.0	133.0
pH	4.8	10.0	7.1	4.5	8.2	7.6
EC ($\mu\text{S}/\text{cm}$)	52.-0	296.0	142.0	489.0	1199.0	699.0
Turbidity (NTU)	27.0	255.0	80.0	1.0	20.0	3.0
Total Dissolved Solids [TDS] (mg/l)	35.0	198.0	97.0	328.0	719.0	484.0

3.5.2 Major ion geochemistry

Deep wells

Ca^{2+} is the dominant cation in deep wells, with 64.3% of the samples being Ca^{2+} -rich water while the remaining 35.7% either have no dominant cation or are Na^+ dominated. The concentration of the alkaline earth Ca^{2+} and Mg^{2+} ions range from 6.2 to 117.7 mg/l and 9.5 to 41.0 mg/l with a mean of 68.6 and 24.8 mg/l respectively (Fig. 3.5). Concentration of the alkalis ions (Na^+ and K^+) range from 0.7 to 75.0 mg/l and 2.7 to 114.0 mg/l with a mean value of 29.7 and 25.9 mg/l respectively. The dominant anion in all deep wells is HCO_3^- , which has concentrations ranging from 223 to 783 mg/l with a mean of 326.7 mg/l. Concentrations of the anions Cl^- , F^- , SO_4^{2-} and NO_3^- range from 0.7 to 25.1 mg/l, 0.3 to 4.5 mg/l, 1.0 to 6.7 mg/l and 0.1 to 296 mg/l, respectively, with mean values of 7.4, 1.9, 3.4 and 64.7 mg/l respectively. Therefore the abundance of major ions in deep wells can be grouped in the order $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+$ for cations and $\text{HCO}_3^- > \text{NO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{F}^-$ for anions. Ca^{2+} , Mg^{2+} , Na^+ , Cl^- , SO_4^{2-} concentrations fall within the WHO limits of 200, 100, 100, 1,000 and 400 mg/l respectively; however, a number of samples for K^+ , NO_3^- and F^- show concentrations above permissible limits of 10, 50 and 1.5 mg/l respectively as recommended by WHO, 2008 (Fig. 3.5).

Shallow wells

Shallow wells are dominated by the alkali ions Na^+ and K^+ with concentrations ranging from 0.8 to 39 mg/l and 2 to 30 mg/l with mean values of 14 and 11.3 mg/l, respectively (Fig. 3.5). The alkaline earth Ca^{2+} and Mg^{2+} have concentrations between 0.9 and 16.8 mg/l and 0.5 and 4.6 mg/l with mean values of 7.7 and 2.5 mg/l, respectively. HCO_3^- is the dominant anion in 65% of the

samples while the remainder percentage is water dominated by Cl^- and SO_4^{2-} . Concentrations of all anions range from 1.8 to 90.3 mg/l for HCO_3^- , 0.8 to 28.0 mg/l for Cl^- , 0.01 to 0.6 mg/l for F^- , 0 to 50 mg/l for SO_4^{2-} and 0.5 to 46.3 mg/l for NO_3^- with mean values of 35.8, 8.3, 0.2, 12.4 and 8.7 mg/l. The abundance of major ions in shallow wells is in the order of $\text{Na}^+ > \text{Ca}^{2+} > \text{K}^+ > \text{Mg}^{2+}$ for cations and $\text{HCO}_3^- > \text{NO}_3^- > \text{SO}_4^{2-} > \text{Cl}^- > \text{F}^-$ for anions. All cations and anions concentrations are within permissible WHO limits, with an exception of K^+ , which is above the limit in 50% of the samples (Fig. 3.5).

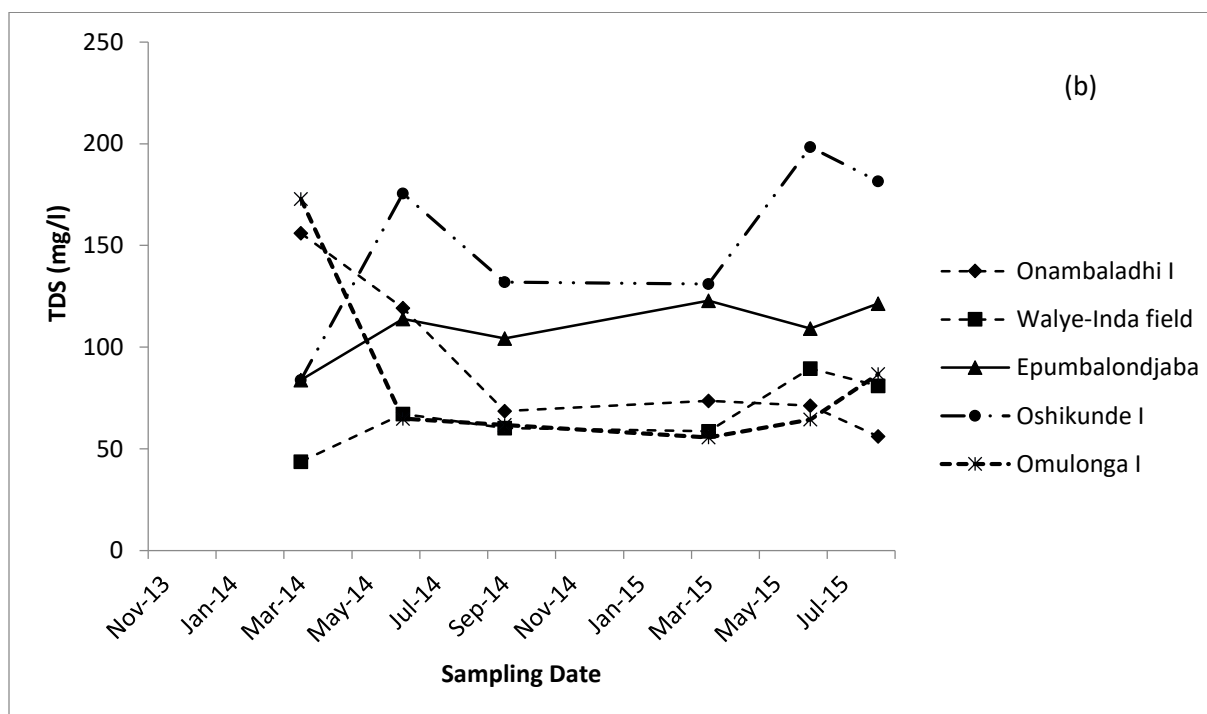
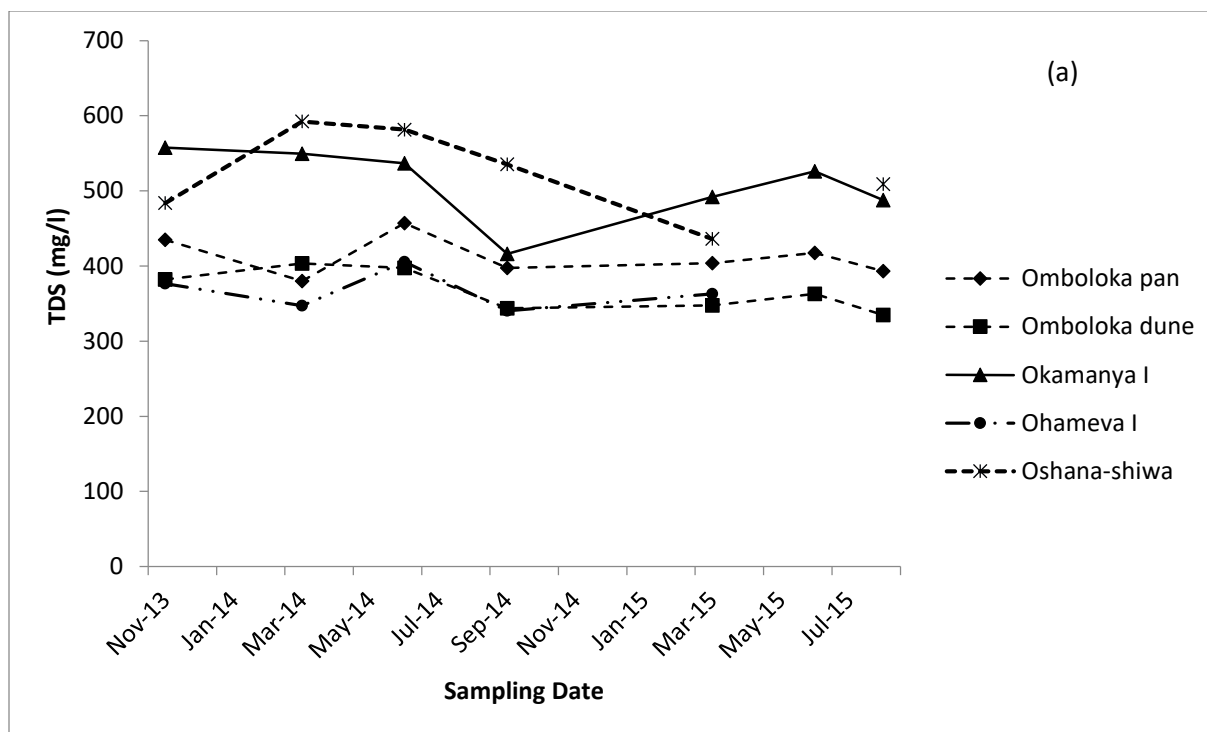


Figure 3-4: Temporal variations of TDS in from 10 of the sampled wells, (a) Show 5 examples of deep wells (b) show 5 examples of shallow wells

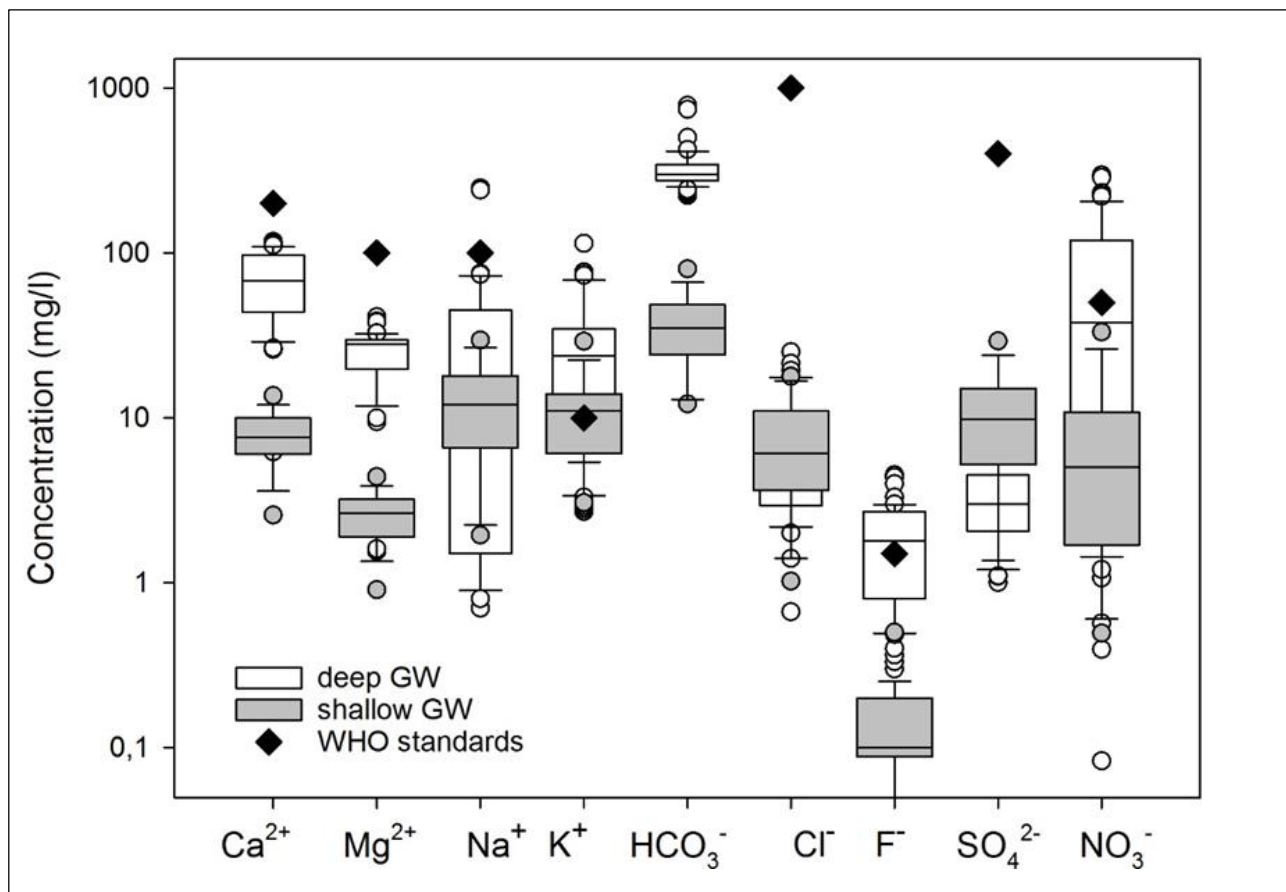


Figure 3-5: Boxplot showing maximum, minimum and median values of cation and anion of deep wells (in open colour) and shallow wells (in grey colour). The box outlines the interval between the 25th and 75th percentiles. Circles indicate outliers. The black diamond symbol indicate the WHO guideline values.

Geochemical processes in groundwater

In Fig. 3.6 and 3.7, a Piper diagram (Piper, 1944) and a Gibbs plot (Gibbs, 1971) are illustrated. Subsequently, the ionic relationships of major ions are discussed in regard to hydrochemical evolution and grouping. Piper diagrams are widely used in order to interpret the chemistry of water samples and to identify different water types (Piper, 1944). Gibbs plots enable an assessment of precipitation, rock weathering and evaporation effects on the geochemical evolution of groundwater in semi-arid and arid areas (Gibbs, 1971). Since the wells were sampled multiple

times and no strong temporal difference was found (indicated by TDS values; Fig. 3.4), average values for each well were used. The Piper diagram (Fig. 3.6) suggests two water types in the deep wells; $\text{Ca}^{2+}\text{-Mg}^{2+}\text{-HCO}_3^-$ and $\text{Na}^+\text{-K}^+\text{-HCO}_3^-$, with $\text{Ca}^{2+}\text{-Mg}^{2+}\text{-HCO}_3^-$ being the dominant type. Shallow wells are characterised by three water types; the mixed water type with neither a dominant cation nor anion, $\text{Na}^+\text{-K}^+\text{-HCO}_3^-$ and $\text{Ca}^{2+}\text{-Mg}^{2+}\text{-HCO}_3^-$ water types. $\text{Ca}^{2+}\text{-Mg}^{2+}\text{-HCO}_3^-$ water type indicates that groundwater is formed in carbonate-rich rocks or derived from an active recharge zone with short residence times (Ravikumar and Somashekar, 2015). Therefore it can be argued that the $\text{Ca}^{2+}\text{-Mg}^{2+}\text{-HCO}_3^-$ water type in deep wells is a result of dissolution of calcrete, which is outcropping in some areas of the pans, as well as weathering of the silicate minerals. Most deep wells are located in depressions and pans characterised by layers of calcrete embedded into unconsolidated sands. Higher EC in deep wells can be interpreted as a result of longer residence times in deep groundwater than in the shallow groundwater. Obiefuna and Orazulike (2011) state that evaporation increases the concentration of ions in the remaining water and leads to precipitation and deposition of evaporates. Therefore the data tend to suggest that evaporation processes are responsible for the observed geochemical composition in the CEB especially in the shallow wells. Furthermore, a widely accepted view is that in semi-arid regions, low rainfall and high evaporation rates cause evaporites to be leached into the saturated zone and this reduces dilution effects on groundwater. Conversely, $\text{Na}^+\text{-K}^+\text{-HCO}_3^-$ demonstrates that groundwater formed in formations where alkali carbonates are present. The mixed water, where no particular water type could be identified, indicates cation exchange as the main processes responsible for the groundwater chemistry.

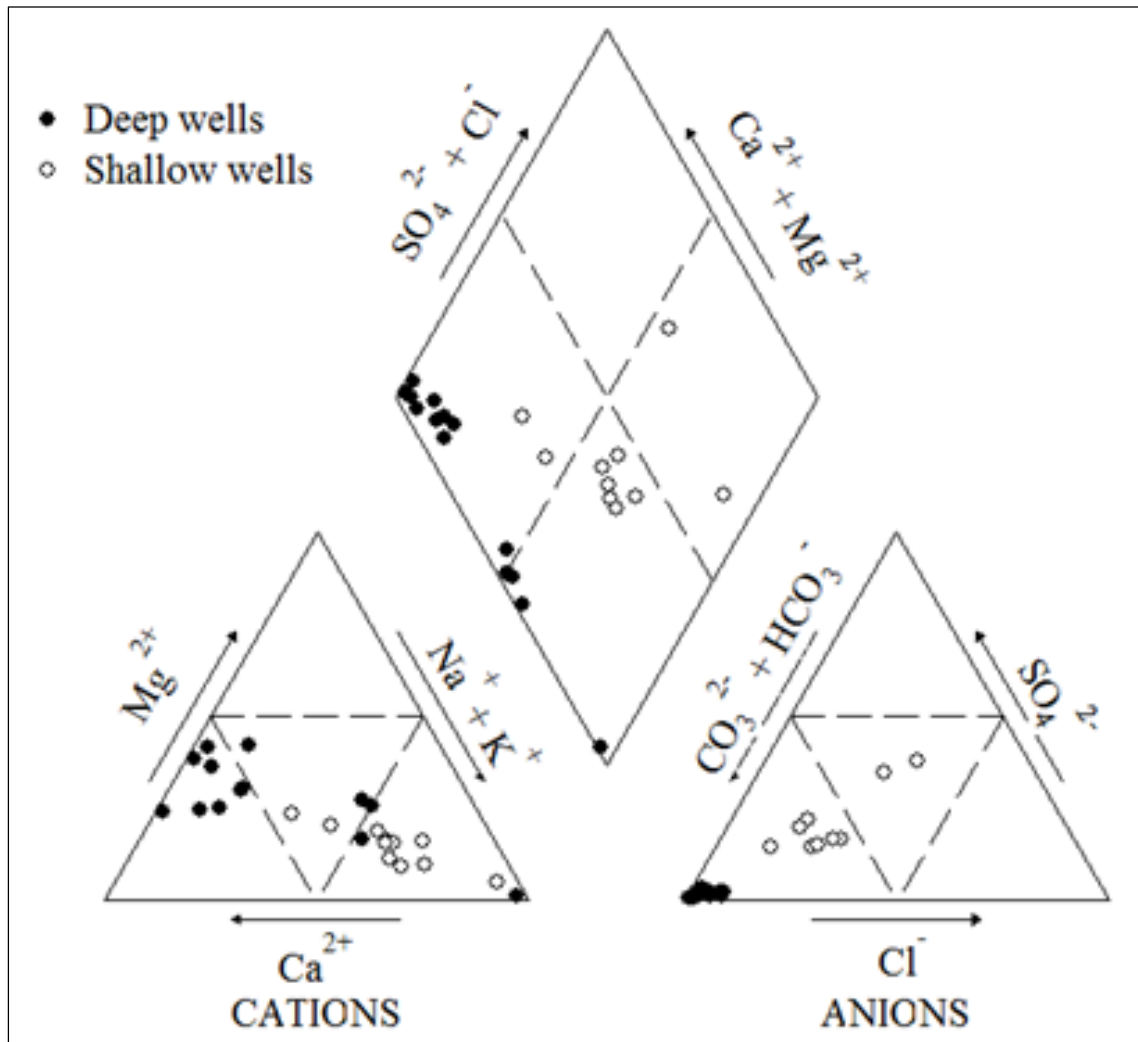
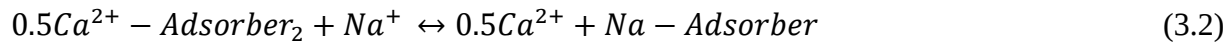


Figure 3-6: Piper plot showing hydrogeochemical facies in meq/l

The relationship of different ions was further used to distinguish between different geochemical processes that control groundwater chemistry. In carbonate rocks, dissolution is both the simplest and most common weathering reaction which is specified by 1:2 ratio of Ca^{2+}/HCO_3^- (Appelo and Postma, 2005). The plots of Ca^{2+} versus HCO_3^- (Fig. 3.7a and b) point out that a majority of the shallow well samples plot near the 1:4 and 1:2 lines while samples from deep wells are scattered

without a particular trend; however, all plot above the 1:2 regression. Plotting of $\text{Ca}^{2+} + \text{Mg}^{2+}$ versus $\text{HCO}_3^- + \text{SO}_4^{2-}$ (Fig. 3.7c and d) was used to indicate where these ions derived from. When data points plot along the 1:1 line, samples are influenced by carbonate dissolution and weathering while data points shifting away from this line indicate either one of these process as dominant. Excess $\text{HCO}_3^- + \text{SO}_4^{2-}$ over $\text{Ca}^{2+} + \text{Mg}^{2+}$ in the groundwater suggests weathering of Ca^{2+} - Mg^{2+} minerals such as calcite and plagioclase feldspars, while excess $\text{Ca}^{2+} + \text{Mg}^{2+}$ indicates reverse ion exchange process (Rao and Rao, 2010; Rao et al., 2015).

The ionic exchange between Ca^{2+} and Na^+ is explained by the adsorption equation (Appelo and Postma, 2005):



During ion exchange, there is excess $\text{HCO}_3^- + \text{SO}_4^{2-}$; therefore Ca^{2+} is desorbed from the absorber and released into solution whilst Na^+ is adsorbed. During carbonate dissolution there is an excess of $\text{Ca}^{2+} + \text{Mg}^{2+}$; therefore Ca^{2+} is adsorbed while Na^+ is released into solution. In this study shallow wells are clustered around the 1:2 line, while deep wells are divided into two subgroups; one group plots along the 1:4 regression line while the other group plots around the 1:2 line. The two groups also correlate to differences in the depth to water table: all samples in the first group have depth to water table of greater than 17 m b.g.l. and second group reflects depths to water table shallower than 17 m b.g.l. Shallow wells are characterised by a high amount of Na^+ (0.8 to 39 mg/l) and high amounts of HCO_3^- (1.8 to 90.3 mg/l). To determine whether this composition is a result of silicate weathering or cation ion exchange Jahnke plots (Jahnke, 1999) were used. Jahnke (1999) compared alkali excess over chloride (calculated as $\text{Na}^+ + \text{K}^+ - \text{Cl}^-$), to HCO_3^- and alkaline-earth

metals ($\text{Ca}^{2+} + \text{Mg}^{2+}$). During cation exchange $\text{Ca}^{2+} + \text{Mg}^{2+}$ decreases at a 1:1 ratio while HCO_3^- remains uninfluenced compared to $\text{Na}^+ + \text{K}^+ - \text{Cl}^-$. In contrast, $\text{Ca}^{2+} + \text{Mg}^{2+}$ remains uninfluenced while HCO_3^- content increases at a 1:1 ratio compared to $\text{Na}^+ + \text{K}^+ - \text{Cl}^-$ during silicate weathering. The Jahnke plots for the shallow wells have very low R^2 (0.55 and 0.34), which shows that both processes are playing a major role in controlling the groundwater chemistry (Fig. 3.7 e and f). In a Gibbs plot (Fig. 3.8) samples from shallow wells plot in the area of evaporation of rainfall, deep wells plot in two groups; one group with a low ratio of $\text{Na}^+ + \text{K}^+$ to $\text{Na}^+ + \text{K}^+ + \text{Ca}^{2+}$ plots in the field of rock dominance, while the second group plots towards evaporation dominance.

3.5.3 Isotopic composition of oxygen ($\delta^{18}\text{O}$) and hydrogen ($\delta^2\text{H}$)

The isotopic composition of the shallow wells ranges between -6.95‰ to 0.86‰ and -49.1‰ to -7.6‰ for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ respectively. For deep wells $\delta^{18}\text{O}$ values range between -9.00‰ and -1.30‰ and $\delta^2\text{H}$ from -61.5‰ to -22.1‰ (Table 3.3). Deuterium excess (d-excess) ranges between -16‰ and 11‰ for shallow wells and from 3‰ to 14‰ for deep wells. One deep well in Ongalangobe village was identified as an outlier and exhibits the lowest and highest d-excess values of -12‰ to 15‰ respectively. All groundwater samples are compiled in $\delta^2\text{H}$ vs. $\delta^{18}\text{O}$ space and plotted against the Global Meteoric Water Line (GMWL) as well as the Local Meteoric Water Line (LMWL) for the CEB (Fig. 3.9). The CEB LMWL has a slope of 7.2 and an intercept of +4.4 ($\delta^2\text{H} = 7.2 \delta^{18}\text{O} + 4.4$; $R^2 = 0.99$) and was developed from rainfall data collected within SASSCAL between 2013 to 2015 and historic data compiled by Turewicz (2013). Most groundwater samples, particularly those from deep wells plot close to the LMWL (Fig. 3.9) and this indicates that they originated from modern precipitation infiltration. The isotopic variations may be attributed to local climate factors (Farid et al., 2013; Kpegli et al., 2015).

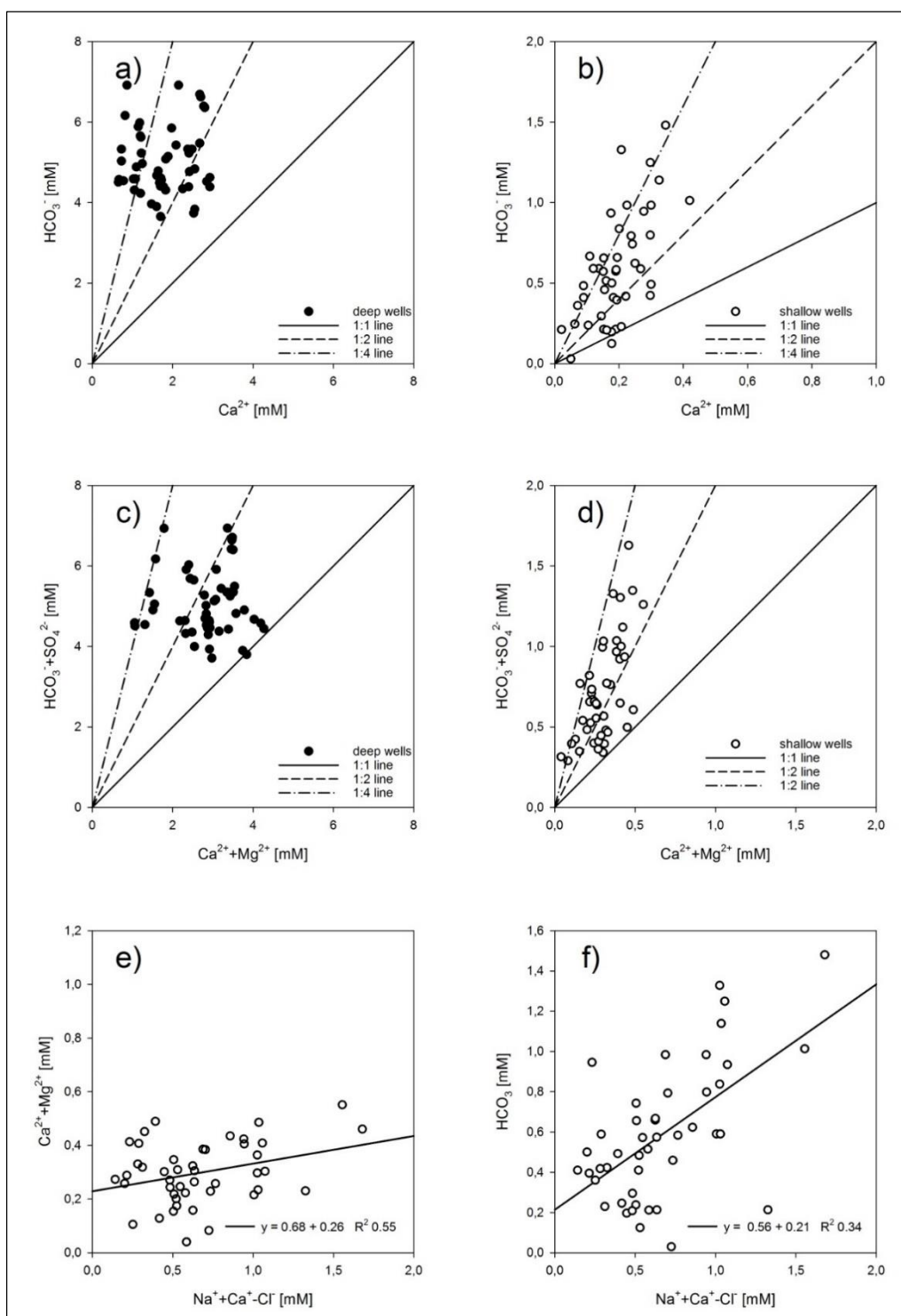


Figure 3-7: Plots of ionic relationships to explain geochemical reactions. (a) and (b) shows $\text{Ca}^{2+}/\text{HCO}_3^-$ plots, (c) and (d) shows $\text{Ca}^{2+} + \text{Mg}^{2+}/\text{HCO}_3^- + \text{SO}_4^{2-}$ plots and (e) and (f) shows $\text{Na}^+ + \text{K}^+ - \text{Cl}^-$ against $\text{Ca}^{2+} + \text{Mg}^{2+}$ and HCO_3^- respectively

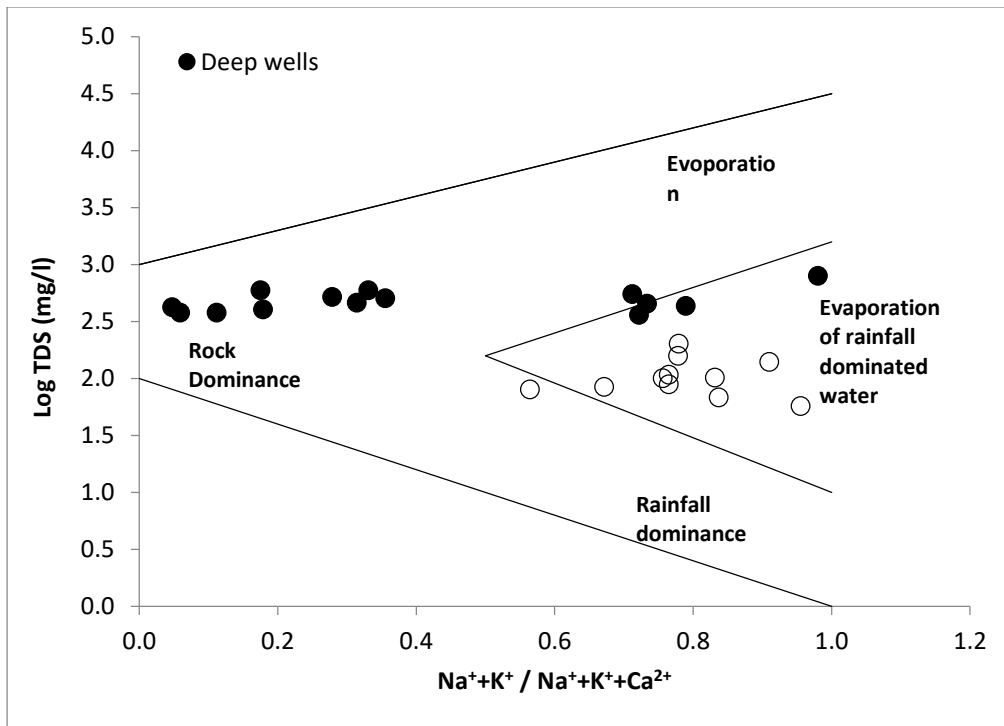


Figure 3-8: A Gibbs plot indicating the mechanism that determines the major ion composition in the study area

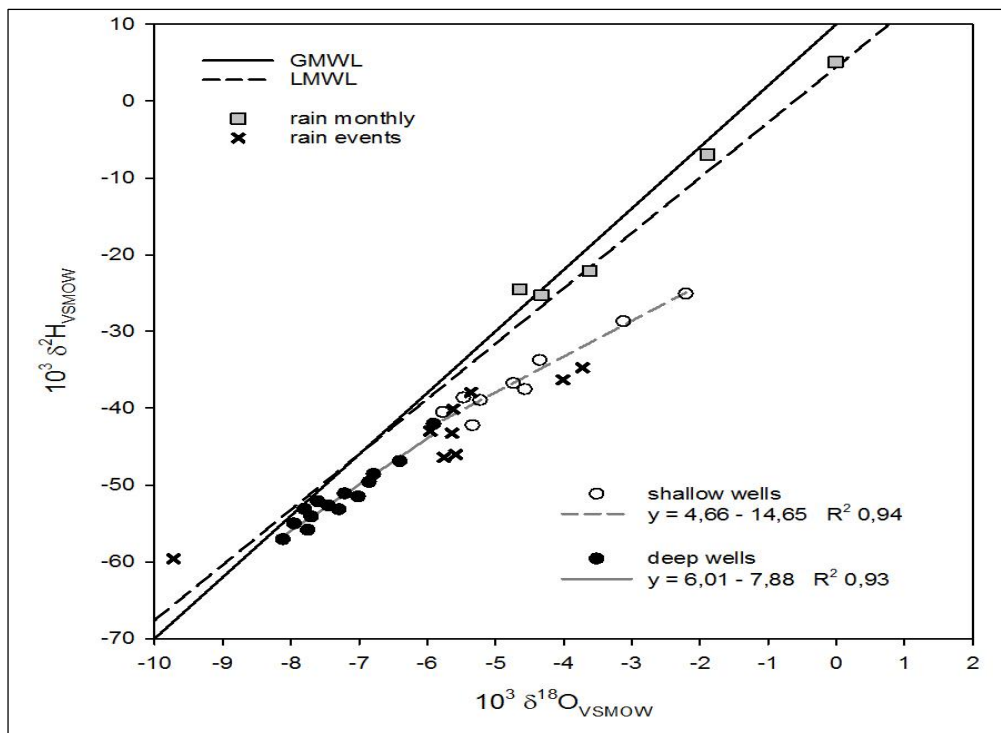


Figure 3-9: $\delta^2\text{H}$ vs. $\delta^{18}\text{O}$ plot including GMWL and LMWL and regression lines

Table 3-3: Minimum, mean and maximum values for isotopes for all the sampling sites. DW=deep well (14), SHW=shallow well (10)

Sample location	Well type	Min		Max		Mean		d-excess		
		$\delta^{18}\text{O}$	$\delta^2\text{H}$	$\delta^{18}\text{O}$	$\delta^2\text{H}$	$\delta^{18}\text{O}$	$\delta^2\text{H}$	Min	Mean	Max
Ohameva I	DW	-7.71	-53.7	-7.30	-51.8	-7.45	-52.7	5	7	10
Ohameva II	DW	-7.80	-56.3	-7.71	-55.4	-7.75	-55.9	6	6	6
Okamanya	DW	-7.64	-54.1	-6.64	-47.2	-7.21	-51.1	6	7	8
Okamanya I	DW	-8.25	-56.7	-7.42	-49.9	-7.96	-55.0	7	9	11
Oluwaya	DW	-7.02	-51.5	-7.02	-51.5	-7.02	-51.5	5	5	5
Oluwaya field	DW	-6.88	-49.5	-5.90	-43.9	-6.40	-46.9	3	4	6
Oluwaya I	DW	-7.38	-51.1	-6.58	-48.1	-6.86	-49.6	3	5	10
Omboloka dune	DW	-7.62	-52.1	-6.22	-46.3	-6.79	-48.6	4	6	9
Omboloka Pan	DW	-8.24	-56.4	-6.41	-46.4	-7.70	-54.1	5	8	12
Ongalangobe	DW	-8.31	-53.5	-1.30	-22.1	-5.91	-42.0	-12	5	14
Ongalangobe I	DW	-9.00	-61.2	-6.60	-45.1	-7.80	-53.1	8	9	11
Ongalangobe II	DW	-8.78	-61.5	-5.82	-44.8	-7.30	-53.2	2	5	9
Oshana-shiwa	DW	-8.00	-55.7	-6.36	-37.2	-7.61	-52.1	6	9	14
Oshana-shiwa I	DW	-8.38	-58.7	-7.88	-54.7	-8.12	-57.1	7	8	9
Epumbalondjaba	SHW	-6.29	-43.4	-4.94	-36.0	-5.47	-38.6	4	5	8
Omulonga I	SHW	-6.95	-49.1	-3.09	-31.1	-5.34	-42.2	-6	1	7
Omulonga II	SHW	-5.93	-46.5	-3.98	-30.9	-4.74	-36.7	0	1	2
Onambaladhi I	SHW	-6.34	-47.3	-3.28	-24.9	-5.23	-38.9	0	3	9
Onambaladhi II	SHW	-5.05	-41.2	0.17	-14.1	-3.12	-28.7	-16	-4	4
Onambaladhi III	SHW	-4.81	-36.1	-4.81	-36.1	-4.81	-36.1	2	2	2
Oshikunde I	SHW	-3.49	-33.1	0.86	-7.6	-2.21	-25.1	-15	-7	-2
Oshikunde II	SHW	-6.29	-44.2	-5.12	-34.6	-5.77	-40.5	2	6	11
Walye-inda	SHW	-5.34	-40.1	-3.76	-30.3	-4.35	-33.7	-1	1	3
Walye-inda field	SHW	-5.96	-42.6	-3.21	-31.2	-4.57	-37.5	-7	-1	5

All collected groundwater samples plot below both the LMWL and the GMWL; hence, they reflect a relative enrichment of heavier isotopes (Fig. 3.9). The samples collected from shallow wells follow a regression line of $\delta^2\text{H} = 4.66 \delta^{18}\text{O} - 14.65$; $R^2 = 0.94$. Samples from deep wells plot on a regression line with an equation of $\delta^2\text{H} = 6.01\delta^{18}\text{O} + 7.88$; $R^2 = 0.93$. The intersection of the evaporation line with the GMWL or LMWL identifies the mean isotopic composition of the parent rainwater (Clark and Fritz, 1997). For the sampled locations the two regression lines intersect with

the LMWL at different points: (-7.48‰, -44.5‰) for shallow wells and (-10.31‰, -69.8‰) for deep wells. This shows that the parent water is different. The shallow aquifers are recharged by rainfall with lighter isotopic signature. This means even small/lighter rain events can replenish them. On the contrary, the regression line of deeper wells crosses the LMWL at a much lower point (-10.31‰, -69.8‰), indicating that only high amount or intense rain events can recharge this aquifer. Samples from shallow wells plot further away from parent water than those from deep wells. Moreover, shallow wells and rain events show the same signature range of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ which is highly enriched, and this is a sign of water exchange and imply direct recharge for the shallow wells. However, highly enriched isotope values might also indicate that shallow wells are influenced by evaporation in comparison to deep wells. It should be noted, however, that the annual rainfall is higher in the area with deep wells (500 mm/a) compared to the area with shallow wells (450 mm/a). This might further influence the actual groundwater recharge rates, which are also reflected by higher chloride concentrations (average 8.3 mg/l) in the area with the shallow wells.

Under relative low humidity and semi-arid conditions, the slope of evaporation from an open water body is characterized by 4.5 to 5 indicating evaporation as a major process. Therefore the observed slope of 4.6 in shallow wells indicates evaporation before or during infiltration. The slope of 6.0 falls between a slope of evaporation of 4.6 and that of the LMWL of 7.2. This indicates mixing of water influenced by evaporation and water that infiltrates through fast or preferential paths through fractures and cracks in the calcrete layers coinciding with observations during the field campaigns. Fractures and cracks cause an increase of effective porosity and allow direct infiltration during high-intensity rainfall. Large differences in $\delta^{18}\text{O}$ are observed in shallow wells rather than in deep wells (Fig 3.10). However, there was no trend in the variation between the isotopic composition

of groundwater samples collected during the rainy and dry seasons. This point towards a lack of seasonal variation in isotopic composition of the parent water and also that processes after the rainy season are not influencing the isotopic composition of groundwater.

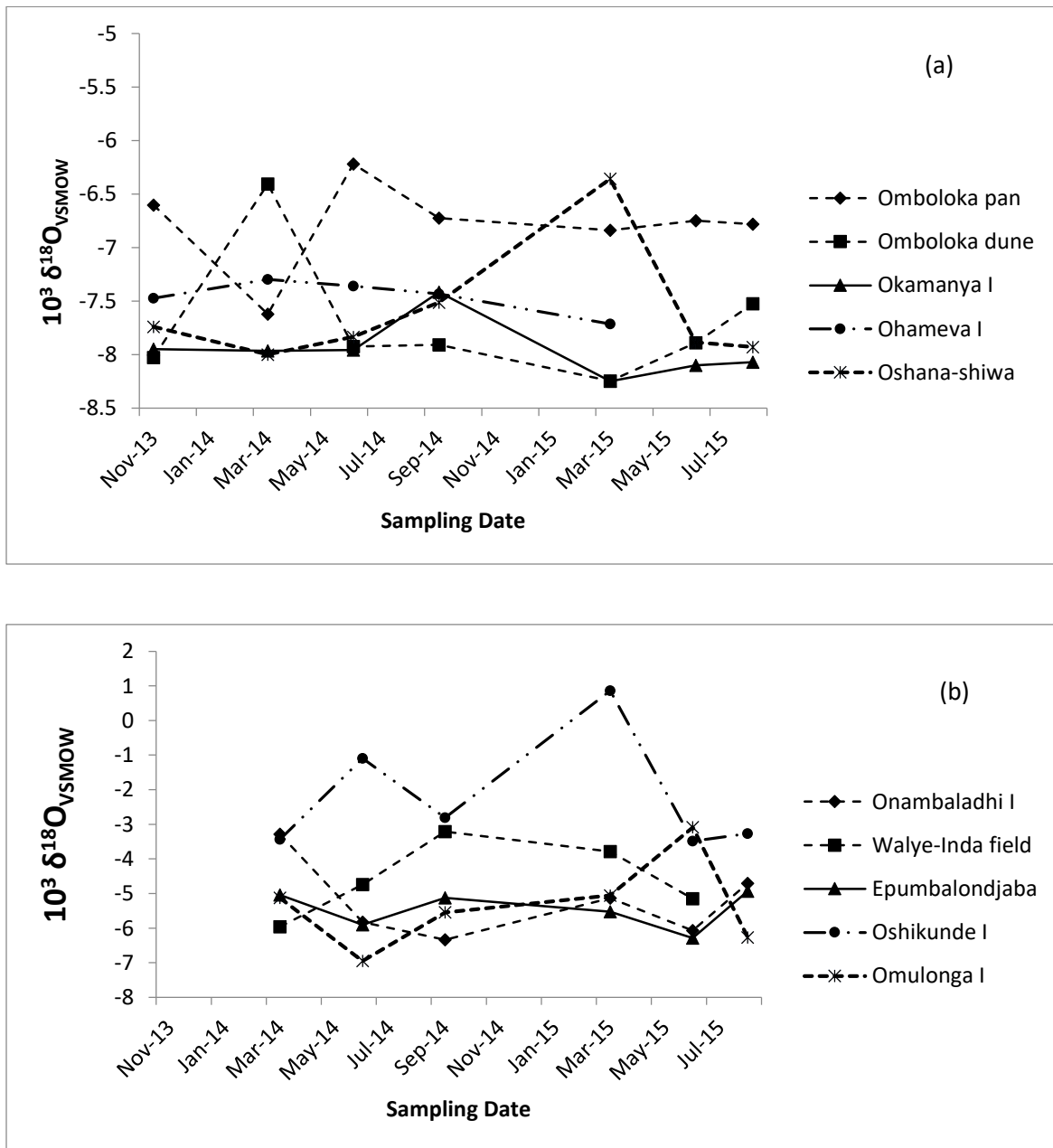


Figure 3-10: Temporal variations of $\delta^{18}O$ in from 10 of the sampled wells, (a) Show 5 examples of deep wells (b) show 5 examples of shallow wells.

3.6 Conclusion

The study aimed to characterise the groundwater geochemistry and understanding recharge mechanisms of the perched aquifers using major ion chemistry and the stable water isotopes ^{18}O and ^2H . According to WHO recommendations, the water quality in most wells is (theoretically) not permissible for drinking and domestic purposes because of high turbidity, potassium, fluoride and nitrate values, which are above the accepted values for drinking water. This study shows that depth to water table plays a major role in groundwater chemistry and isotope hydrogeology of the perched aquifers as a clear distinction can be made between the shallow and deep wells in the CEB. The deep wells are characterised by two water types; predominantly $\text{Ca}^{2+}\text{-Mg}^{2+}\text{-HCO}_3^-$ and $\text{Na}^+\text{-K}^+\text{-HCO}_3^-$, whereas shallow wells have three major groups; $\text{Na}^+\text{-K}^+\text{-HCO}_3^-$, $\text{Ca}^{2+}\text{-Mg}^{2+}\text{-HCO}_3^-$ and the mixed water type. Dissolution of carbonate minerals such as calcite and dolomite and silicate weathering and cation exchange are the dominant geochemical processes affecting the groundwater chemistry. The isotopic composition of the deep wells suggests distinguishing between two distinct recharge processes: i) water that is affected by evaporation either before or after infiltration and ii) water that infiltrates through fast preferential paths. The shallow well isotopic composition indicate evaporation. These isotopic compositions imply that groundwater is recharged under climatic conditions similar to the modern climate as they plot close to rainfall. It can also be concluded that deep groundwater must be recharged by high-intensity or large rainfall events while the shallow wells might also be recharged by lighter rainfall events. No temporal variation of the groundwater isotopic composition was identified. For a clear characterization of groundwater flow and recharge areas, it is necessary to further investigate spatial distribution and temporal variations of both groundwater chemistry and isotopic composition (both shallow and

deep wells). Use of other tracers such as ^3H , ^{14}C would help to determine ages of young and old groundwater but were not available for this work.

3.7 Acknowledgments and funding

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4 Spatio-temporal variations of hydrochemical and isotopic patterns of groundwater in hand-dug wells: the Cuvelai-Etosha Basin, Namibia

This chapter is an edited version of: J.T. Hamutoko, H. Wanke, M. Beyer, M. Gaj & P. Koeniger. Spatio-temporal variations of hydrochemical and isotopic patterns of groundwater in hand-dug wells: the Cuvelai-Etosha Basin, Namibia. A manuscript has been accepted in PIAHS.

4.1 Abstract

The rural population in parts of the Cuvelai-Etosha Basin (CEB) in Namibia depends on groundwater as a source for drinking and livestock watering. Groundwater recharge can influence both water availability and quality and thus a thorough understanding of groundwater recharge mechanisms is essential. Hence, the aim of this study is to investigate spatial-temporal patterns for understanding water origins and recharge processes of perched aquifers in the CEB. The study uses hydrochemical data and water stable isotope signatures ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) of samples collected during (10) ten field campaigns over a three-year period (from 2014 to 2016), originating from two regions within the basin (Ohangwena and Omusati). A clear distinction between the shallow groundwater in the two regions (Omusati and Ohangwena) is documented by TDS values, hydrochemical water types as well as the isotopic signatures of water. These differences are influenced mainly by their location in the landscape, depth to water table, the type of well infrastructure and aquifer material. Spatial and temporal variations indicate that although these perched aquifers are both within the same basin, they are chemically different because of their local aquifer lithologies. Therefore, these differences in the hydrochemical composition as well as the processes governing perched aquifers must be taken into account when planning groundwater management in the basin.

Keywords: Perched aquifers, Hydrochemistry, Stable isotopes, Seasonal variations, Recharge mechanisms

4.2 Introduction

More than half of the rural communities in the Namibian part of the Cuvelai-Etosha Basin (CEB) depend on groundwater as a main source of domestic water supply. The shallow groundwater is trapped on both local, discontinuous impermeable layers (perched aquifer) and shallow regional aquifers. It is commonly tapped by traditional hand-dug wells that are more affordable and cheaper in comparison with deep boreholes. However, because of the shallow depth to the water table and small catchments of these local aquifers, the perched aquifers face both natural and human induced challenges, for example population growth and agricultural activities; lack of proper water abstraction infrastructure; lack of improved sanitation facilities and changes in the climatic regimes that may promote both contamination and over-exploitation of the water resources of the shallow aquifers (Hamutoko et al., 2016). Additionally, the pressure for the development of water resources in dry land regions is high because of the overall scarcity and insecurity of supply (Young et al., 2006). Therefore, there is an urgent need to understand different elements that may affect the groundwater systems such as the processes governing groundwater recharge.

Groundwater recharge is an essential element of the hydrological cycle but it is generally very difficult to estimate (Scanlon et al., 2002), particularly in semi-arid to arid environments where potential evapotranspiration excessively exceeds precipitation, as well as limited vegetation cover

and thick unsaturated zones which result in low groundwater recharge (Allison & Hughes, 1983; Skrzypek et al., 2015; Stadler et al., 2010). Integrated isotopic and hydrochemical tracers along with standard hydrological data are used to understand such complex dry land hydrological processes on different spatial and temporal scales (Cartwright & Morgenstern, 2012; Conrad et al., 2004; Okkonen & Kløve, 2012; Vanderzalm et al., 2011; West et al., 2014). Different spatial and temporal scales are particularly important for arid environments due to high heterogeneity that is associated with these environments. Ledesma-Ruiz et al., (2015), highlight that spatial and temporal variability evaluation of major ions is commonly used in groundwater to give insight to the aquifer's heterogeneity and processes controlling the groundwater chemistry. Furthermore, an understanding of the different temporal and spatial scales of groundwater resources is extremely important for assessing the potential impact of groundwater extraction or the contamination of water resources, as well as assessing the vulnerability of the groundwater resources to changes in climatic conditions.

Previous studies in the CEB pointed out the existence of the hand-dug wells, but attention was given to borehole water from the deep seated aquifers (Christelis & Struckmeier, 2001; Lindenmaier et al., 2014), since hand-dug wells are considered rather small and not important for large-scale water supply. However, given the facts above, the importance of these aquifers for the rural population is immense. Wanke et al. (2014) described water quality from hand-dug wells in different areas in Namibia, and concluded that the water in hand-dug wells is not acceptable for drinking and domestic purposes, mainly because of its high turbidity, total dissolved solids (TDS), fluoride and nitrate values. Hamutoko et al. (2017) characterized the hydrochemical and isotopic

composition of the hand-dug wells in the Ohangwena region and concluded that the groundwater is bi-carbonate dominated, while the isotope signatures imply recharge through both fast infiltration and indirect recharge. Nevertheless, spatio-temporal variations of both hydrochemical composition and isotopic signatures are still not well understood and this hinders an effective management of this important local water resource. Groundwater recharge can influence both water availability and quality and thus a thorough understanding of groundwater recharge mechanisms is essential. Hence, in this study we sought to understand the spatial and temporal variations of major ions and water stable isotope signatures (^{18}O and ^2H), to determine the predominant processes that contribute to groundwater recharge and the evolution of hydrochemistry of hand-dug wells in the CEB.

4.1 Study area

4.1.1 Location and climate

The study area is located in the CEB (Fig. 4.1). CEB is the Namibian part of the Cuvelai catchment, which is a vast sedimentary basin extending from the southern Angolan highlands into north central Namibia, covering an area of about 165,000 km² (Lindenmeier et al., 2014). Two core study areas were defined, namely the Ohangwena and Omusati regions. The majority of inhabitants in Ohangwena and Omusati regions use hand-dug wells tapping from perched aquifer. In Ohangwena region, the mean annual rainfall ranges between 450 mm/a in the west up to 550 mm/a in the east, while potential evapotranspiration ranges between 2600 and 2800 mm/a. In the Omusati region, the mean annual rainfall varies between 350 and 400 mm/a, while the potential evapotranspiration ranges from 2800 to 3200 mm/a (Mendelsohn, et al., 2013). The rainy season

starts in November and ends in April, whilst the amount and spatial distribution of the rain is extremely variable (Fig. 4.2). Nevertheless, there are still limited and inadequate rainfall stations in the basin to record variations in rainfall patterns at a small scale.

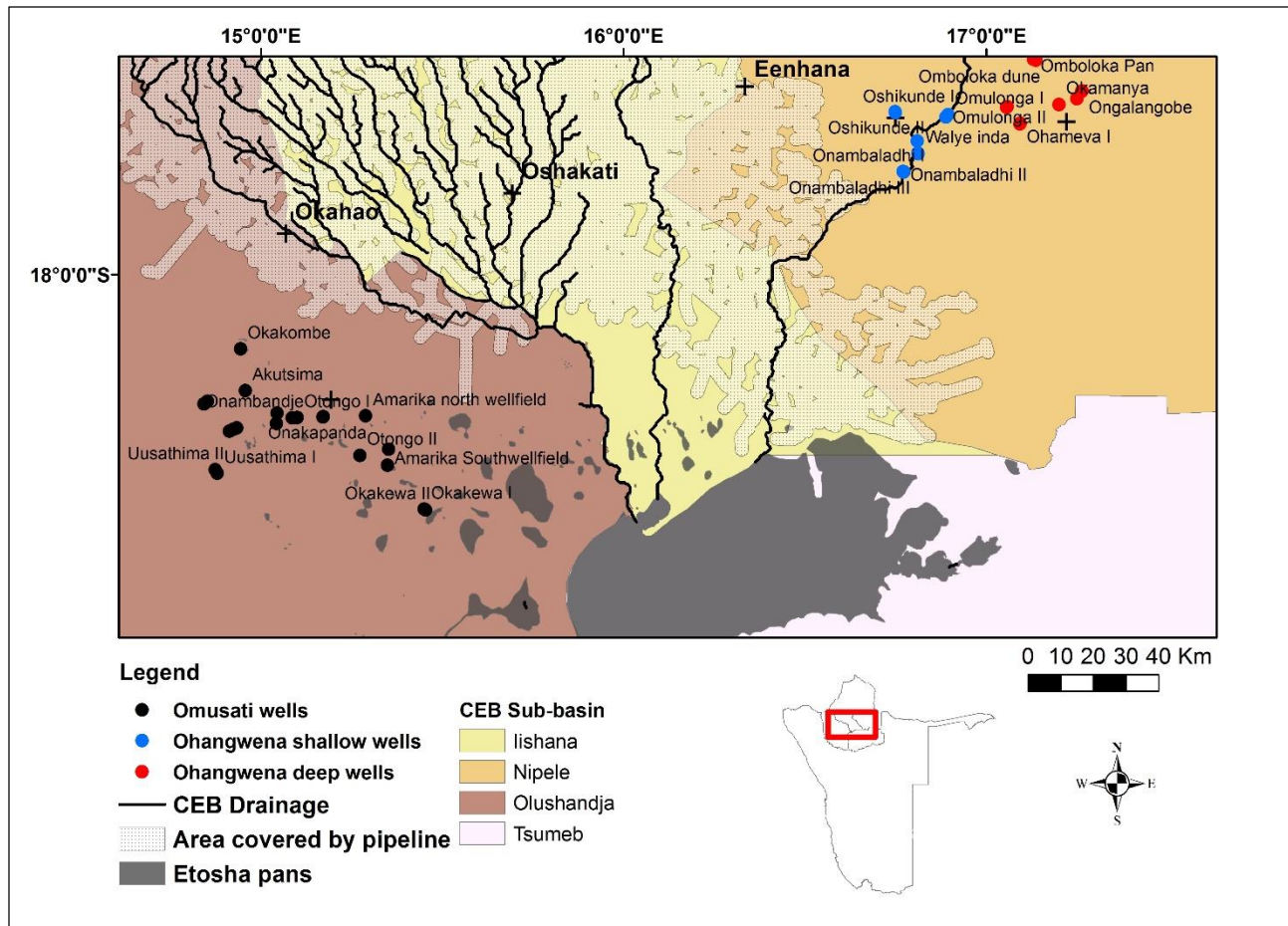


Figure 4-1: Location of the study area and sampling sites. The map also shows the area that is connected to the national water supply pipeline

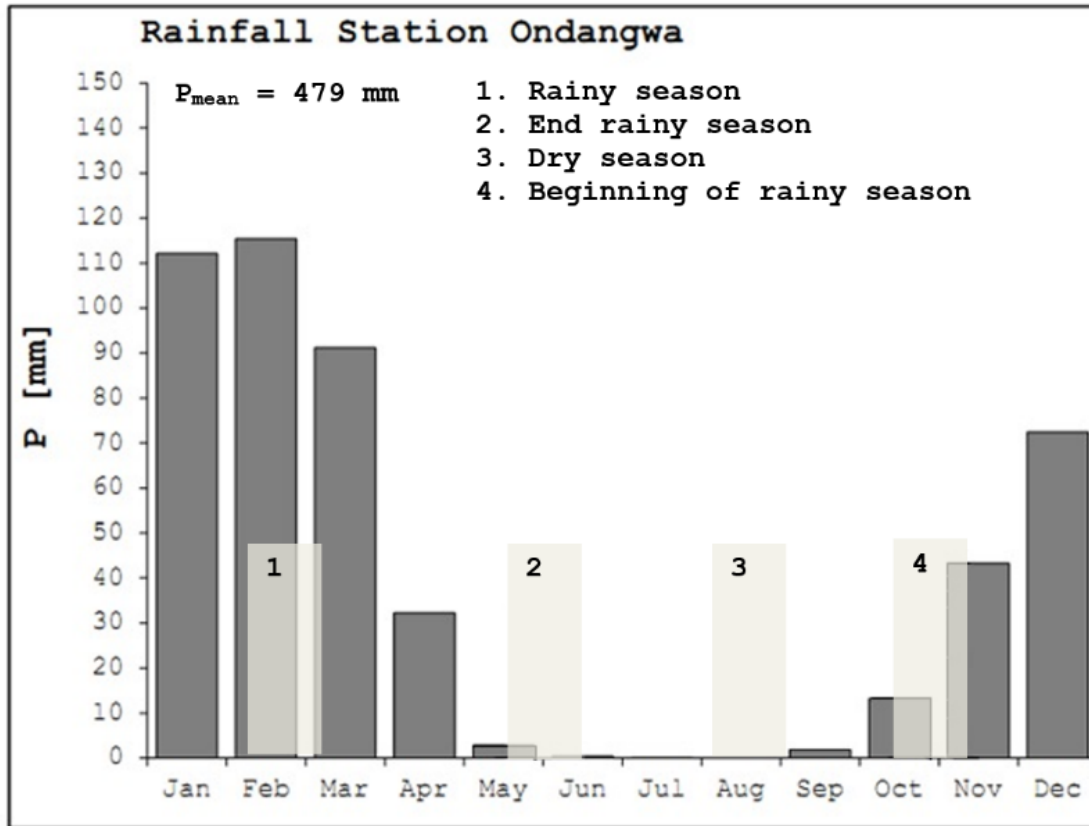


Figure 4-2: Mean monthly precipitation at the closest meteorological station with longer term records (1902 – current). The four labelled represent the time field campaigns took place (edited from Beyer, 2016)

4.1.2 Geological and hydrogeological setting

The geological setting of the CEB is described in detail by Lindenmaier et al. (2014), Miller and Becker (2008), Miller, Pickford, and Senut (2010), and Miller (1997). The land surfaces of the study area are covered by different sand and clay successions, with outcrops of calcrete and dolomite occurring mainly in pans and depressions. These sand and clay successions are part of the thick sediments (can be up to more than 600 m locally) of the Kalahari Sequence, with ages ranging from late Cretaceous to the recent times. The Kalahari Sequence has four formations:

Ombalantu, Beiseb, Olukonda and Andoni. These formations are described in details in Miller, 1997 and stratigraphy is shown in Table 4.1.

Table 4-1: Stratigraphy of the Kalahari sequence (modified after Ploethner et al., 1997 and GWK & Bicon, 2003 in Bittner, 2006)

System	Sequence (AGE)	Formation	Lithology	Maximum thickness (m)
Quaternary	Kalahari Sequence (< 120 Ma)	Alluvium	Calcrete, Sand	n/a
Tertiary		Etosha Limestone Member	Limestone, calcrete, sand	100
		Andoni	Sand, sandstone, silt	275
		Olukonda	Sand, sandstone, silt	175
		Beisep	Sandstone, mudstone, gravel	50
Cretaceous		Ombalantu	Mudstone	100

Hydrogeologically, there are six main aquifer systems that can be distinguished within the CEB, namely the “Otavi Dolomite Aquifer (DO) located on the western and southern rim, followed to the north by the Etosha Limestone Aquifer (KEL), the Oshivelo Multi-layered Aquifer (KOV) in the eastern area of the CEB, the Ohangwena Multi-layered Aquifer (KOH) in the north-eastern parts, the Oshana Multi-layered Aquifer (KOS) covering the area of the Cuvelai drainage system and the Omusati Multi-zoned Aquifer (KOM) situated in the west adjacent to the KOS” (Bittner, 2006). The distribution of the aquifers is shown in Fig. 4.3.

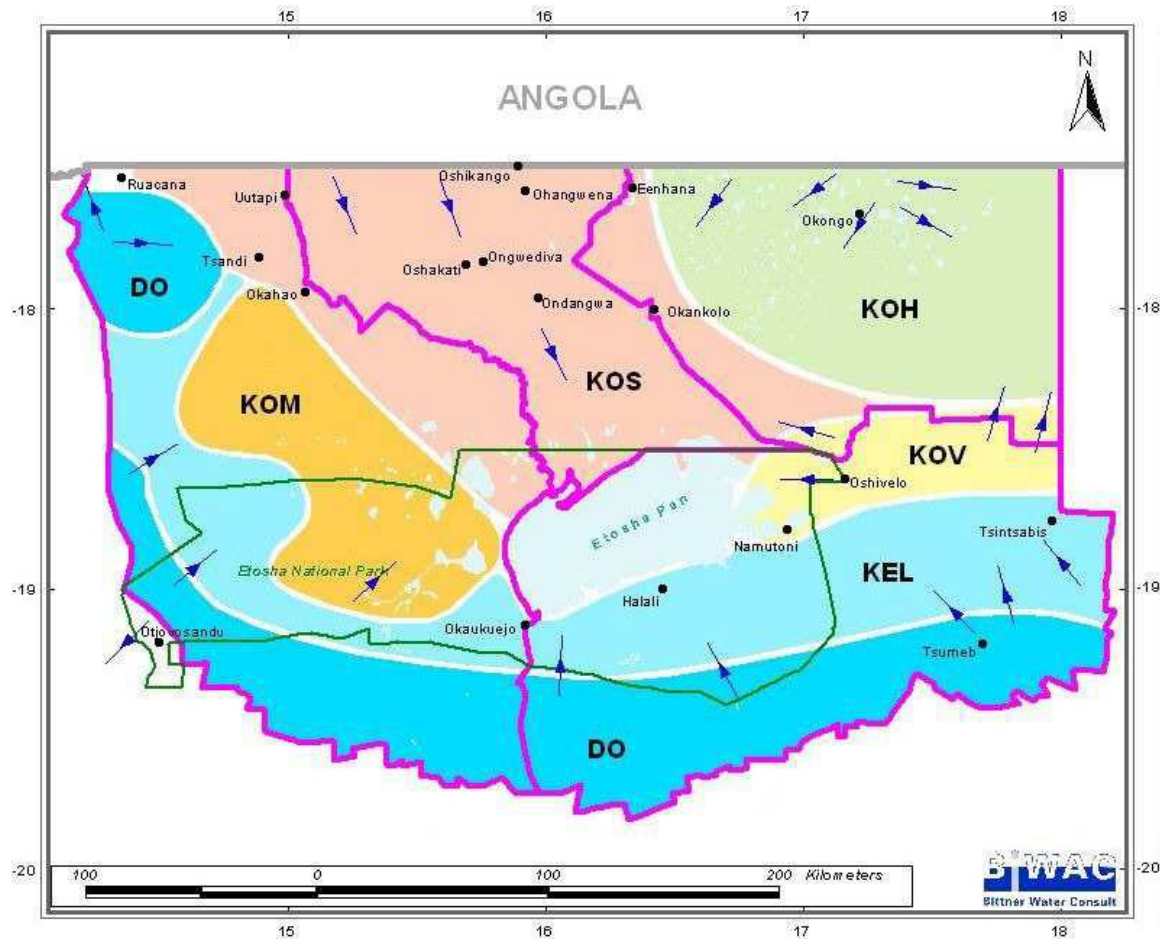


Figure 4-3: Main groundwater systems of the CEB (Bittner, 2006)

The two core study areas are in the Kalahari multi-layered Ohangwena aquifer (KOH) and the Kalahari multi-zoned Omusati aquifer (KOM). KOH is contained within the unconsolidated to semi-consolidated sediments of the Andoni and Olukonda formations (Bittner, 2006). KOH consists of local perched aquifers (KOH-0) that lie between 0 and 40 m on top, underlain by the regional Ohangwena 1 aquifer (KOH-I), which is between 60 and 160 meters below groundwater level (m b.g.l.), and at the bottom is the Ohangwena 2 aquifer (KOH-II), which is between 250 to 350 m b.g.l. (Bittner, 2006). KOM as the name implies, is hosted in all four formations of the

Kalahari sequence, with rocks ranging from semi-consolidated to consolidated sediments, mainly sand, clay and calcrete/dolocrete but also large evaporitic deposits (Bittner, 2006). The depth to the water table is shallow, ranging between 10 m to 100 m, with perched aquifers occurring in fewer places as compared to the KOH region.

The Ohangwena region is characterized by two types of hand-dug wells (Fig. 4.4): shallow wells (funnel-shaped, hand-dug wells) locally known as “Omifima” and the deep wells (cylindrical-shaped, hand-dug wells) known as “Eendungu”. The depth of the shallow wells ranges from surface to a maximum depth of about 5 m b.g.l. The depth of the deep hand-dug wells is between 5 m b.g.l to 30 m b.g.l. In the Omusati region, all hand-dug wells are of the funnel-shaped type (Fig. 4.5). In the Ohangwena region, all hand-dug wells are tapping the perched aquifers, while in the Omusati region some hand-dug wells are tapping both perched aquifers and the shallow parts of the regional aquifer KOM. Additionally, all hand-dug wells in Omusati are situated in pans while in Ohangwena they are either located in pans / depressions or in old, ephemeral rivers.



Figure 4-4: Two types of hand-dug wells: a) the deep wells (cylindrical-shaped hand-dug wells) known as “Eendungu” and b) shallow wells (funnel-shaped hand-dug wells) locally known as “Omifima”



Figure 4-5: Examples of hand-dug wells in Omusati region

4.2 Sampling methods and laboratory analysis

Water samples were collected from 48 hand-dug wells from the two core study areas. Sampling took place over a period of three years (between 2014 and 2016) within ten campaigns. Some wells were not sampled at all times because they were not in use and/or they were dry during the particular field campaign; thus samples would have been unrepresentative. In the field, the physical parameters pH, electrical conductivity (EC), oxidation-reduction potential (Redox), oxygen content (O_2) and temperature (T) were measured with Hach field portable instruments (HQ 11d pH meter, HQ 14d conductivity meter, HQ 40d multi-meter) (Fig. 4.6). The water level was measured with an electrical contact gauge. Major ions samples and stable isotopes were collected following standard procedures.



Figure 4-6: On-site parameter measurements in the field

Chemical analyses were performed at the Analytical Laboratory Services in Windhoek, Namibia and at the hydrochemistry laboratory of the German Federal Institute for Geosciences and Natural Resources (BGR) in Hanover, Germany, using several chemical analytical methods such as Ion Chromatography (IC) and Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES). The methods used at each laboratory are discussed in detail section 3.6. Stable isotopes were measured at the University of Namibia (UNAM) and BGR laboratories using an off-axis integrated cavity output spectroscope (OA-ICOS, Los Gatos DLT-100) and a cavity ring down spectroscope (CRDS, Picarro L2120-i,) respectively. All values are given as δ -values in per mil (‰) against the international standard Vienna Standard Mean Ocean Water (V-SMOW, normalized to V-SMOW/SLAP scale) as defined by equation (4.1),

$$\delta = \left[\left(\frac{R_{SA}}{R_{ST}} \right) - 1 \right] \times 1000 \quad (4.1)$$

Where R_{SA} (-) denotes the isotope ratio of $^2\text{H}/\text{H}$ or $^{18}\text{O}/^{16}\text{O}$ of the sample and R_{ST} (-) of the standard respectively. Analytical errors of a quality check sample measured within each run are better than 0.20‰ for $\delta^{18}\text{O}$ and 0.8‰ for $\delta^2\text{H}$ measurements at BGR and 0.30‰ for $\delta^{18}\text{O}$ and 1.0‰ for $\delta^2\text{H}$ for measurements at UNAM. Major ions and isotopes were plotted with ArcGIS to find the spatial patterns, piper diagrams were produced using GW_chart (USGS) and a spreadsheet was used to find the temporal variations.

4.3 Results

4.3.1 Spatial patterns

4.3.1.1 Water quality and chemistry

Hydrochemical data indicate differences between samples from Omusati and Ohangwena regions. A piper diagram (Fig. 4.7) shows the hydrochemical water types for all the collected samples. In Ohangwena region, bicarbonate is the dominant anion, whereas in Omusati region the groundwater is dominated by sulphate, while cation changes from calcium and magnesium (Ca-Mg) dominated water to sodium and potassium (Na-K) dominated water (Fig. 4.7). In the study area, five main water types are observed: CaMgHCO_3 , NaHCO_3 , CaSO_4 and NaSO_4 as well as mixed water type. CaMgHCO_3 water type occurs mainly in Ohangwena deep wells and a few samples from the shallow wells. NaHCO_3 water type is mainly found in the shallow wells in Ohangwena and also samples from deep hand-dug wells water with level more than 17 m below ground surface. CaSO_4 and NaSO_4 water types are dominant in Omusati wells. The mixed water types where all ions have

almost equal concentrations are found in both regions; however it is most common for the shallow wells in the ephemeral river in Ohangwena. Furthermore, sub-groups within the main five water types were recognized, for example, CaNaSO_4 and CaMgSO_4 within the CaSO_4 water type.

TDS, fluoride and nitrates are some of the main elements of concern for drinking water in the study area. To show the spatial variability (Fig. 4.8), average values for all the sampling campaigns were used for each sampling site. Figure 4.8 shows the distribution of average total dissolved solids (TDS) and water types in the study area. Relatively high TDS values are observed in Omusati region compared to Ohangwena region. In Ohangwena region, all the sampled wells have TDS within the WHO drinking guidelines limit (WHO, 2008), however in Omusati region only seven wells out of 22 wells (31 %) have TDS within the WHO drinking guidelines limit. The water types in Ohangwena region generally change from NaHCO_3 in the north-east to CaMgHCO_3 , and to mixed water types in the south-west. However, it must be noted that this spatial pattern is also observed for the depth to water table. The depth to water table decreases towards the south-west. In the Omusati region, the water becomes fresher (lower TDS and HCO_3 water types) towards the east. There is however, an interesting observation where one village (Olumpelengwa) has two hand-dug wells approximately two km apart, but they have totally different chemistry. Olumpelengwa I has relatively deeper depth to water table (approx. 10 m), water is brackish with TDS ranging from 3209 to 7980 mg/l with an average value of 6709 mg/l and the dominant water type is NaSO_4 . On the other hand, Olumpelengwa II has depth to water table of approximately five m, the water is fresh with TDS between 70 and 582 mg/l and an average value of 477 mg/l and CaMgHCO_3 is the dominant water type.

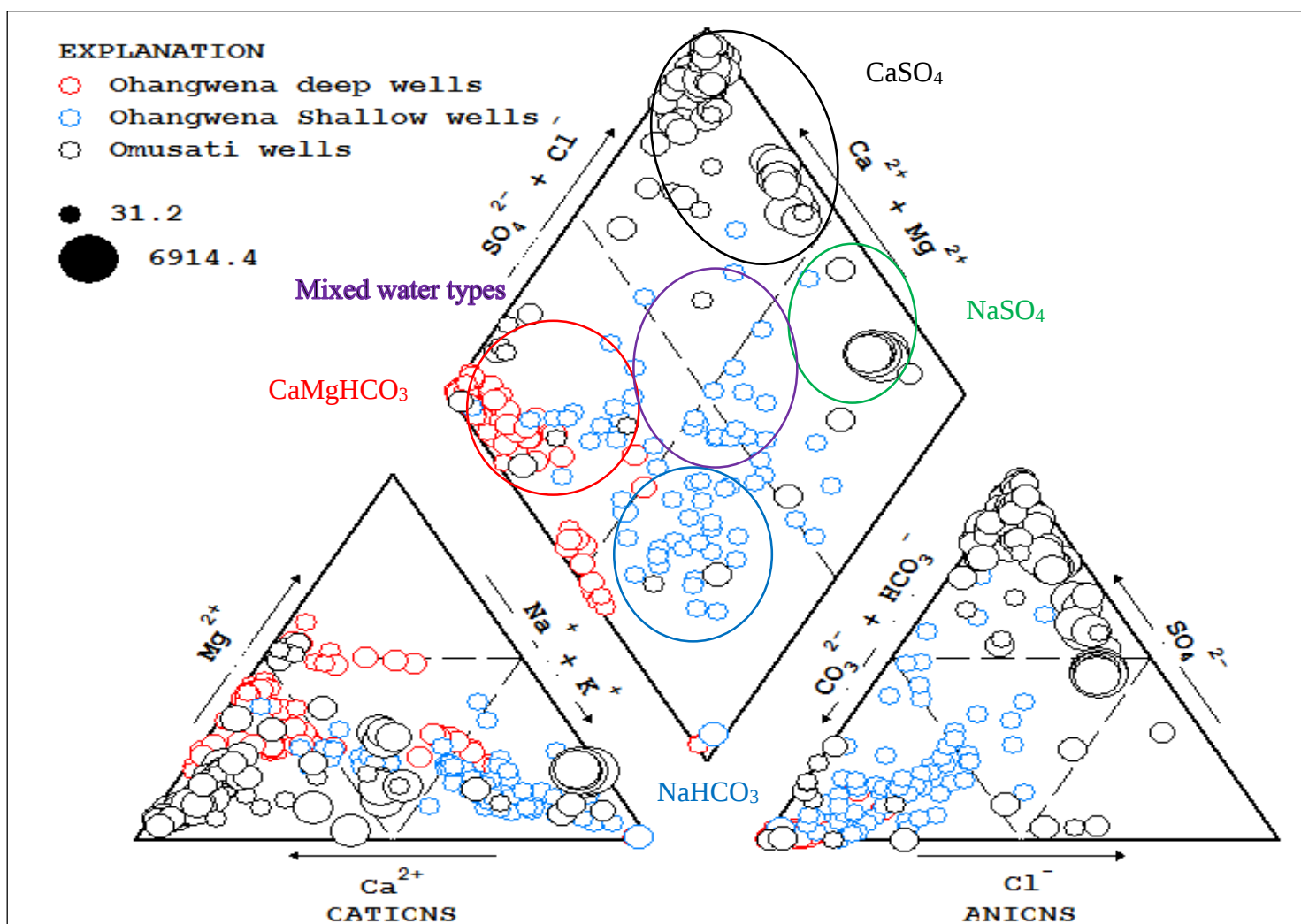


Figure 4-7: Piper diagram showing hydrochemical facies for all samples. The size of the symbol represent the amount of TDS in mg/l

Generally, Ohangwena deep wells show higher values of both nitrate and fluoride as compared to the shallow wells in Ohangwena and Omusati (Fig. 4.9 and 4.10). The ten shallow wells in Ohangwena have no fluoride and nitrate values exceeding the WHO drinking water standards. On the other hand, out of 14 deep hand-dug wells, nine hand-dug wells (64%) and eight hand-dug wells (57%) exceed drinking limit for fluoride and nitrate respectively. In Omusati, eight out of 22 sampled hand-dug wells (36%) exceed fluoride WHO drinking standards, while only one well has an average value exceeding the nitrate WHO drinking guideline value and with average nitrate content of 344 mg/l.

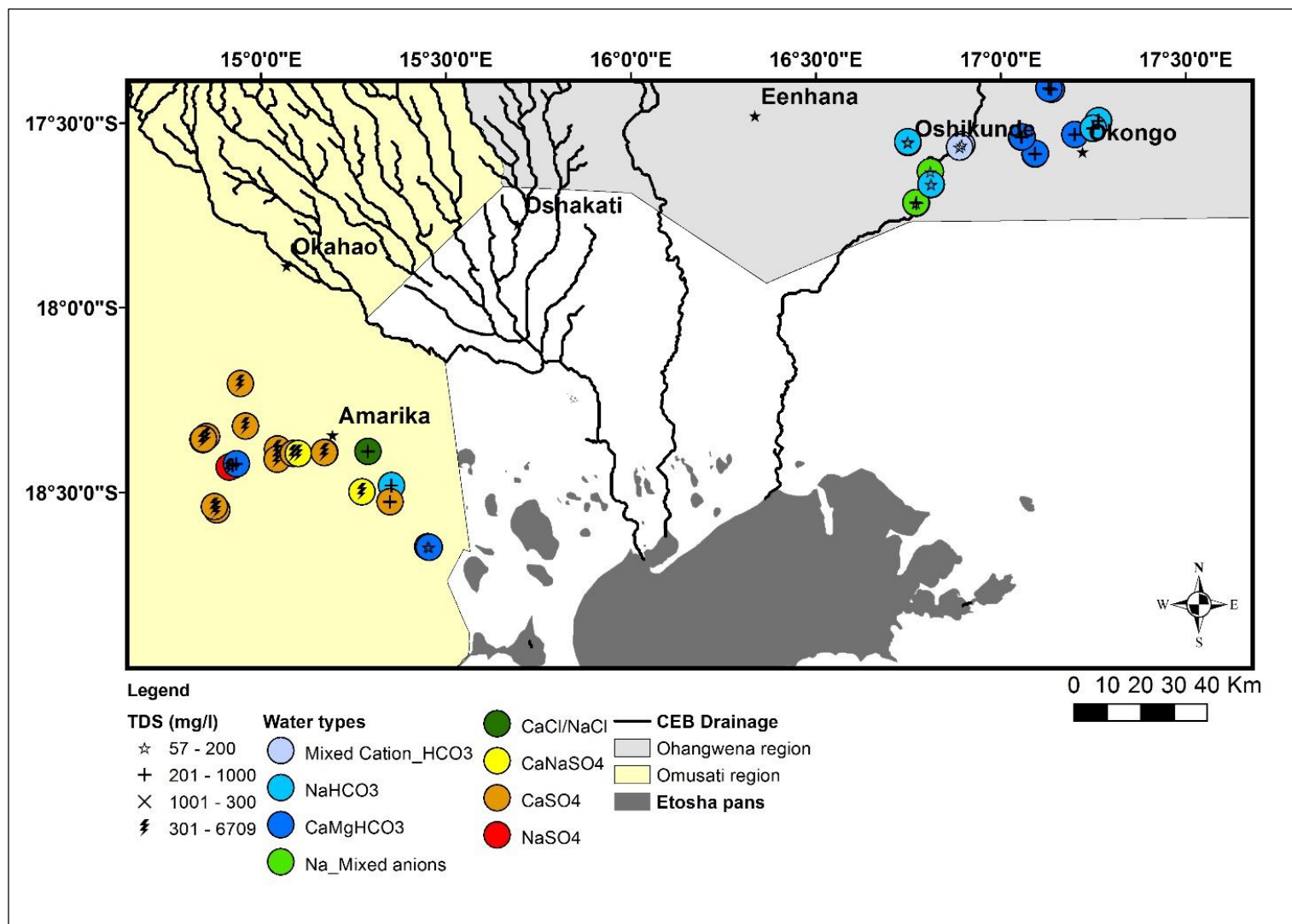


Figure 4-8: Spatial distribution of TDS and water types in the study area. WHO guideline value for TDS is 1000 mg/l therefore all values above that are unacceptable for drinking (WHO, 2008)

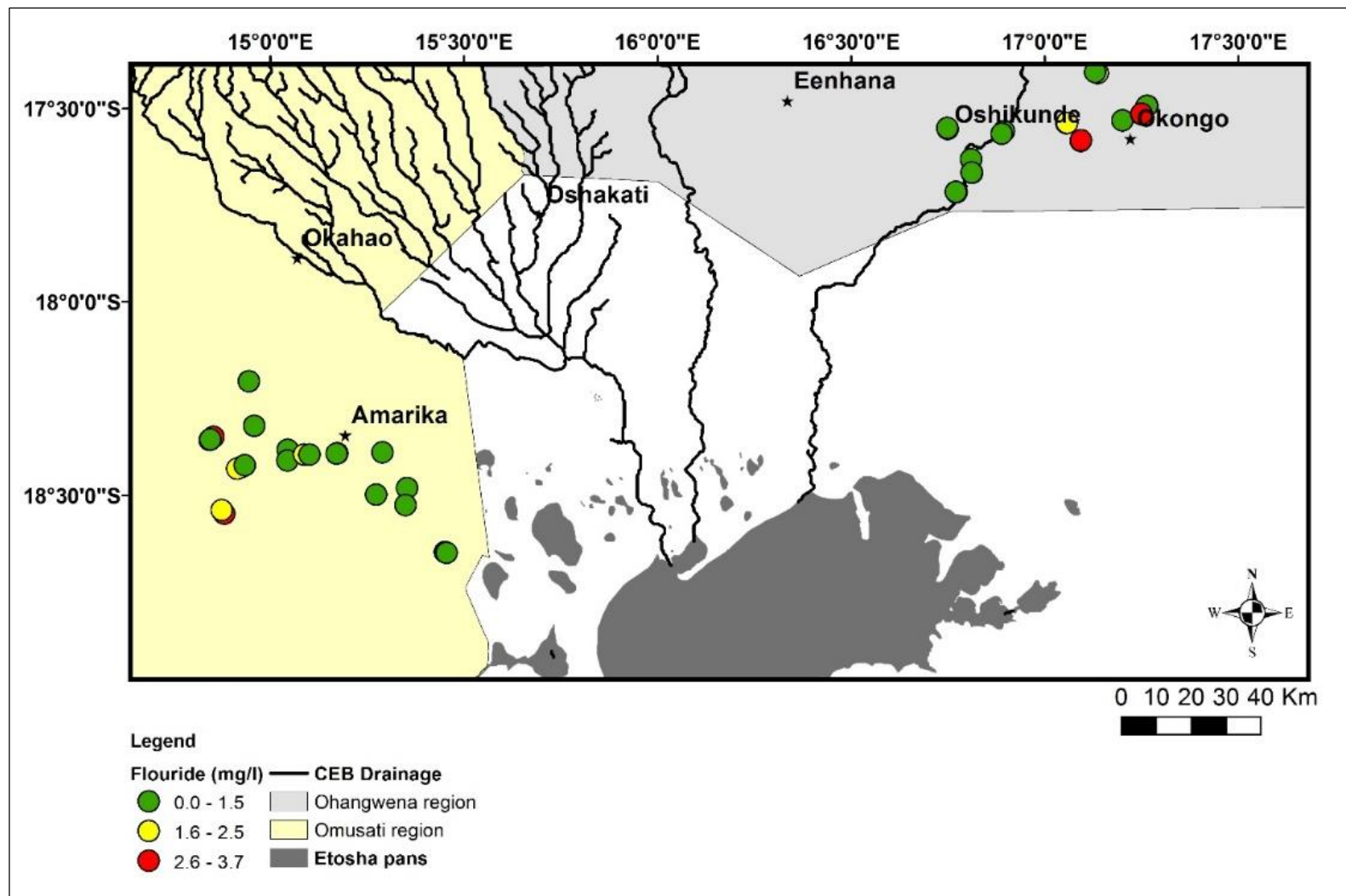


Figure 4-9: Spatial distribution of Fluoride [mg/l] values in the Ohangwena and Omusati regions. WHO guideline value for Fluoride is 1.5 mg/l therefore all values above that are unacceptable for drinking (WHO, 2008)

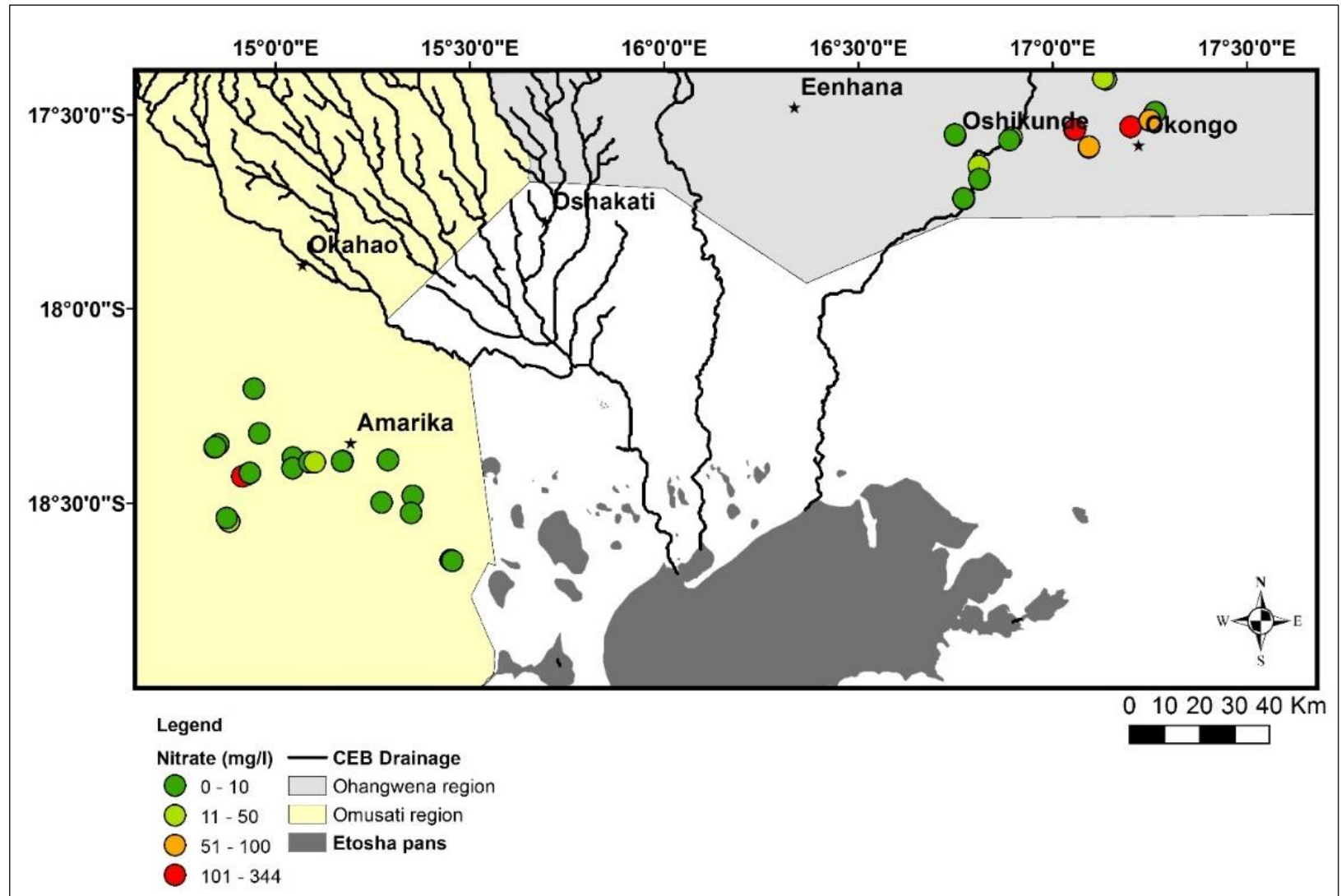


Figure 4-10: Spatial distribution of Nitrate [mg/l] values in the Ohangwena and Omusati regions. WHO guideline value for nitrate is 50 mg/l therefore all values above that are unacceptable for drinking (WHO, 2008)

4.3.1.2 Water stable isotopes ($\delta^{18}\text{O}$ and $\delta^2\text{H}$)

The stable isotope values of all collected samples are plotting close to the Global Meteoric Water Line (GMWL) (Fig. 4.11). The samples from Omusati region cover a wide isotopic range from -7.81 ‰ to 1.32 ‰ for $\delta^{18}\text{O}$ and from -54.77 ‰ to -13.28 ‰ for $\delta^2\text{H}$, while in Ohangwena region there are two distinct groups (Fig. 4.11). One group represents samples from deep wells that are depleted in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values ranging between -9.00 ‰ to -5.82 ‰ and from -61.51 ‰ to -37.18 ‰ for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ respectively; and the second group comprises of samples from shallow wells with isotope values ranging between -6.95 ‰ to 0.86 ‰ for $\delta^{18}\text{O}$ and from -49.14 ‰ to -7.64 ‰ for $\delta^2\text{H}$. The collected water samples have isotopic composition strongly affected by evaporation as indicated by the slopes of the regression lines on which the samples plot. In Ohangwena region, the deep wells plot on regression line with equation $\delta^2\text{H} = 5.2 \delta^{18}\text{O} - 13.80$, while shallow wells plot of regression line with equation $\delta^2\text{H} = 5.0 \delta^{18}\text{O} - 12.78$. The samples from Omusati plot on regression line with equation $\delta^2\text{H} = 5.2 \delta^{18}\text{O} - 10.88$. These lines intersect the LMWL at (-8.7, -58.2), (-7.8, -51.8) and (-8.6, -57.5) for Ohangwena deep wells, Ohangwena shallow wells and Omusati wells, respectively. The intersection of the regression line identifies the mean isotopic composition of the parent/source water. Ohangwena deep wells and Omusati wells both plot on regression line with a slope of 5.2 and the mean isotopic composition plot very close to one another. The spatial distribution of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ shows that the deep wells are more depleted than the shallow wells regardless of the region (Fig. 4.12 and 4.13).

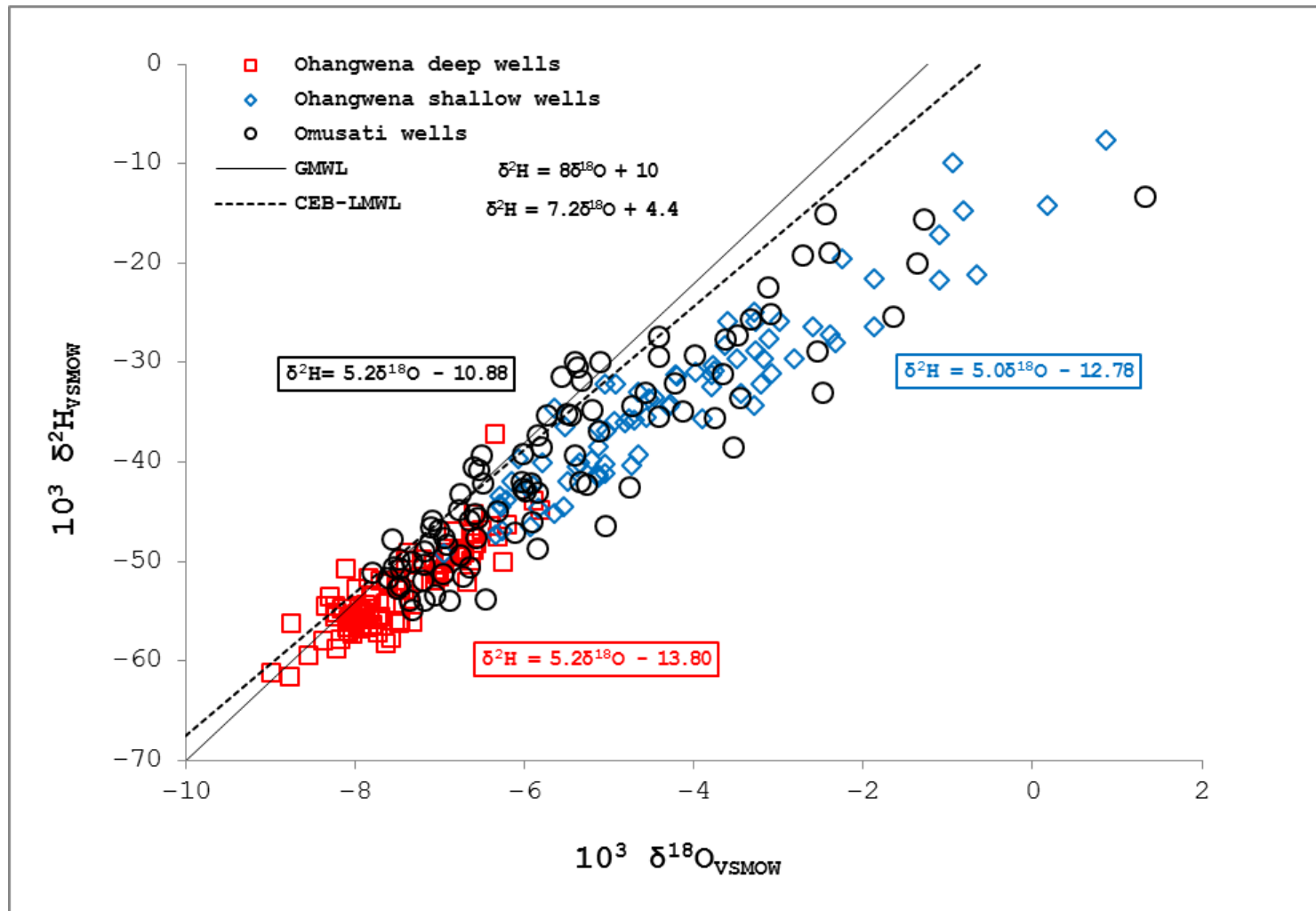


Figure 4-11: $\delta^2\text{H}$ vs. $\delta^{18}\text{O}$ plot of all collected samples including the global meteoric (GMWL) and local meteoric (LMWL) water lines

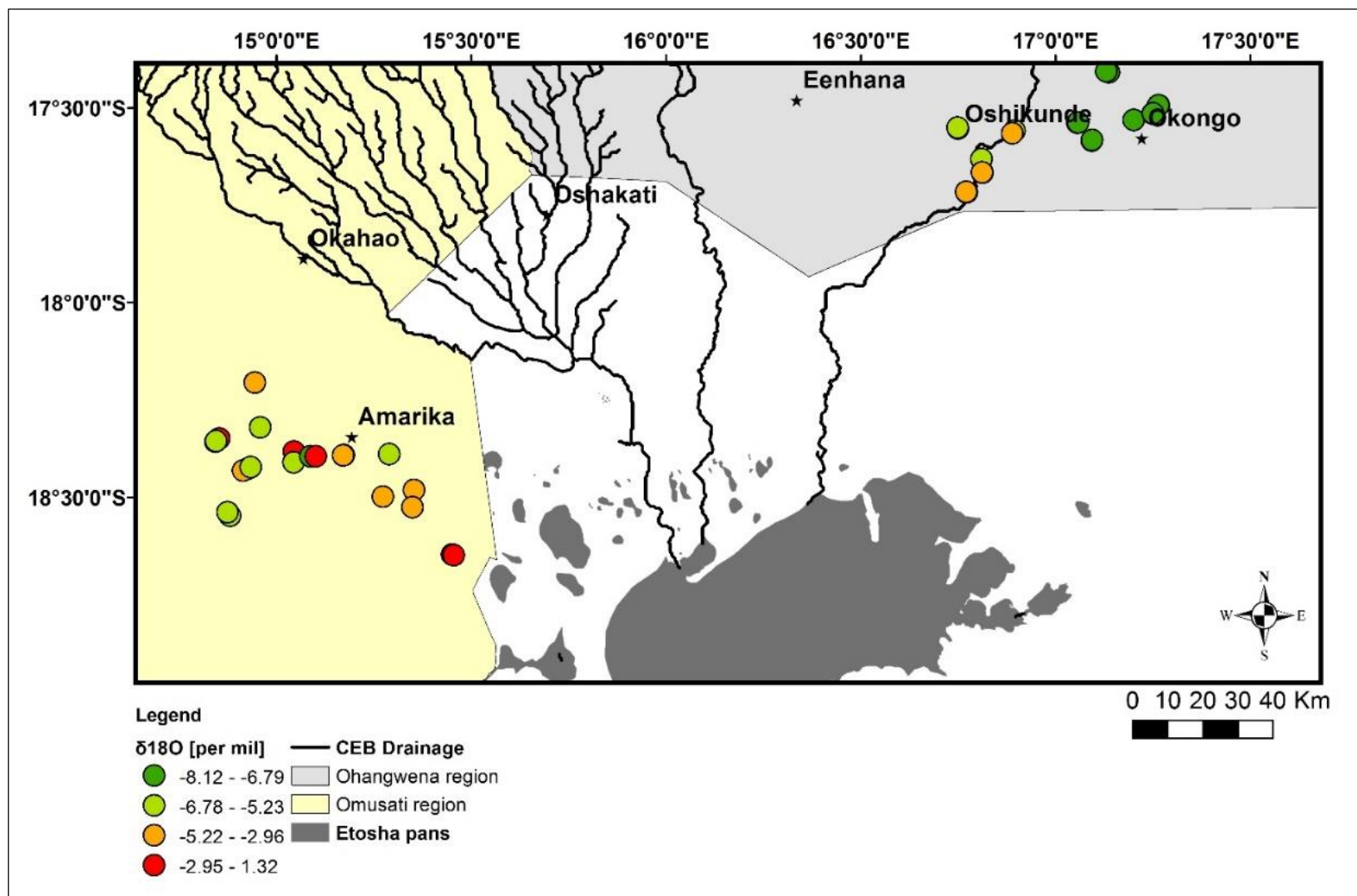


Figure 4-12: Spatial distribution of $\delta^{18}\text{O}$ [per mil] values in the Ohangwena and Omusati regions

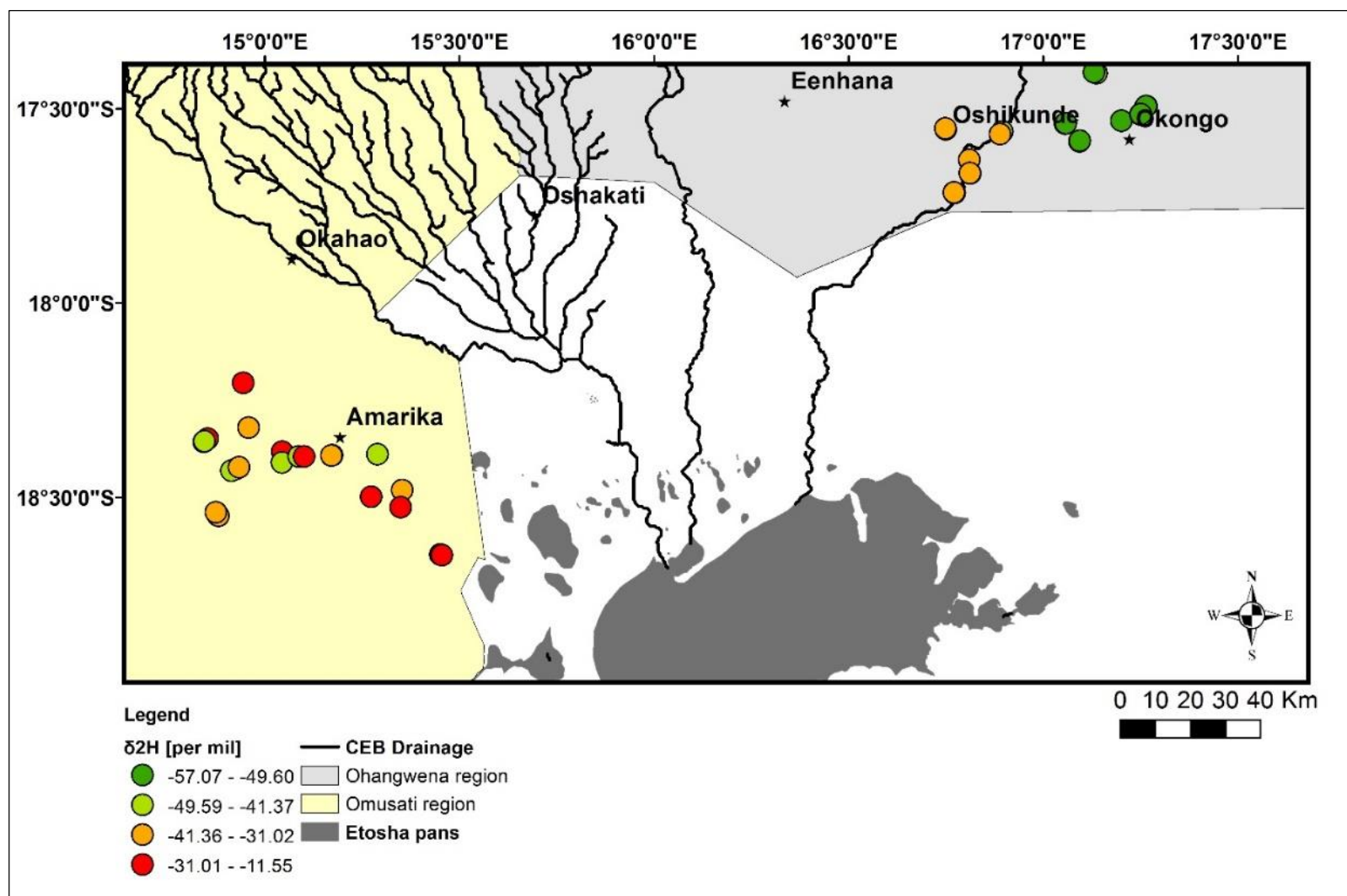


Figure 4-13: Spatial distribution of $\delta^2\text{H}$ [per mil] values in the Ohangwena and Omusati regions

4.3.2 Temporal patterns

4.3.2.1 Water quality and chemistry

Temporal patterns were observed for the different water types, TDS, Cl as well as F and NO_3 for ten hand-dug wells.

Ohangwena deep hand-dug wells

The deep wells in Ohangwena show consistent or very little change in the dominant water type. HCO_3 is dominant in all seasons for all the wells. As for cations, an increase in calcium is observed during the dry season, especially in the year 2014 and 2016 at the Omboloka site, but the overall water type is always CaMgHCO_3 (Fig. 4.14). In Oshana-shiwa, the water type changes from CaMgHCO_3 to NaHCO_3 between different sampling campaigns. The TDS changes slightly between the different years, but appear rather similar for each year. A trend of decreasing chloride and nitrate concentration is observed from March to June in 2015 and 2016, while in 2014 this decrease in chloride happened later, from June to September (Fig. 4.17). So the highest values are recorded at the end of the rain season and they become low in the dry season. High fluoride concentration above the WHO drinking guideline value are observed, however no temporal trend could be established.

Ohangwena shallow hand-dug wells

The shallow wells show a different trend in major ions than that of deep wells (Fig. 4.15). The samples from Epumbalondjaba are plotting in various anion fields, where an increased sulphate content is observed from June to September 2014. On the other hand, at Omulonga it is the cations that are mixed. The overall main water type is the mixed water type, mainly CaMgHCO_3 and

NaHCO₃, but some samples are of the sulphate and chloride water types. The TDS and chloride show a similar trend observed for the deep wells. All shallow hand-dug wells have low fluoride below the WHO drinking guideline value. Nitrate is also low, with one exception at Epumbalondjaba in October 2016 which is above the WHO drinking guideline value. Nitrate and fluoride show similar temporal patterns as those observed in deep wells.

Omusati wells

In Omusati, the dominant cations are constant per well over the whole sampling period. An exception is observed at Olumpelengwa II where cation changes slightly from magnesium to sodium during the dry season. The anions show a slight increase in sulphate content during the dry season at Olumpelengwa II, while the rest of the wells increase in chloride during the dry season (Fig. 4.16). TDS concentrations during the dry season are higher in comparison to the rain season. Nitrate is higher in June as compared to the dry and rain season (Fig. 4.18). Fluoride concentration is generally low in this area and it is almost constant for each well throughout the sampling period.

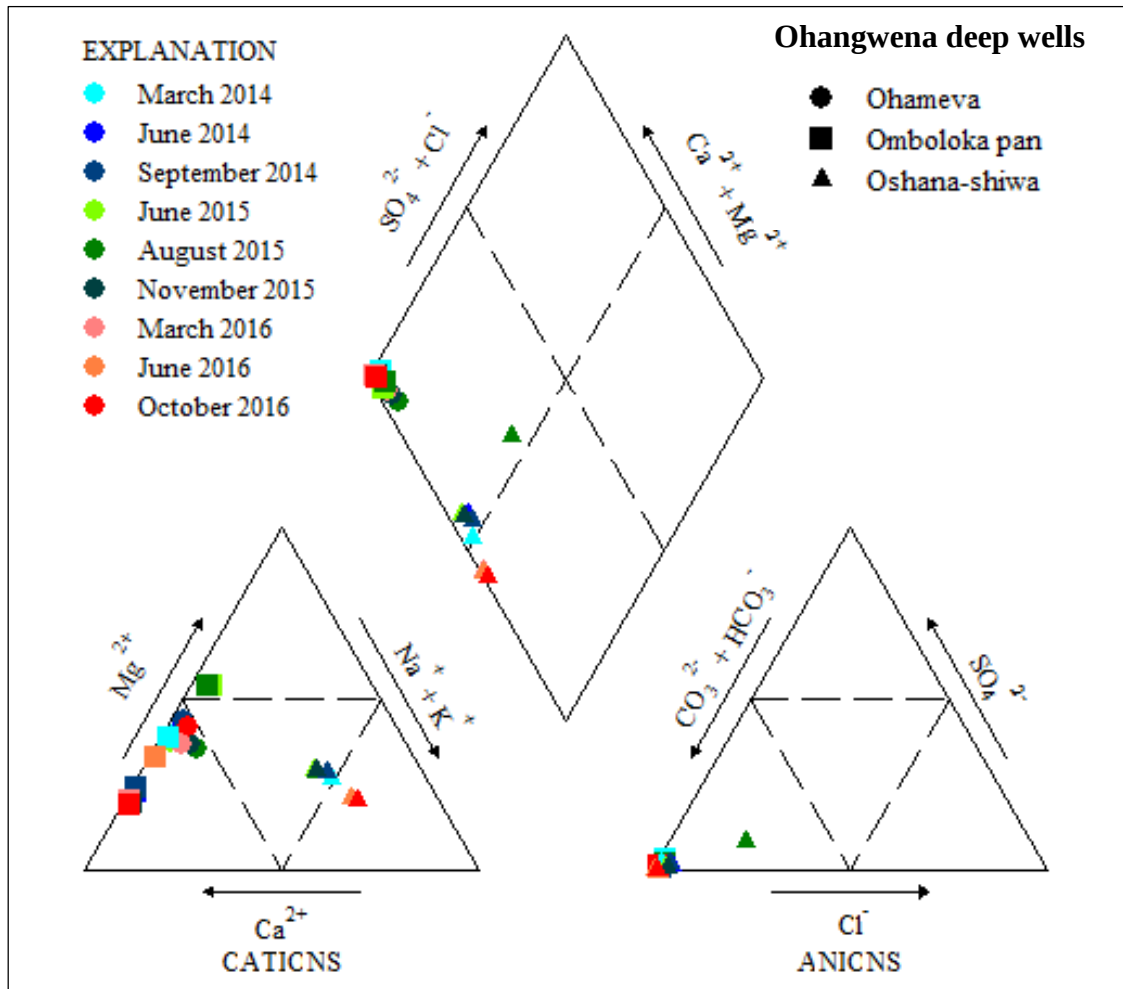


Figure 4-14: Piper diagram show the temporal variation in major ion composition of the Ohangwena deep wells

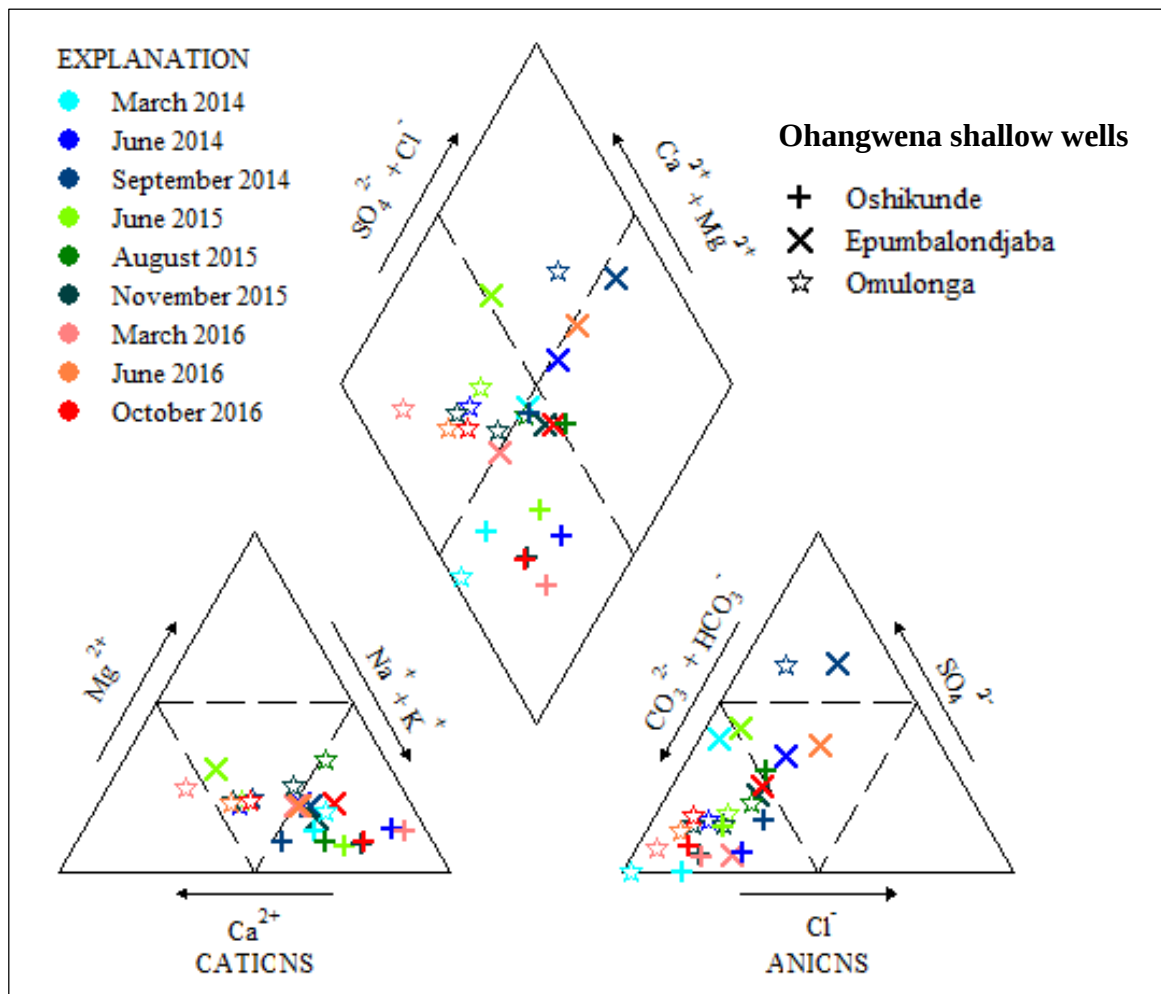


Figure 4-15: Piper diagram show the temporal variation in major ion composition of the Ohangwena shallow wells

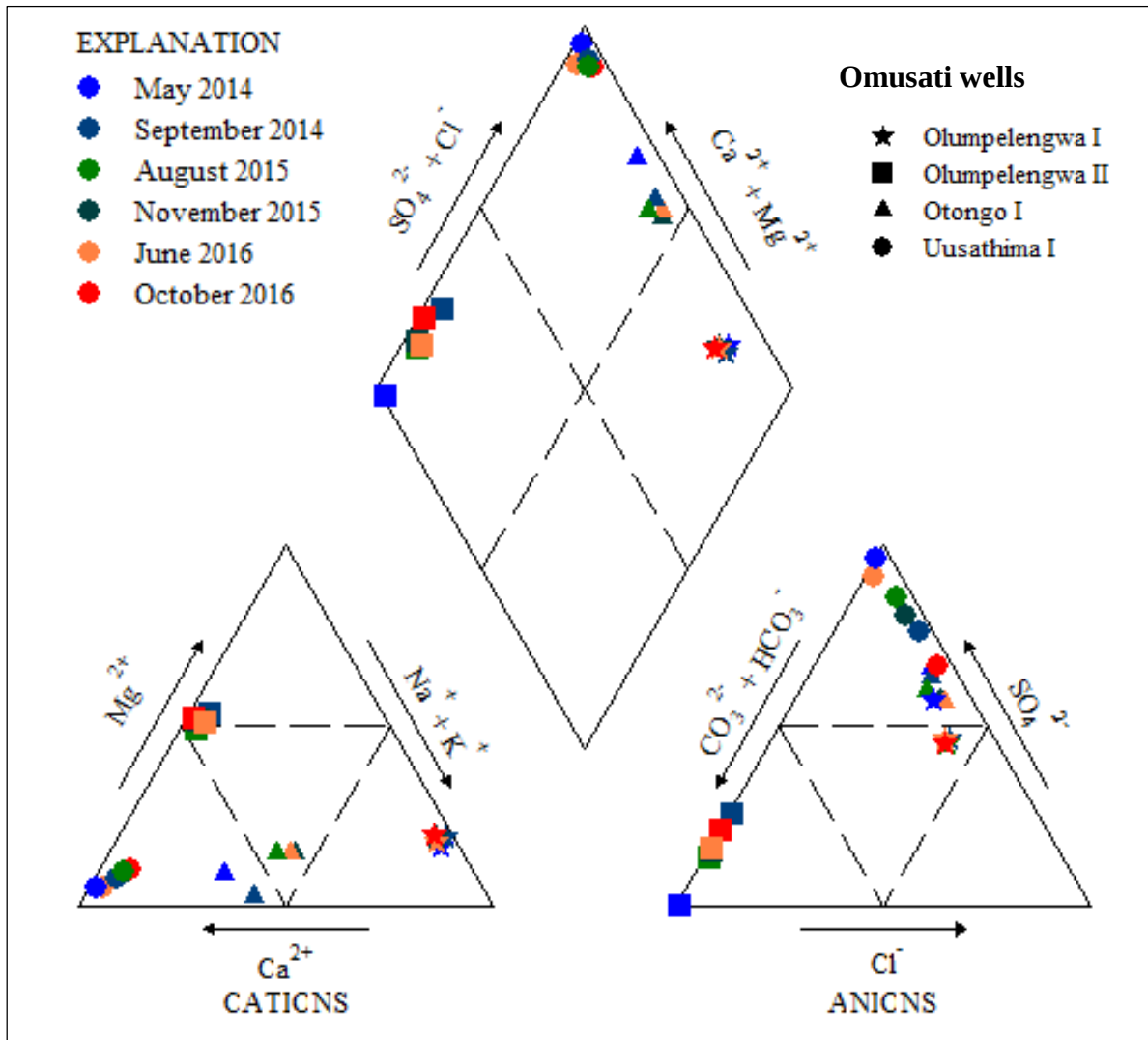


Figure 4-16: Piper diagram show the temporal variation in major ion composition of the Omusati wells

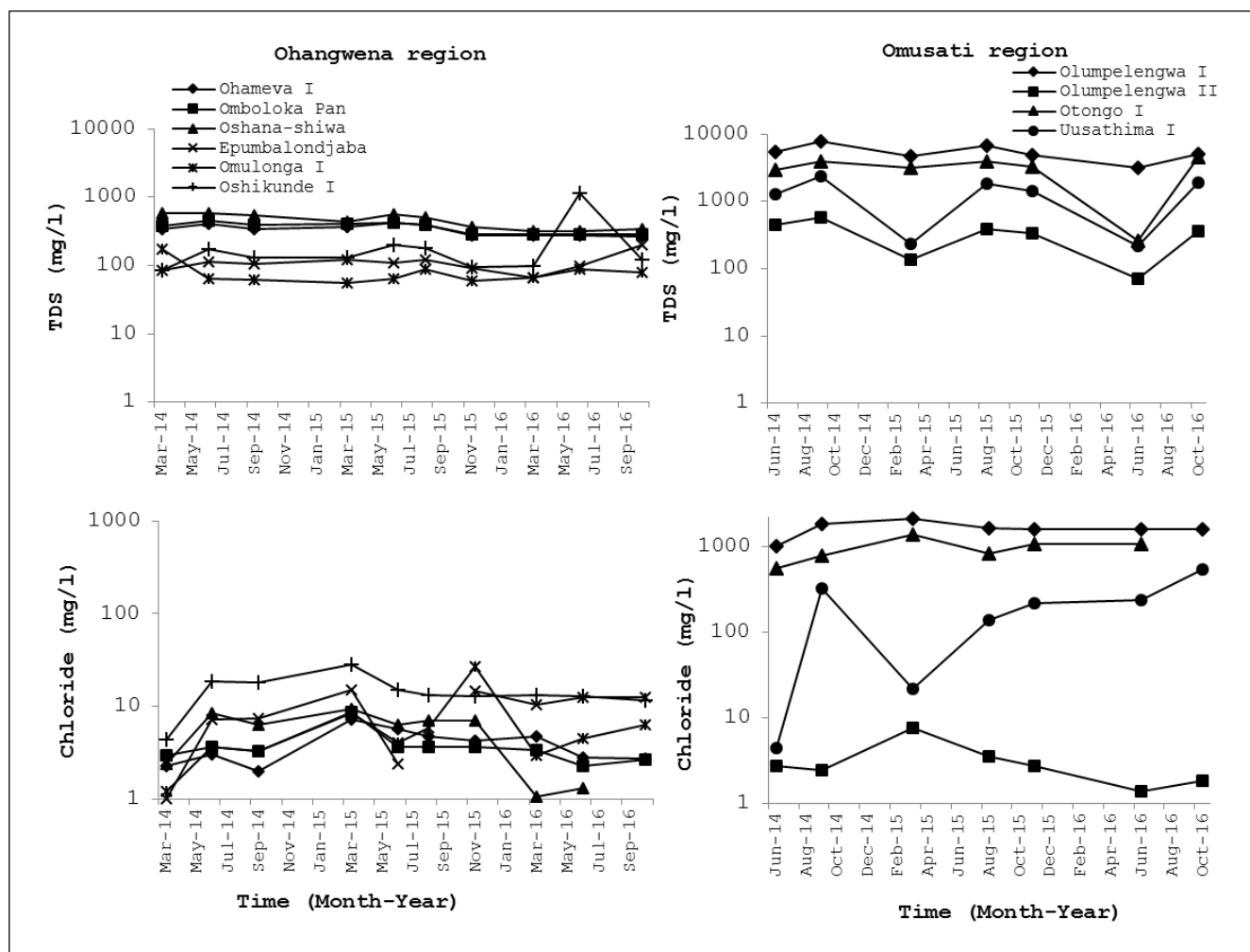


Figure 4-17: Temporal variation of TDS and chloride concentrations of hand-dug wells in Ohangwena and Omusati regions

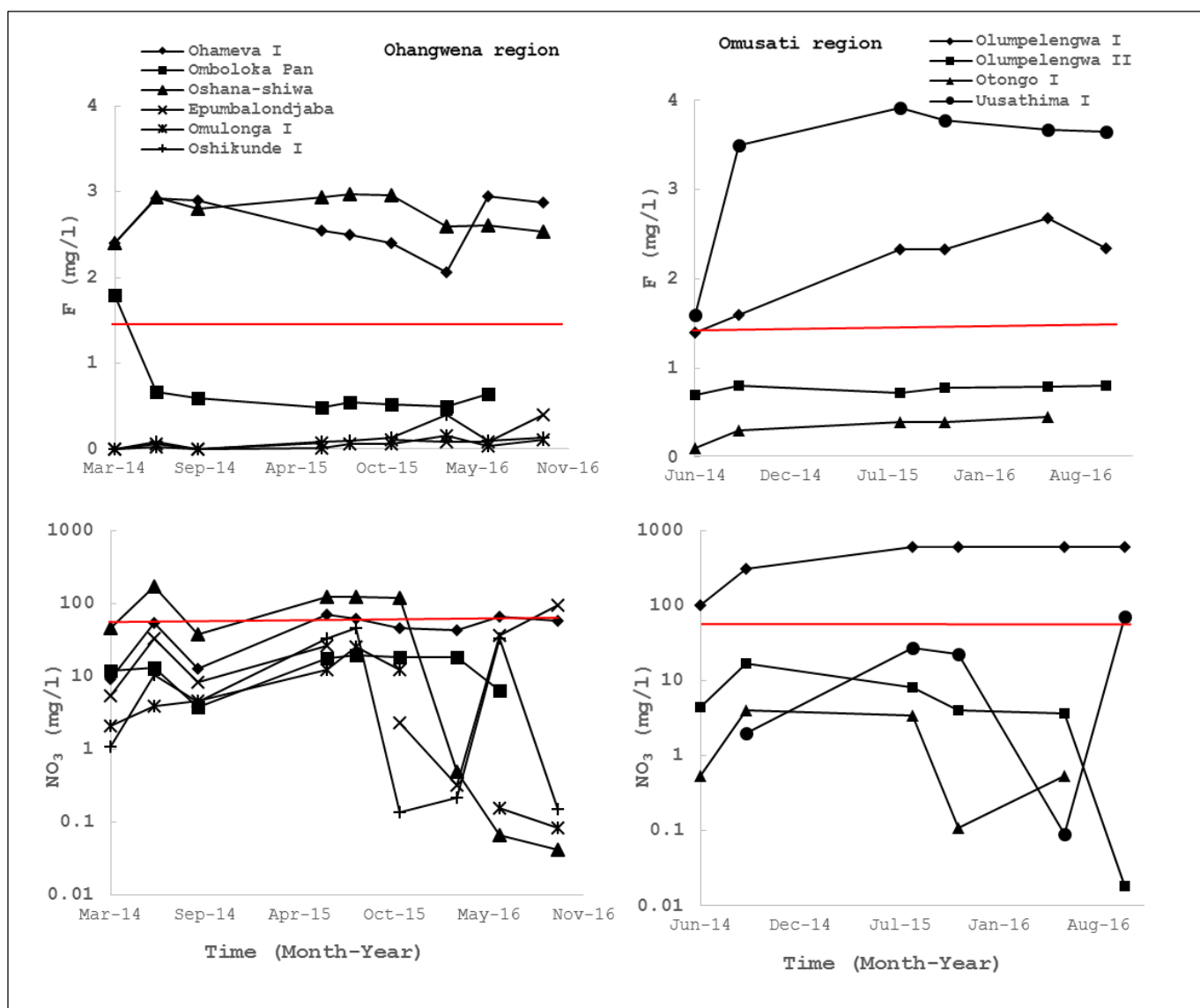


Figure 4-18: Temporal variation of fluoride and nitrate concentrations of hand-dug wells in Ohangwena and Omusati regions. The red line represent the WHO guideline value which is 1.5 mg/l for Fluoride and 50 mg/l for nitrate

4.3.2.2 Water stable isotopes

The relative abundance of stable isotopes ^{18}O and ^2H shows very little changes in the deep wells, while the shallow wells (open funnel-shaped wells) in both regions show large variations between different sampling times. A temporal pattern is observed in Ohangwena, where both deep wells

and shallow wells generally have isotopically more depleted groundwater in June (after the rain season) than the other months, but this trend could not be established for wells in Omusati (Fig. 4.19). The isotope values and chloride follow a similar trend, when chloride drops in the rain season, the isotope values become depleted and during the dry season, groundwater becomes more enriched with heavier isotopes, and the chloride concentration increases.

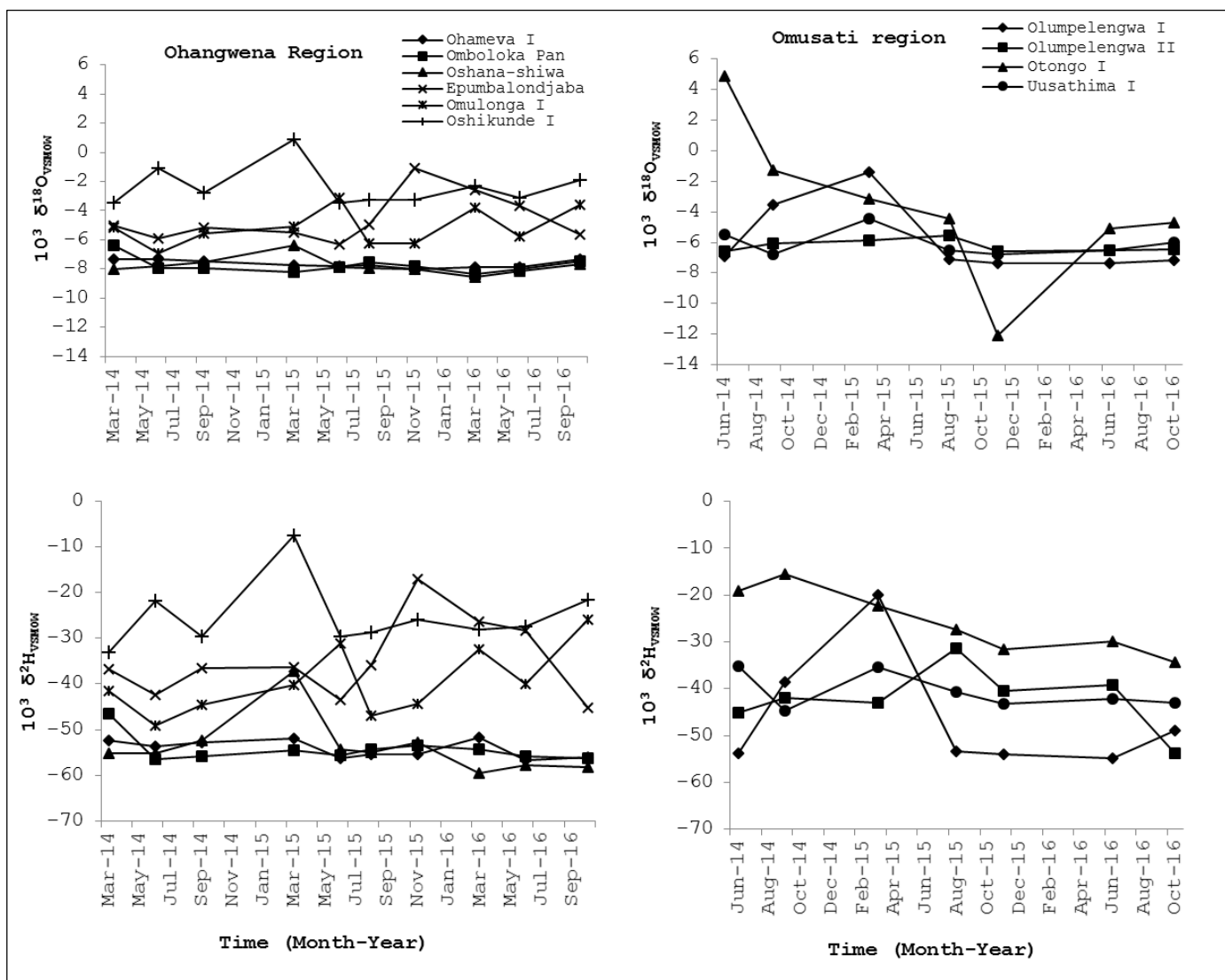


Figure 4-19: Temporal variation of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ concentrations of shallow perched in Ohangwena and Omusati regions

It must be noted here that the hand-dug well at Epumbalondjaba village in Ohangwena region is located in close proximity (approximately 10 m) to an ephemeral river which has standing water. Isotope values for samples taken from the river were always enriched as compared to samples taken from the hand-dug wells sampled at the same time (Fig. 4.20). Furthermore, samples taken during the rainy season (i.e. March 2014 and March 2016) show depleted isotope values as compared to samples taken during the dry season.

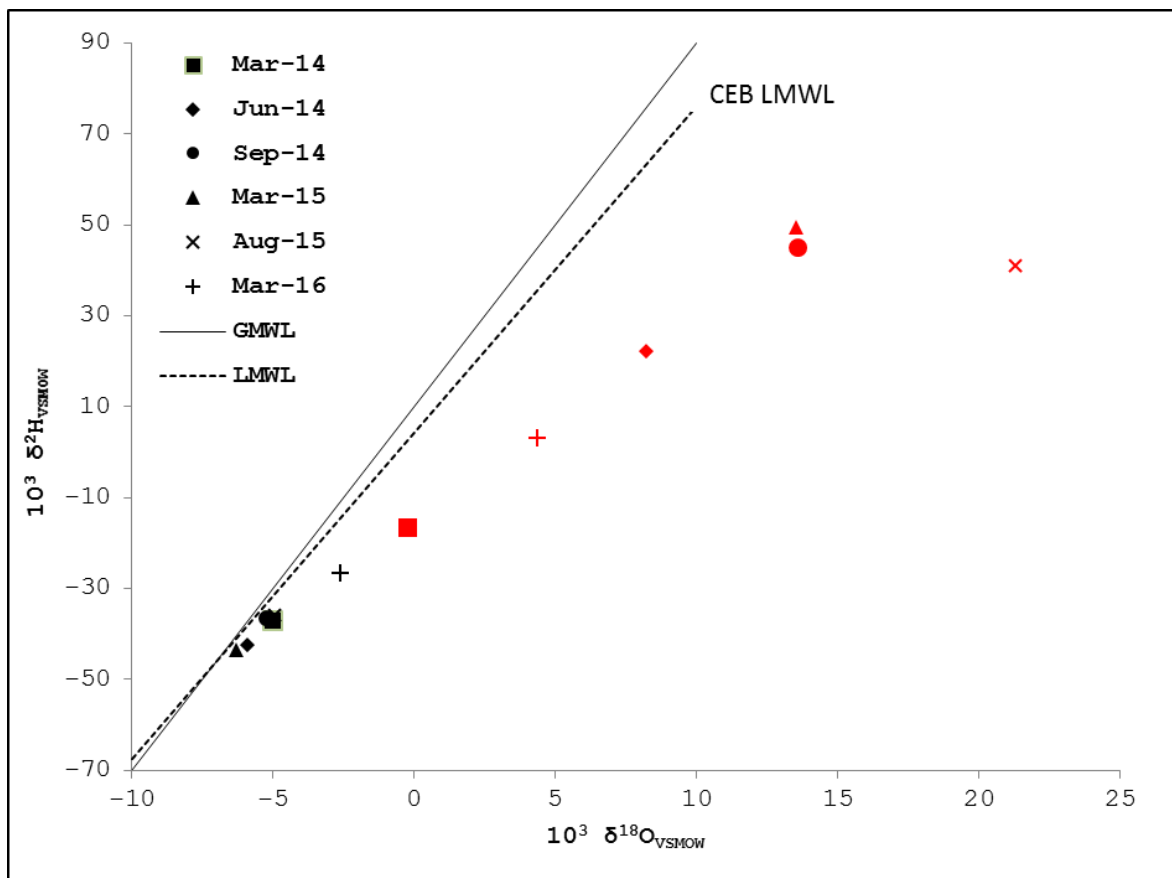


Figure 4-20: $\delta^2\text{H}$ vs. $\delta^{18}\text{O}$ plot of shallow hand-dug well and surface water at Epumbalondjaba. The black colour represent the hand-dug well while the red is the standing surface water in the ephemeral river

4.3.3 Case study of recharge scenario at Uusathima village in Omusati

A recharge scenario was observed at Uusathima village in March 2016. Water was standing in a small pond after a night of heavy rainfall and it was infiltrating into the ground and flowing laterally into the well through cracks and fractures within the calcrete (Fig. 4.21). Samples were taken from the pond, the flowing recharging water, the hand-dug well currently receiving inflow and from another hand dug well with no inflow. For these samples, a clear geochemical evolution process is shown from rain water to the groundwater water type (Fig. 4.21). There is a progressive increase in the sulphate content and dominant water is CaSO_4 (Fig. 4.22). Stable isotopes (Fig. 4.23) show that the flowing water was less depleted, while the recharged well and surface water pond have a similar composition.

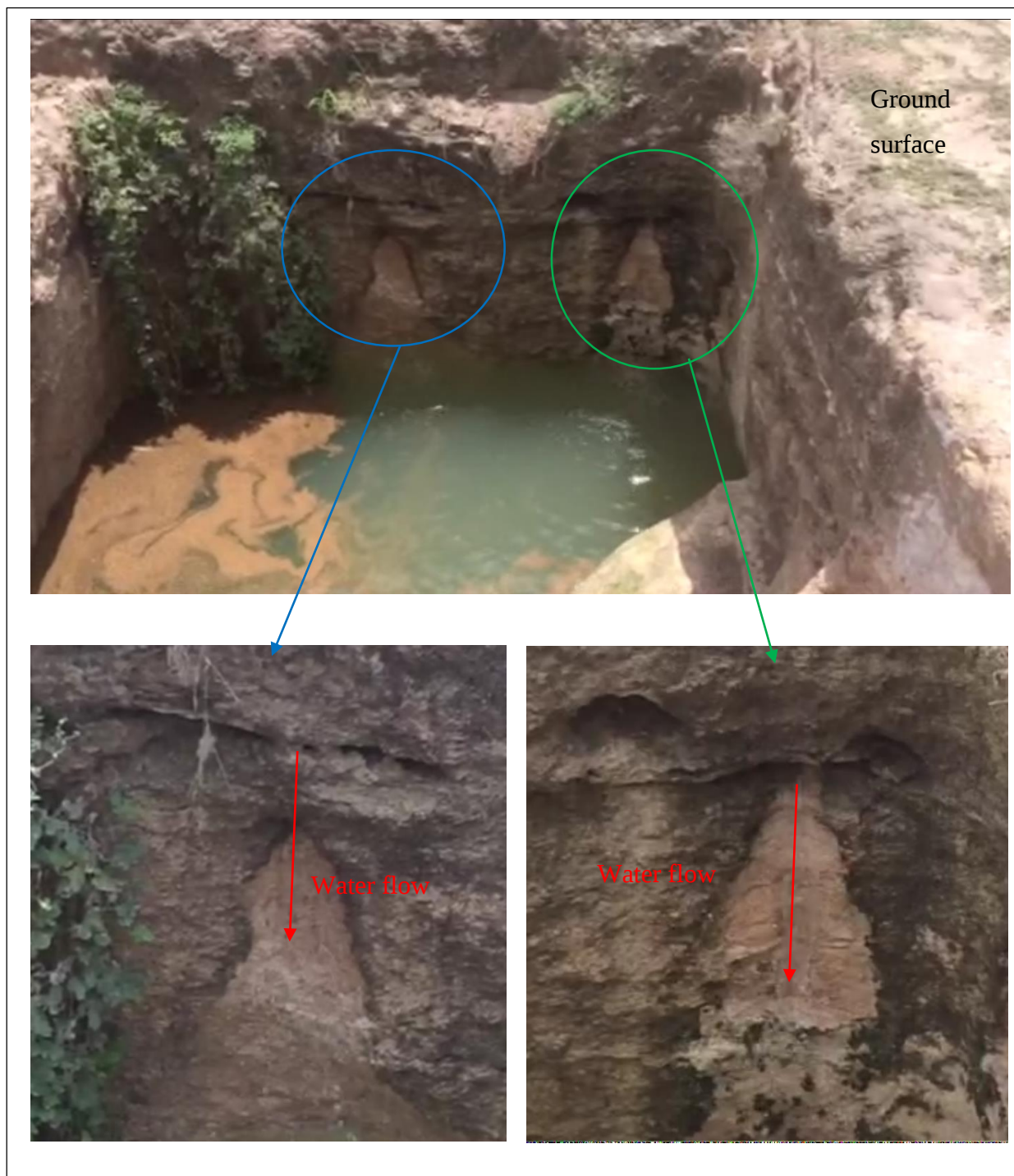


Figure 4-21: Pictures illustrating fresh groundwater inflow after a night of heavy rainy at Uusathima village

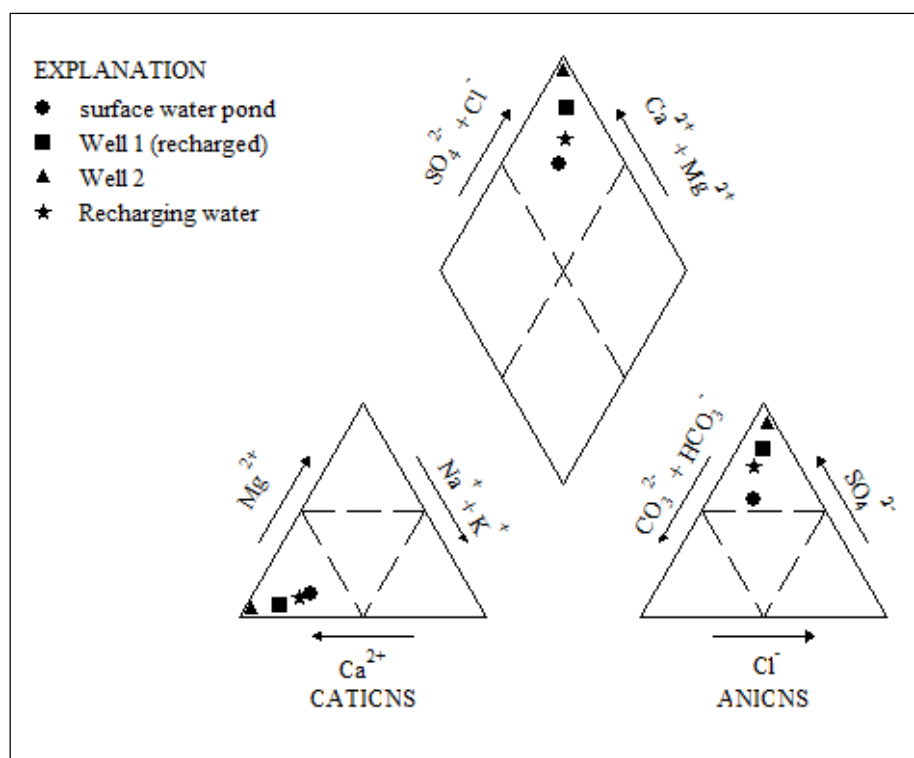


Figure 4-22: Piper diagram of the fresh recharge scenario at Uusathima village in Omusati region

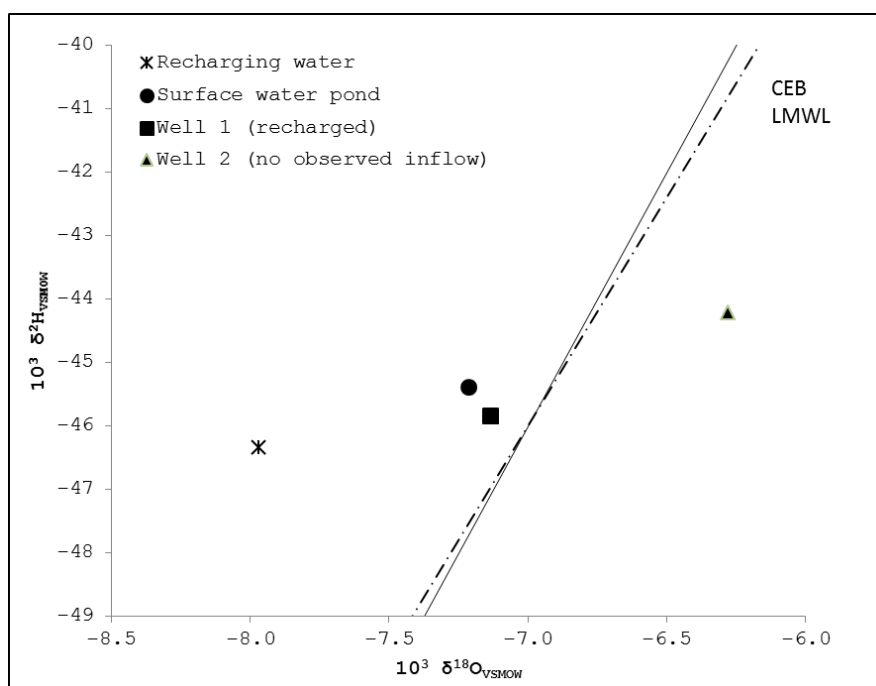


Figure 4-23: $\delta^2\text{H}$ vs. $\delta^{18}\text{O}$ plot of the fresh recharge scenario at Uusathima village in Omusati region

4.4 Discussion

This study reveals a clear distinction between the shallow groundwater in the two regions, Omusati and Ohangwena. This is documented by the TDS values, hydrochemical water types, as well as the isotopic compositions of water. Ohangwena is dominated by HCO_3 water types, while Omusati is dominated by SO_4 water types. TDS is generally higher in Omusati than in Ohangwena. The spatial heterogeneity is controlled mainly by their location in the landscape, depth to the water table, the type of well infrastructure and lithological, climatic and anthropogenic factors.

Ohangwena deep wells are characterized by CaMgHCO_3 and NaHCO_3 water types, while Ohangwena shallow wells are mainly characterized by mixed water type and NaHCO_3 . CaMgHCO_3 type is common in recharge zones and they normally infer fast infiltration through preferential paths or can result from the dissolution of calcite and dolomite when they react with CO_2 -rich water (Freeze & Cherry, 1979). NaHCO_3 water is commonly formed as a result of evaporative concentration of these ions at or near the surface, or by weathering of pedogenic carbonate minerals and sodium rich silicate minerals by action of dissolved CO_2 in the soil zone (Freeze & Cherry, 1979). Mixed water type normally indicates the mixing of two water sources and this implies that the shallow wells have at least two sources and or experience at least two different hydrochemical processes.

Omusati region is dominated by sulphate and chloride water types, mainly CaSO_4 and CaNaSO_4 , with NaSO_4 , CaCl and NaCl occurring locally. These water types typically originate from the dissolution of evaporitic rocks (i.e. gypsum) and they indicate water that has gone through major evaporation before recharge to concentrate the ions. This is typical for flat and poorly drained areas

such as the Omusati region. Thus pans in Omusati can be categorized as discharge areas rather than recharge zone. The scenario observed at Olumpelengwa village, where two wells in close proximity have totally different chemistry, implies that the two wells are tapping from different aquifers. Bittner (2006) indicates that the regional aquifer in Omusati is relatively shallow and it has high salinity. Therefore, it can be assumed that the brackish Olumpelengwa I is tapping from the regional aquifer, while Olumpelengwa II which has freshwater is tapping the perched aquifer. Therefore, it can be inferred that differences in water chemistry are influenced mainly by their location in the landscape, depth to water table as well as aquifer material.

Since the collected samples are plotting close to the LMWL and within the range of modern local precipitation, this implies that these aquifers in both regions were recharged under climatic conditions similar to modern climate. The groundwater originated from local rainfall and the variation in the isotopic compositions may be a result of natural variations in the regional and local climate, depth to water table as well as the type of well infrastructure. The water in the deep wells in the Ohangwena and Omusati wells have a slightly more depleted source water (-8.7, -58.2 and -8.6, -57.5 respectively). This could indicate that recharge to the aquifers which these wells are tapping from is limited to larger amount events, while for the shallow wells also small amount events are contributing as the mean parent water source is slightly enriched (-7.8, -51.8). In addition, the deep wells are plotting closer to the LMLW; this indicates that the component from recharge without significant evaporation is larger than for the shallow wells. This means that for deep wells, recharge through preferential flow paths is dominant, while for the shallow wells (experiencing more evaporation), infiltration through the matrix plays a major role. Samples from the open funnel-shaped hand-dug wells are enriched in $\delta^{18}\text{O}$ and $\delta^2\text{H}$, irrespective of their latitude

or longitude, and they are strongly affected by evaporation due to exposure to the atmosphere. Bittner (2006) highlights that high evaporation rates in the CEB cause the drying up of pans and ephemeral rivers, resulting in the precipitation of salt and increased salinity of the shallow aquifers, in particular in waterlogged areas and areas comprising a low permeable lithology. In Ohangwena, the type of well changes spatially and this influences the isotopic compositions. The depth to water table and the type of well infrastructure abstracting water from those aquifers influences the dominant processes that control that aquifer. Shallow wells are exposed to the atmosphere and this intensify evaporation while deep wells are less affected by evaporation.

The deep wells are commonly found in the pans and depressions, and it is commonly discussed (e.g. de Vries et al., 2000) that these areas are recharge zones in the Kalahari. Focused, indirect, or localized recharge is the dominant process in these kinds of areas, according to Scanlon (2006), where by water infiltrates through cracks and fractures. These cracks and fractures are seen in Figure 4.21 and thus fast infiltration can be confirmed as a major recharge process for this area. The shallow wells are all located in the ephemeral river. Lindenmaier (2014) showed that the water is flowing in the subsurface of this ephemeral river, with recharge occurring in the Angolan highlands. Therefore, the water in these shallow wells is a mixture of subsurface flow and the water that is infiltrating from local rainfall. The NaHCO_3 water type in the shallow wells could also indicate evaporative concentration of these ions at or near the surface. This argument is in agreement with the isotopic signatures which show that evaporation is a dominant process in these wells.

Temporal variations within each region are different for both regions. In Ohangwena, temporal patterns were mainly observed in chloride, nitrate and isotopes. The decrease in chloride content

and depletion of isotopes values during the rainy season indicate recharge events and visibly occur at different times depending on the rainfall. It is interesting to notice that the recharge events occur in the same period even though the aquifers have different depths to water table. If one assumes that they are recharged by the same rainfall events and same mechanisms, it would be expected that recharge will be delayed for the deep wells because of the depth the water has to percolate to reach the aquifer in comparison to the shallow wells. Therefore, this accounts for the results that the shallow wells and deep wells in Ohangwena are recharged through different mechanisms, whereby the deep wells are recharged through fast preferential paths and shallow wells by diffuse recharge. In Omusati, variations in chloride and isotope ratios are observed but they are not following a particular pattern; however TDS increases during dry season. This indicates dissolution of evaporites and evaporation as the dominant process that influences the change. It should be noted that in both regions, the sampled wells are used for water abstraction, but there are no estimations of how much is extracted and thus this could have an impact on accounting for temporal variations.

Stadler et al. (2008) discussed four different possible sources of nitrate in the semi-arid Kalahari in Botswana (which is a similar environment to this study site), which are “(i) surficial input by nitrogen through precipitation and/or anthropogenic activities. Nitrogen from this source may enter the groundwater directly through preferential pathways, or it may contribute to the soil N pool. (ii) Nitrogen leaching from the unsaturated zone. This may include remobilized N from several individual sources such as the fixation of atmospheric N in plants, bacterial fixation, or N from soil, which here are only assessed as total N contribution from the unsaturated zone to the groundwater, (iii) nitrate from aquifer material and (iv) groundwater-immanent nitrate input from

other aquifers that may be hydraulically connected to the investigated aquifer” (Stadler et al., 2008). Wanke et al. (2014) determined the source for nitrate in Erongo region in Namibia with a similar hydrogeological setting to be from manure. These hand-dug wells are located in areas where agricultural activities such as livestock farming are common; therefore, high nitrate is likely to have resulted from manure. High nitrate content are very local as even wells within the same well-field, meaning located a few meters from one another can have very different nitrate content.

Fluoride is also an element of concern and it notably increases with depth. Globally, high fluoride contents in groundwater are normally of geogenic source (Banerjee, 2015). They are associated with fluoride-rich minerals which are commonly found in granites and volcanic rocks or unconsolidated sedimentary aquifers. Strong cyclic evaporation that is experienced in shallow aquifers in semi-arid areas also increases fluoride concentration. Banerjee (2015) discussed in detail the groundwater fluoride contamination. Wanke et al. (2017) concluded that fluoride in Namibia is mainly because of the aquifer material together with climatic and hydrogeological factors. Groundwater in the study area is hosted in unconsolidated to semi-consolidated sedimentary aquifers and it experiences evaporation, thus it can be concluded that the observed high fluoride content is derived from the geogenic sources.

4.5 Conclusions

In the present study, an attempt was made to understand the spatial and temporal variations of major ions and water stable isotope signatures (^{18}O and ^2H), to determine the predominant processes that contribute to groundwater recharge and the evolution of hydrochemistry of hand-dug wells in the CEB. A distinct spatial difference was noted between samples from Omusati and

Ohangwena regions. The spatial heterogeneity as shown by the TDS, hydrochemical water types, chloride, nitrate and fluoride, can be attributed to lithological, climatic and anthropogenic factors. The combination isotope and hydrochemical data provided information on recharge sources and the mechanisms for recharge. Deep wells are recharged by fast infiltration through preferential flow paths during large events, with mean isotopic compositions of -8.7 and -58.2 for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ respectively. The mean parent isotopic composition for shallow wells is -7.8 for $\delta^{18}\text{O}$ and -51.8 for $\delta^2\text{H}$, which is slightly enriched as compared to that of the deep wells. For the Omusati wells, the mean parent isotopic composition is similar to that of the deep wells (-8.6, -57.5) but it was also established that hand-dug wells in Omusati are tapping from both the perched aquifer and the regional aquifer, and it is sometimes difficult to determine from which aquifer each well is tapping as the regional aquifer has a relatively shallow water table. The hydrochemical water type implies that pans in Ohangwena are recharge zones, while in Omusati they are discharge zones. However, the areas with potential high recharge also show high concentrations of nitrate and fluoride above permissible drinking values, which is less of a problem in the discharge area. The discharge areas (Omusati) have a rather high concentration of sulphate and chloride that results in very high TDS amounts.

This study is the first of its kind to look at spatial and temporal patterns in hand-dug wells at a very local scale in Namibia and thus the results have important implications for future research. The data generated here can be used in other areas or it can be used as a baseline and guidance for future research. There are no piezometers and boreholes in these perched aquifers so far and thus the water level fluctuation data is missing. Therefore it is recommended to establish monitoring stations for both water levels and the quality. Currently the abstraction rate from these aquifers is

not known and this threatens water security as it is not known if the current abstraction is done safely. Furthermore, nitrate contamination is associated with anthropogenic sources (manure) and therefore proper planning of better infrastructure and protection zones will be required to avoid pollution in the future.

4.6 Acknowledgement

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5 Interaction of perched and regional aquifers in semi-arid environments: an example from the Cuvelai-Etосha Basin, Namibia

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5.1 Abstract

The influence of perched aquifers as a determinant of groundwater recharge at a regional scale remains poorly known, especially in southern Africa where scarcity of data still limits our understanding of recharge and groundwater flow more generally. This hinders effective groundwater management. Thus the objective of this study is to understand the interaction between perched aquifer KOH-0 and the regional Ohangwena 1 aquifer KOH-1, including the development of a conceptual and geochemical models for recharge mechanisms and geochemical processes in the (CEB) and quantify recharge rates. Groundwater samples were collected and analyzed for major ions and stable isotopes ($\delta^{18}\text{O}$ and $\delta^2\text{H}$). The conceptual model suggests that groundwater originates from precipitation that undergoes strong evaporation, carbonate dissolution and alkali enrichment as a result of silicate weathering and cation exchange during percolation through both unsaturated and the saturated zones. Both hydrochemical and isotopic signatures point toward preferential flow paths and diffuse infiltration through the soil matrix as main recharge mechanisms for pans/depressions and ephemeral river respectively. Mean groundwater recharge rates calculated with chloride mass balance method vary from 7.9% to 17.8% and from 7.3% to 25.5% for perched aquifers in the ephemeral rivers and pans/depressions, while for the regional aquifer it ranges from 5.5% to 19.4% and 5.1% to 32.4% respectively. The most outstanding

difference between the two hydrotopes is that in the pans/depressions the groundwater in both aquifers from the same location have similar hydrochemical and isotopic compositions whereas in the ephemeral river, the genesis of the water in the two aquifer is different. Overlapping hydrochemistry and isotopic compositions suggest mixing of the aquifers/ groundwater of a common origin for aquifers in pans/depressions while no relation was established for the ephemeral river hydrotape. Thus, it is recommended that special care must be taken to avoid contaminating the shallow perched aquifer because these contaminants could potentially contaminate the regional aquifer.

5.2 Introduction

It is expected that by 2025, 1.8 billion people will be living in countries with absolute water scarcity and two-thirds of the world population could be under water stress conditions (UN-Water, 2017). In semi-arid regions, most communities depend on groundwater for their drinking water. Groundwater resources are already facing challenges of over-exploitation and contamination, which are expected to be exacerbated by environmental change and increase in population. In order to develop effective strategies to reduce the pressure on the hydrologic systems, there is an urgent need to improve the understanding of existing groundwater resources in terms of aquifer distributions and interactions, as well as processes that control the groundwater dynamics, recharge and chemistry.

There have been several studies on inter-aquifer interactions (Cartwright et al., 2012, 2010; Mondal et al., 2010; Weitz and Demlie, 2013), focusing mainly on water fluxes and cross-contamination. There appears to be very few investigations on the influence of perched aquifers

on deeper aquifers. A perched aquifer is defined as an isolated and unconfined water body that occurs above the regional water table and this is typically controlled by stratigraphy or structures (Fetter, 1994; Freeze and Cherry, 1979). They are most-easily distinguished in environments where the regional water table is deep. As a result of their shallow depth they are vulnerable to contamination as well as changes in both land use and climatic conditions.

It is hypothesized that perched aquifers are highly important for groundwater recharge processes, as they prevent infiltrating meteoric water from percolating to deeper depths, outside the influence of evapotranspiration. These aquifers channel subsurface water to flow quasi-horizontally. Yet the influence of perched aquifers as a determinant of groundwater recharge at a regional scale remains poorly known, especially in southern Africa where scarcity of data still limits our understanding of recharge and groundwater flow more generally. Moreover, the episodic nature of recharge caused by extreme events like flooding makes reliable recharge estimates difficult (Scanlon et al., 2006). Episodic recharge events are expected to be relatively important in areas underlain by perched aquifers, for the same strata that prevent the vertical percolation of soil water are likely to impede the infiltration of surface water.

Hydrogeochemistry and isotope geochemistry have been used in all parts of the world to understand groundwater recharge mechanisms and aquifer interactions. The low recharge rates of arid and semi-arid regions are difficult to quantify (Allison and Hughes, 1983; De Vries et al., 2000; Skrzypek et al., 2015; Stadler et al., 2010). Allison et al. (1994) Stadler et al. (2010) and Lapworth et al. (2013) discussed the advantages of using hydrogeochemical and isotopic methods over physical methods (e.g. lysimeters) in semi-arid regions. Hydrogeochemical and isotopic methods are specifically important for semi-arid remote areas where other hydrological data is

scarce. Moreover, they provide significant information on groundwater recharge patterns on both local and regional scales. For example Kpegli et al. (2015) demonstrated that geochemical processes are influenced by recent recharge and mixing of aquifers using stable isotopes in the Kandi Basin of Benin. In Mexico, Ledesma-Ruiz and Mahlkecht (2017) used major ions to show that water-rock interaction and cation exchange are the main processes that modify the groundwater chemistry using major ions in Tecate. Liu et al. (2015) used hydrochemistry and stable isotopes in the Subei Lake Basin, China to identify the origin and geochemical evolution of groundwater and concluded that dissolution of carbonate minerals is the main geochemical process. Vanderzalm et al. (2011) showed that the alluvial basins in arid central Australia have multiple recharge sources that varied spatially with proximity of the recharge source.

The objective of this study is to understand the interaction between perched aquifer KOH-0 and the regional Ohangwena 1 aquifer KOH-1, including the development of a conceptual and geochemical models for recharge mechanisms and geochemical processes in the (CEB) and quantify recharge rates. Recharge processes were assessed using natural hydrochemical and isotope tracer data, and hydrochemical processes relevant to recharge mechanisms will be discussed in this article as well.

5.3 Study site

The study was carried out in the CEB, which is the Namibian part of the Cuvelai catchment (Fig. 5.1). The Cuvelai catchment is a large, trans boundary sedimentary basin extending from Southern Angolan highlands into northern and central Namibia, covering about 165 000 km² (Lindenmaier et al., 2014; Mendelsohn et al., 2013). The majority of inhabitants in the basin live in rural areas

and use groundwater by means of hand-dug wells and boreholes that tap both shallow and deep aquifers. The study area is located in the Okongo constituency, where people mainly use hand-dug wells tapping from perched aquifers of moderate potential thickness. The CEB is topographically flat, with elevation ranging between 1092 and 1110 metres above sea level (m a.s.l.) and has no perennial rivers. It is characterized both by a thick unsaturated zone composed of Kalahari sands and extreme climatic conditions, i.e. low rainfall but high evapotranspiration. The hydrogeological setting studied is representative for many semi-arid regions elsewhere, including other parts of Africa, Australia and the western United States. Typical semi-arid climatic conditions characterise the study area, with precipitation between 450 – 500 mm during an annual rainy season from October to April while potential evapotranspiration is in the range of 2000 - 3000 mm/a which is more than four times the annual precipitation (Mendelsohn et al., 2013).

The geological setting of the Cuvelai-Etosa Basin is described by Miller et al. (2010), Miller, (1997 and 2008). The land surfaces of the study area are covered by sand and clay, and outcrops of calcretes and dolomites occur mainly in pans and depressions. These sands and clays are part of the thick Kalahari Sequence which can locally be up to more than 600 m in thickness, with ages ranging from late Cretaceous to recent. The Kalahari Sequence has four formations: Ombalantu, Beiseb, Olukonda and Andoni. The Ohangwena multi-layered aquifer system that has been identified in the study region is contained within the unconsolidated to semi-consolidated sediments of the Andoni and Olukonda Formations (Bittner, 2006; Miller, 1997). Perched aquifers (KOH-0) are located between 0 and 40 meters below ground level (m.b.g.l) while the regional unconfined KOH-1 aquifer is between 60 and 160 m.b.g.l (Bittner, 2006). KOH-0 has hydraulic conductivities between 10^{-6} and 10^{-4} m/sec while the multi-layered aquitard below, ranges from

10^{-9} to 10^{-4} m/sec (Ananias, 2015). The area with perched aquifers extends in south-west to northwest direction (Fig. 5.2). Ananias (2015) and Lohe et al. (2013) suggested that in some areas the perched aquifers in the CEB are connected to the regional aquifer Ohangwena KOH-1, and that recharge to the regional aquifer may occur via perched layers. A volume of 2.01×10^{-3} and 5.02×10^{-3} m³/day m², may potentially flow from the perched KOH-0 into the unconfined KOH-1 through the aquitard (Ananias, 2015). However, this volume is relatively small.

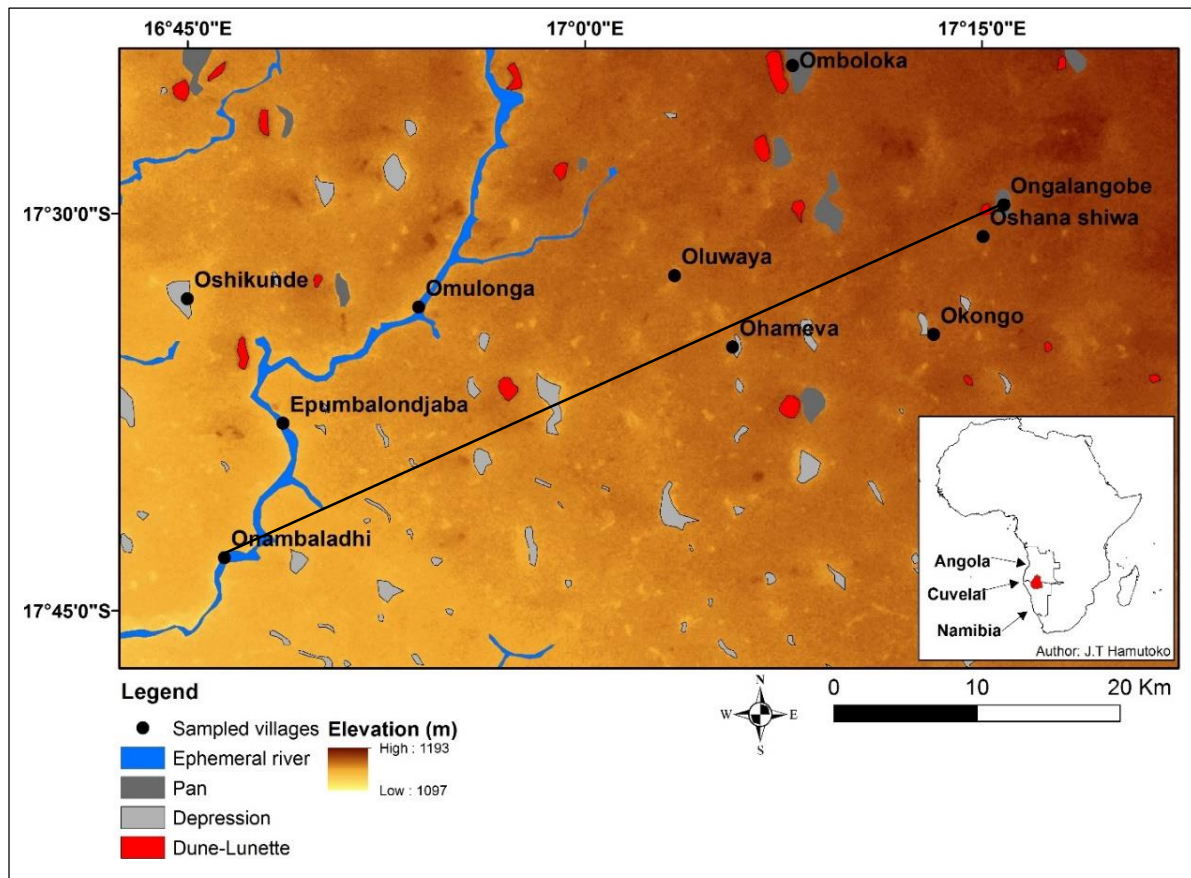


Figure 5-1: Map showing the location of the study area. The map also shows four different hydrotopes that are demarcated from the different elevation and field observations. The line indicate where the cross section (figure 5.7) was taken

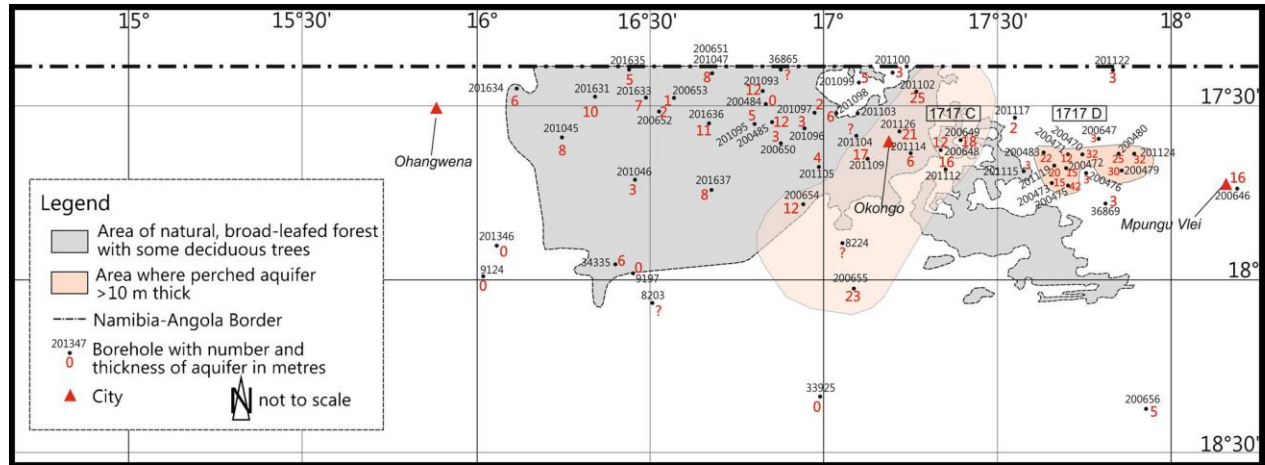


Figure 5-2: Thickness of perched aquifer in the Ohangwena region based on texture (Lohe et al., 2013)

Since perched aquifers occur as discontinuous aquifers in the unsaturated zone, they are very heterogeneous and thus they are very difficult to characterise as a single aquifer. Therefore a hydrotope approach was adopted for close examination. A hydrotope approach groups different land surfaces according to their natural mosaic structure and each group is treated as one modelling unit (Becker and Braun, 1999). The use of this approach is becoming increasingly important especially in hydrological modelling though different users use different names. For example Gao et al. (2014) and Savenije (2010) used the so called topography driven conceptual modelling (FLEX-Topo), which classifies the catchment into functional units depending on topography. Savenije (2010) emphasised that even though there is significant heterogeneity in the landscape, soil, terrain and rainfall, patterns with striking simple emergent behaviour still exist at the larger scale. Therefore the FLEX-Topo conceptualises the dominant physical processes in key elements of the landscape, and classify them into groups according to topography, geology, geomorphology and land-use criteria (Fenicia et al., 2014; Gharari et al., 2011). On the other hand, Flügel (1995) and Legesse et al., (2003) used the term hydrological response units (HRU) but basically following

the same principle to address the heterogeneity and complexity of hydrological processes without using complicated or over-simplified models.

Five hydrotopes for this study area were classified in Hamutoko et al. (2016), namely pans, depressions, dunes, sandfield and ephemeral rivers. These were characterised from field observations, mapped from digital elevation models and satellite images. However it was observed that perched aquifers in the CEB occur mainly underneath large pans, depressions and ephemeral river hydrotopes. Ephemeral rivers are associated with dryer climates and are normally perched systems (Xu and Beekman, 2003). Pans are geomorphological features that appear as shallow sub-circular to sub-elliptical isolated depressions; they are predominantly accompanied by crescent dunes which can rise to a height of 30 – 40 m above the pan floor (Lancaster, 1978). In this work pans and depressions are considered as one hydrotope as they have similar physical characteristics with the main difference being that depressions lack crescent dunes in their proximity. Bowler (1986) suggested that pans can serve as either discharge or recharge point, depending on the present hydrologic dynamics and their soil hydraulic properties. Moreover, their ground surface may be covered or partly covered by grass, bare clay and/or calcrete with few shrubs mainly from the acacia species, while the dunes are covered by thick forest. Perched aquifers in the pans/depression hydrotope are tapped by cylindrical-shaped hand-dug wells with water levels in the ranges of 5 to 30 m b.g.l while in the ephemeral river they are tapped by funnel shaped hand-dugs with water level below 5 m b.g.l. The deeper regional aquifer (KOH-1) extends to both hydrotopes and is tapped by boreholes which are drilled with a standard depth of 150 m in the area.

Table 5-1: Description of the hydrotopes with perched aquifers in the study area

	Pans/depressions	Ephemeral river
Type of hand-dug well	 Omahangu field Deep wells at e.g. Omboloka wellfield. It is observed that generally in all the pans/depressions the hand-dug wells are positioned along south-west to northwest line as indicated by the red arrow.	 Shallow well
Vegetation	Partly covered by grass, sparsely distributed throne trees, <i>Combretum imberbe</i> , <i>Acacia</i> spp. bushes and grass, also covered in Mahangu fields that a cultivated yearly during rainy season	Covered by forest savannah and woodlands
Depth to water table	5 to 30 m b.g.l	0 to 5 m b.g.l
Water inflow possible	Surface runoff into well	Ephemeral river is still flowing in the subsurface, surface water only flow in years with high rainfall

	They are topographically lowest point in the area and thus groundwater flows toward the centre	
Soil type	Fine sand, clay and calcrete Calcrete outcrop at Omboloka 2 meters of calcrete and gravel at recently dug hole in Okamanya	Medium to coarse grained Sand
Standing water	During rainy season, water accumulates around the wells	No standing water around the wells, however some parts of the river have standing water during the rainy season

5.4 Materials and methods

5.4.1 Sampling and analytical techniques

Groundwater samples were collected from hand-dug wells and boreholes in 10 villages (Fig. 5.1). In each village a minimum of one hand-dug well and a borehole was sampled. Samples from the hand-dug wells are representative of the perched aquifer while samples from the boreholes are representative of the regional aquifer. Samples were collected between the period of November 2013 and October 2016. However additional data especially for the boreholes was taken from Nakwafila (2011), and the BGR hydrocensus database. Four of the sampled villages are situated in the ephemeral river hydrotope while six are located in the pans/depressions hydrotope. Hach field portable instruments (HQ 11d pH meter, HQ 14d conductivity meter, HQ 40d multimeter) were used to measure pH, electrical conductivity (EC), redox potential (Redox), oxygen content (O_2) and temperature (T) in the field. The water level in hand-dug wells was measured with an electrical contact gauge.

Three samples were taken at each sampling point: a 100 ml polypropylene bottle for cations, a 500 ml polypropylene bottle for anions and a 50 ml glass bottle for stable isotopes. The cation samples were filtered through 0.45- μ m filters and subsequently preserved with nitric acid, whereas anion samples were kept cool using a cooler box and refrigerator until analysed in the laboratory. Major ion analyses were performed at the Analytical Laboratory Services in Windhoek, Namibia, and at the hydrochemistry laboratory of BGR in Hanover, Germany. The analytical procedures used at each laboratory are described in details in Hamutoko, 2017. The glass bottle for stable isotopes was carefully sealed to prevent evaporation during transport.

Stable isotopes were measured at the University of Namibia (UNAM) and BGR laboratories using an off-axis integrated cavity output spectroscopy (OA-ICOS, Los Gatos DLT-100) and a cavity ring down spectrometer (CRDS, model L2120-i, Picarro Inc.) respectively. All isotopic ratios are given as δ -values in per mil (‰) against the international standard Vienna Standard Mean Ocean Water (V-SMOW, normalized to V-SMOW/SLAP scale) as defined by equation (1),

$$\delta = \left[\left(\frac{R_{SA}}{R_{ST}} \right) - 1 \right] \times 1000 \quad (5.1)$$

Where R_{SA} (-) denotes the isotope ratio of $^2\text{H}/\text{H}$ or $^{18}\text{O}/^{16}\text{O}$ of the sample and R_{ST} (-) of the standard respectively. Analytical errors of a quality check sample measured within each run are better than 0.30‰ for $\delta^{18}\text{O}$ and 1.0‰ for $\delta^2\text{H}$ measurements.

5.4.2 Chloride Mass Balance (CMB)

The CMB method is a well-established method for estimating recharge in arid and semi-arid regions. The method assumes that chloride is a chemically-inert tracer, which enters rainwater from marine aerosols and atmospheric dust. Its concentration increases after infiltration by evaporation and/or uptake of water by plants (Edmunds et al., 2002; Harrington et al., 2002). Wrabel, 1999, Mainardy, 1999; Külls, 2000 in Klock (2001) assumed that the dry input is negligible for the Kalahari because it is relatively small comparing to the wet deposition. Yet, Wanke et al. (2014) contended that dry deposition contributes 20 to 50 % to the total deposition of chloride.

The groundwater recharge rate is estimated using the equation:

$$R = (P * Cl_p) * DDF / Cl_{gw} \quad (5.2)$$

where R recharge in mm/a, P is mean annual rainfall in mm/a, Cl_p mean concentration chloride in precipitation in mg/l, Cl_{gw} is chloride concentration in groundwater in mg/l and DDF is dry deposition factor and is assumed to be between 1.2 and 2.

As surface runoff is limited to a very local extend and mainly occurs around the wells and chloride uptake by plants is also insignificant, all assumptions are met in this study and CMB could be applied. Twenty three (23) rain water samples were analysed for chloride content. The mean concentration chloride in precipitation was calculated from the collected twenty three (23) rain water samples to a value designated Cl_p . 188 groundwater samples were analysed for chloride, 148 from the perched aquifers and 40 from the regional aquifer.

5.4.3 Geochemical modelling

Inverse chemical modelling, checking of charge balance, computing of the aqueous speciation and calculation of saturation indices (SI) with respect to the main mineral phases were done using the numerical modelling software PHREEQC (Parkhurst and Appelo, 1999). Liu et al. (2015) pointed out that saturation index is a vital geochemical parameter in the fields of hydrogeology and geochemistry, which is often useful for identifying the existence of some common minerals in the groundwater system. When SI of minerals equals zero the groundwater is saturated with respect to those minerals; positive SI values represent oversaturation, and negative SI values show under-saturation (Appelo and Postma, 2005). Inverse modelling was also used in this study. Inverse modelling is a process of evaluating what happened between the initial and final water compositions.

5.5 Results

5.5.1 Hydrochemistry and water quality

The ranges and average values of physio-chemical parameters and major ions results are presented in the Table 5.2. In the ephemeral river hydrotope, pH ranges between 5.4 and 10.4 for the perched aquifers and between 8.0 and 9.0 for the regional aquifer with mean values of 7.5 and 8.6 respectively (Table 5.2). In the pans/depressions hydrotope, pH ranges from 6.4 to 8.4 with mean value of 7.6 for the perched aquifers and from 7.6 to 8.6 with mean value of 8.1 for the regional aquifer. EC ranges from 47 $\mu\text{S}/\text{cm}$ to 296 $\mu\text{S}/\text{cm}$ with mean value of 142 $\mu\text{S}/\text{cm}$ for the perched aquifers and from 461 $\mu\text{S}/\text{cm}$ to 2142 $\mu\text{S}/\text{cm}$ with mean of 1333 $\mu\text{S}/\text{cm}$ for regional aquifer in the ephemeral river. Whereas in the pans/depressions EC for the perched aquifers and regional aquifer range 283 $\mu\text{S}/\text{cm}$ to 1031 $\mu\text{S}/\text{cm}$ with mean of 588 $\mu\text{S}/\text{cm}$ and from 481 $\mu\text{S}/\text{cm}$ to 1784 $\mu\text{S}/\text{cm}$ with mean of 742 $\mu\text{S}/\text{cm}$ respectively. Generally higher pH and EC values were recorded in the regional aquifer than those recorded in the perched aquifers (Table 5.2). The abundance of major ions is arranged based on median values (Table 5.2). In the ephemeral river, the abundance of major ions of perched aquifers can be grouped in the order of $\text{Na}^+ > \text{K}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$ for cations and $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^-$ for anions while for the regional aquifer is $\text{Na}^+ \gg \text{K}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$ for cations and $\text{HCO}_3^- \gg \text{Cl}^- > \text{SO}_4^{2-} > \text{F}^-$ for anions. In the pans/depressions, the abundance of major ions of perched aquifers can be grouped in the order of $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+ > \text{Na}^+$ for cations and $\text{HCO}_3^- > \text{NO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{F}^-$ for anions while for the regional aquifer is $\text{Na}^+ \gg \text{Ca}^{2+} > \text{K}^+ > \text{Mg}^{2+}$ for cations and $\text{HCO}_3^- \gg \text{Cl}^- > \text{SO}_4^{2-} > \text{F}^-$ for anions. In general, bicarbonate is the dominant anion in both hydrotopes as well as in both the perched aquifers and the regional aquifer with few exceptions of SO_4 rich and mixed anion in the perched aquifers within the ephemeral river.

Table 5-2: Minimum, median, average and maximum values of hydrochemical composition of rain water and groundwater. EC in $\mu\text{S}/\text{cm}$, temperature in $^{\circ}\text{C}$ and major ions in mg/l

	Rain n=1	Ephemeral river								Pans/depressions							
		Perched aquifer (KOH-0) n=57				Regional aquifer (KOH-1) n=7				Perched aquifer (KOH-0) n=67				Regional aquifer (KOH-1) n=15			
		Min	Max	Median	Mean	Min	Max	Median	Mean	Min	Max	Median	Mean	Min	Max	Median	Mean
pH	6.7	5.4	10.4	7.4	7.5	8.0	9.0	8.7	8.6	6.4	8.2	7.7	7.6	7.6	8.6	8.0	8.1
Temp	25	15.0	37.6	25.3	25.4	20.3	25.0	25.0	24.0	22.2	29.8	25.3	25.2	21.1	27.4	25.0	24.7
EC	15	47	296	139	142	461	2142	1122	1333	283	1031	558	588	481	1784	596	742
K ⁺	0.37	2.00	54.60	10.00	11.92	5.40	10.00	6.90	7.43	2.70	76.60	12.40	8	7.30	0	12.00	16.79
Na ⁺	0.63	0.80	34.40	10.10	12.74	41.00	398.00	285.00	6	0.60	247.00	4.30	9	10.0	278.	76.00	95.57
Cl ⁻	0.60	1.00	26.90	5.64	8.11	5.00	185.00	20.00	42.86	1.06	25.10	4.32	6.44	0.67	0	5.10	8.57
Mg ²⁺	0.23	0.46	28.10	2.80	3.42	0.10	8.90	0.48	1.69	1.55	57.80	27.80	7	4.10	0	9.60	13.51
Ca ²⁺	0.69	0.85	72.30	8.19	9.60	1.00	42.00	1.45	7.51	6.21	108.00	63.90	1	6.40	0	31.00	30.07
SO ₄ ²⁻	1.26	0.10	34.00	6.02	10.08	2.00	20.20	19.00	16.73	0.60	6.72	2.90	3.30	0.00	0	2.16	3.24
HCO ₃ ⁻	2.40	7.60	330.00	40.20	53.98	248.00	648.00	593.00	1	45.3	783.0	296.0	59	242.	682.	325.0	361.87
Fe ²⁺	0.06	0.03	5.74	1.67	1.93	0.01	0.01	0.01	0.01	0.00	0.40	0.01	0.03	0.00	0.03	0.02	0.02
NO ₃ ⁻	2.39	0.03	46.30	3.74	9.74	0.00	1.40	0.00	0.37	0.04	296.00	45.60	0	0.00	00	2.50	19.07
NO ₂ ⁻	-	0.00	18.80	0.15	0.91	0.00	0.01	0.01	0.01	0.00	6.19	0.13	0.71	0.00	0.38	0.01	0.10
F ⁻	0.02	0.01	2.06	0.10	0.16	0.30	4.70	4.02	3.69	0.30	4.50	2.01	1.93	0.30	2.99	1.50	1.60

The water quality was evaluated based on TDS, fluoride and nitrate (Fig. 5.3) which are identified as some of the elements of concern by previous studies (Hamutoko et al., 2017; Wanke et al., 2014). It is observed that in the pans/depressions all sampled hand-dug wells and boreholes have TDS values within WHO drinking limit, fluoride is high in most sites above drinking limit. Fluoride values are generally higher in the regional aquifer than the perched aquifer. Nitrate is only above drinking limit in the perched aquifer but high values such 46 mg/l were recorded in the regional aquifer. In the ephemeral river, the perched aquifer has very low TDS below drinking limit, while 2 borehole are above and 2 are within the limit. Fluoride in the perched aquifer in all the sampled villages are within the drinking limit, while 3 boreholes have high fluoride content. Nitrate in this hydrotope is not a problem for drinking water as all the values are below the WHO guideline.

Generally for perched aquifers in the pan/depression hydrotope, as the depth to water table increases, the water changes from Ca-Mg rich to Na-K rich water, which can be inferred from the Piper diagram (Fig. 5.4). More specifically, villages where the perched aquifers have water table depths more than 17 metres (Oshana-shiwa and Ongalangobe), the data points for both perched aquifers and regional aquifer straddle the boundaries of CaMgHCO_3 and NaHCO_3 fields. At Omboloka village the perched aquifer has a relatively shallow depth to water table approximately of 10 m and both the perched aquifer and the regional aquifer are characterised by the CaMgHCO_3 water type. Perched aquifers at Oluwaya, Okongo and Ohameva villages have water table depths that vary between 5 m and 17 m and are characterised by CaMgHCO_3 water types while the regional aquifer is characterised by NaHCO_3 (Fig. 5.4). In the ephemeral river hydrotope, in all but one villages the groundwater is of the NaK-mixed anions and NaHCO_3 water type in the

perched and regional aquifers, respectively. The exception is the village of Omulonga where the water type of the perched aquifer is a mixed cation- HCO_3 type while the regional aquifer has a NaHCO_3 water type.

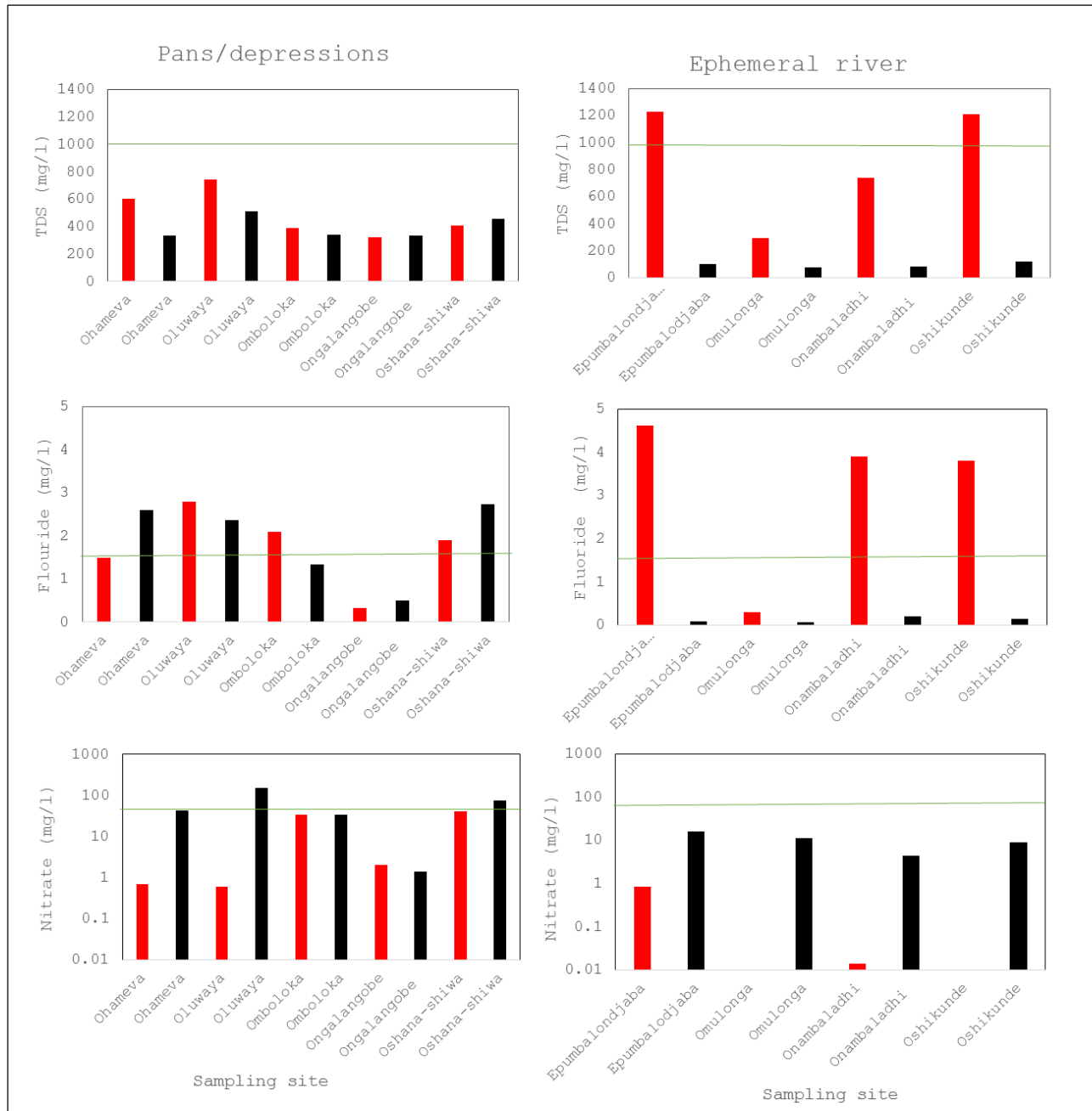


Figure 5-3: Main substances of concern in the perched aquifer and the regional aquifer. Black represent the perched aquifers while red represent the regional aquifer and the horizontal line is the WHO guideline

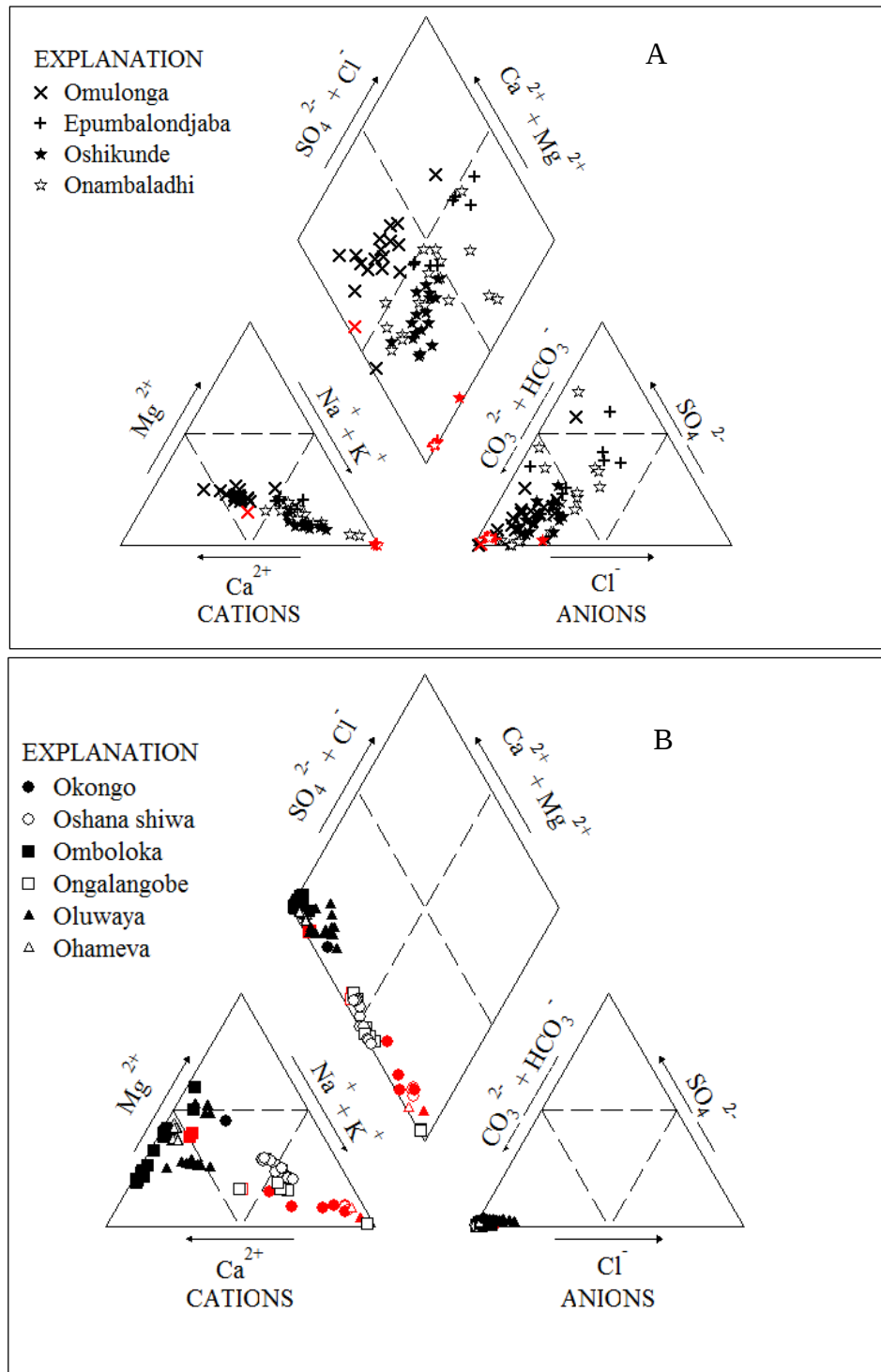


Figure 5-4: A piper diagram showing different water types. (A) Samples from pans and depressions and (B) samples from the ephemeral river hydrotope. Each sample represent one village with the black colour showing perched aquifer while red is the regional aquifer

While the differences and similarities between the water types of the different hydrotopes and aquifers can be indicative of the groundwater's origin and aquifer connectivity, hydrochemical reactions along the groundwater flow path must be understood before final inferences can be made. Bivariate plots of different parameters were therefore used (Fig. 5.5) to get an insight on the geochemical processes in the aquifers. No significant correlation exists between pH and HCO_3^- (Fig. 5.5 A and B). The regional aquifer has slightly higher pH values than the perched aquifers. In the ephemeral river hydrotope the perched aquifers and regional aquifer plot in two distinct fields where by the regional aquifer have very high HCO_3^- as compared to the perched aquifers but perched aquifers cover a wider range of pH values. In the graph of Ca versus HCO_3^- (Fig. 5.5 C and D), in both hydrotopes, more than half of the samples plot around the 1:2 and 1:4 lines.

The Ca + Mg versus $\text{HCO}_3^- + \text{SO}_4^{2-}$ (Fig 5.5 E and F), is used to determine the ion exchange processes. When samples have excess $\text{HCO}_3^- + \text{SO}_4^{2-}$ over Ca + Mg this indicates that ion exchange is the dominant processes while the opposite Ca + Mg over $\text{HCO}_3^- + \text{SO}_4^{2-}$ indicate reverse ion exchange as the dominant process. All samples from both hydrotopes plot above the 1:1 line with exception of two points of Oluwaya perched aquifers that plot on the line and two points from Oshana-shiwa and Omulonga perched aquifers that plot below the 1:1 line. This indicates samples have excess $\text{HCO}_3^- + \text{SO}_4^{2-}$ which imply ion exchange process dominance.

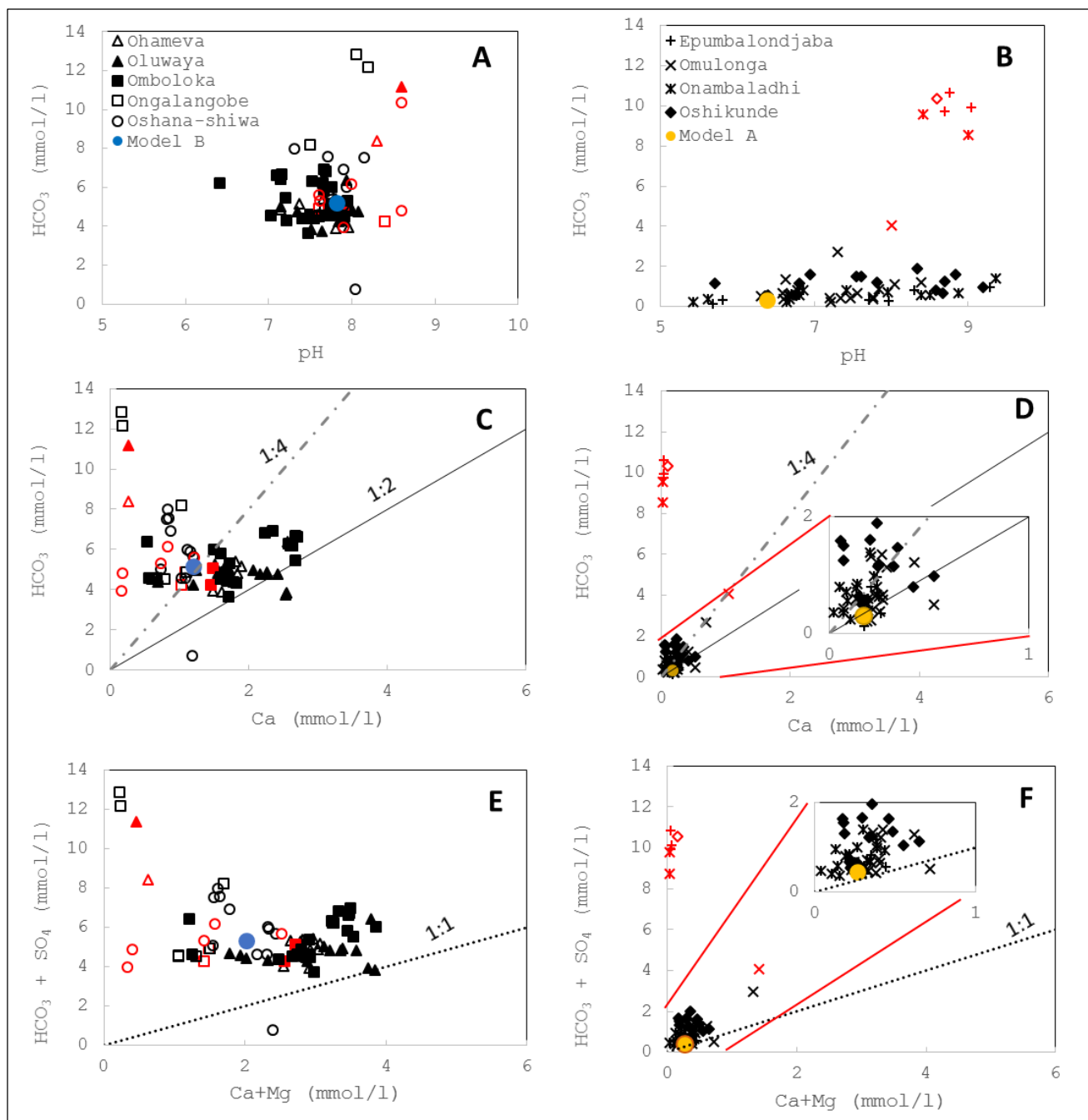


Figure 5-5: Graphs showing relationships between pH and Alkalinity, Calcium and Alkalinity and Calcium + Magnesium, Alkalinity and Sulphate to elucidate geochemical reactions. The graphs A, C and E represents the Pans/Depressions hydrotope while graphs B, D and F represents samples from the ephemeral river

The saturation index (SI) of Calcite, gibbsite, quartz, kaolinite, fluorite, dolomite, gypsum and albite was computed in PHREEQC using the wateq4f.dat database. Table 5.3 shows the saturation indices values for these minerals while in Fig. 5.6 saturation indices of calcite, dolomite, gypsum and fluorite of all the groundwater samples was plotted versus TDS. In the ephemeral river the median SI for calcite, gibbsite, quartz, kaolinite, fluorite, dolomite, gypsum and albite is -1.65, 2.81, 1.05, 8.32, -3.77, -3.40, -3.51 and 0.82 for perched aquifers and 0.07, -0.69, 0.86, 1.20, -1.53, 0.00, -4.11 and 0.27 for the regional aquifer, respectively (Table 5.3). Most of the groundwater in the perched aquifers in the ephemeral river hydrotope is oversaturated with the silicates minerals gibbsite, quartz, kaolinite and albite, while under-saturated with minerals calcite, fluorite, dolomite, and gypsum. On the other hand the regional aquifer in the ephemeral river are oversaturated with calcite, quartz, kaolinite, and albite while under-saturated with gypsum, gibbsite, and fluorite.

The perched aquifers and the regional aquifer the pans/depressions hydrotope have similar saturation indices, whereby they are both over-saturated with calcite, gibbsite, quartz, kaolinite, dolomite and under-saturated with fluorite and gypsum (Table 5.3). The only difference observed is under-saturation of albite in the perched aquifers while in the regional aquifer it is over-saturated. The similarity in the pans/depressions is also shown in Fig. 5.6 where the regional aquifer and perched aquifers plot in the same field. On the other hand, samples from the perched aquifers and regional aquifer in the ephemeral river plot in different field. The regional aquifer plot mainly on a horizontal straight line either on the saturation line for calcite and dolomite or below the saturation line for fluorite and gypsum.

Table 5-3: Saturation indices of common minerals computed from PHREEQC

Unless stated (mg/l)	Rain n=1	Ephemeral river								Pans/depressions							
		Perched aquifer (KOH-0) n=57				Regional aquifer (KOH-1) n=7				Hand-dug wells (KOH-0) n=67				Perched aquifer (KOH-1) n=15			
		Min	Max	Median	Mean	Min	Max	Median	Mean	Min	Max	Median	Mean	Min	Max	Median	Mean
SI Calcite	-4.58	-4.48	0.95	-1.65	1.52	-0.39	0.57	0.07	0.13	-2.65	0.98	0.40	0.33	-0.34	1.07	0.48	0.48
SI CO ₂ (g)	-3.52	-6.33	-0.42	-2.77	2.86	-3.36	-2.62	-2.98	2.98	-3.44	1.03	-2.18	-2.11	-3.18	-2.07	-2.52	-2.55
SI Gibbsite	2.39	0.51	3.78	2.81	2.55	-0.79	-0.26	-0.69	0.58	-6.69	1.22	0.30	0.23	-0.55	0.91	0.15	0.21
SI Quartz	-0.59	0.74	1.22	1.05	1.02	0.77	0.92	0.86	0.86	0.53	1.56	1.16	1.12	0.64	1.26	1.08	1.02
SI Kaolinite	4.42	4.29	10.62	8.32	7.93	0.91	2.12	1.20	1.41	11.28	5.48	3.69	3.49	1.14	4.73	3.61	3.39
SI Fluorite	-6.20	-7.66	-0.42	-3.77	3.91	-2.24	-1.23	-1.53	1.63	-2.46	0.13	-0.47	-0.76	-2.42	-0.30	-1.25	-1.25
SI Dolomite	-9.31	-9.06	2.00	-3.40	3.13	-1.12	0.81	0.00	0.01	-5.38	1.79	0.80	0.64	-0.52	2.16	1.24	0.98
SI Gypsum	-5.12	-5.41	-2.52	-3.51	3.53	-4.26	-3.44	-4.11	3.97	-4.30	2.71	-3.17	-3.25	-4.20	-3.26	-3.78	-3.68
SI Albite	-5.70	-3.72	2.25	0.82	0.72	0.19	0.28	0.27	0.25	12.69	1.09	-1.12	-1.00	-0.84	0.79	0.34	0.10

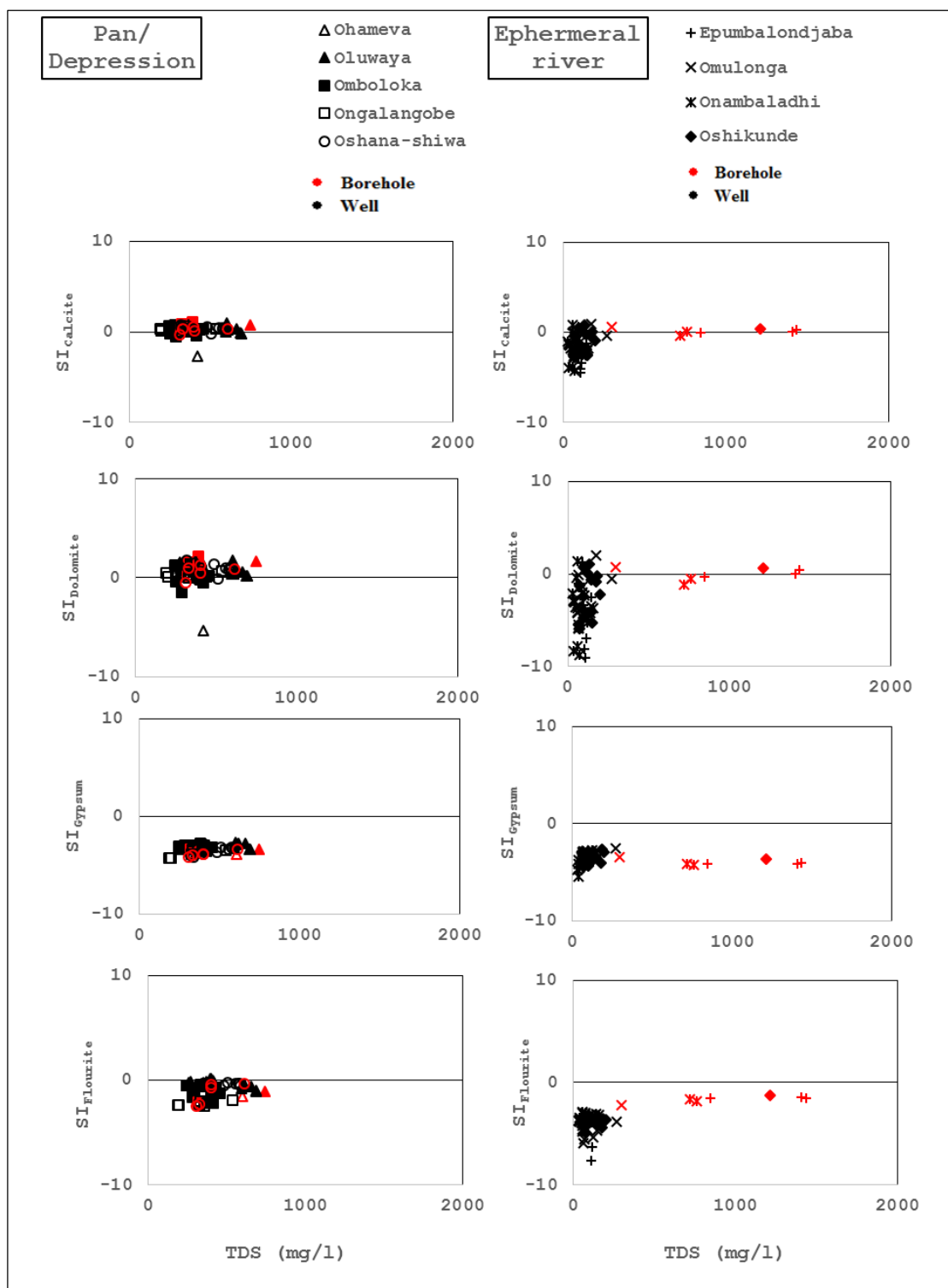


Figure 5-6: Graphs of saturation indices (SI) of water with respect to the selected mineral phases (Calcite, Dolomite, Gypsum and Fluorite) plotted against with TDS

5.5.2 Groundwater recharge rates from CMB

The chloride content of the 22 rain samples ranges from 0.21 to 2.25 mg/l with average of 0.81 mg/l and median of 0.69 mg/l. The average chloride value was used in calculating the groundwater recharge rates. The long term precipitation values are 450 mm/a for the ephemeral river and 500 mm/a for pans/depression hydrotopes, respectively (Mendelsohn et al., 2013). Generally, the perched aquifers in the ephemeral river have higher chloride concentrations with mean values between 5.4 mg/l and 12.1 mg/l as compared to perched aquifers in the pan/depressions with mean values between 3.8 mg/l and 13.1 mg/l. Thus lower recharge rates were recorded in the ephemeral river with mean values from 36 mm/a to 80 mm/a while in the pans/depressions recharge rates have mean values from 37 mm/a to 128 mm/a. These mean recharge values translate into 8% to 18% and 7 to 25% as recharge percentage of mean annual rainfall for perched aquifers in the ephemeral river and pans/depressions respectively (Table 5.4)

Chloride concentrations in the regional aquifer vary from 5.0 mg/l to 15.8 mg/l and 3.0 mg/l to 19 mg/l in the ephemeral river and pans/depressions, respectively. Recharge rates varies from 25 mm/a to 87 mm/a in the ephemeral river and from 26 mm/a to 162 mm/a in the pans/depressions, which converts to 6% to 19 % and 5 % to 32% as recharge percentage of mean annual rainfall respectively (Table 5.4). At Omulonga the regional aquifer behaves quite different from the other villages in the ephemeral river hydrotope as seen in Fig. 5.4, 5.5 and 5.6, it plots closer to the perched aquifers rather than with other samples from the regional aquifer. The recharge as percentage of the mean annual rainfall at Omulonga is 18% for the perched aquifer and 19% for the regional aquifer. Another interesting observation is that the recharge rates are higher for the regional aquifer than for the perched aquifers at Omboloka and Ohameva.

Table 5-4: Median and mean chloride and groundwater recharge rates based on chloride mass balance method and annual precipitation. Average chloride in rainwater is 0.81 mg/l

Hydrotope	Rainfall (mm/a)	Village	Perched aquifer						Regional aquifer		
			Chloride in mg/l		Recharge (mm/a)		Recharge as % of mean annual rainfall				
			Median	Mean	Median	Mean	Median	Mean	Chloride (mg/l)	Recharge (mm/a)	Recharge as % of mean annual rainfall (%)
Pans/ depressions	500	Ongalangobe	2.50	3.8	194.4	127.6	38.8	25.5	5.1	95.2	19.0
		Oshana-shiwa	6.20	5.0	78.3	97.1	15.6	19.4	6.3*	76.2	15.2
		Ohameva	3.03	3.8	160.6	127.7	32.1	25.5	3.0	162.0	32.4
		Oluwaya	14.5	13.1	33.4	36.9	6.6	7.3	19.0	25.5	5.1
		Omboloka	4.5	6.5	105.8	74.0	21.1	14.8	3.2*	150.4	30.0
Ephemeral River	450	Epumbalondjaba	8.9	8.8	48.8	49.1	10.8	10.9	15.8*	27.5	6.1
		Omulonga	4.1	5.4	106.9	80.1	23.7	17.8	5.0*	87.4	19.4
		Onambaladhi	6.1	9.9	71.3	43.9	15.8	9.7	17.4	25.0	5.5
		Oshikunde	11.6	12.1	37.7	35.9	8.3	7.9	-	-	-

*average value

5.5.3 Geochemical model

The calculated SI (Table 5.3) and lithology were used to constrain the inverse geochemical models. Rainfall was used as initial member while the median groundwater composition for the various groups were used as the end member. Two model scenarios were considered; Model A is representative of samples from perched aquifers in the ephemeral river while model B represent samples from the perched aquifers in the pans/depressions. The first scenario (Model A) simulated evapotranspiration of rainfall water, where by 90% of the water was removed in 10 steps. Figure 5.8 shows how major ions were changing during the simulation. The second scenario (Model B) used results of model A, then it is equilibrated with calcite (0.8), dolomite (0.4) and partial pressure of CO₂ was set to -2.5. Half a mole of albite was added to the solution and exchanger was also activated. The models were fitted with a trial-and-error procedure by visually comparing the modelled ion-ion relations to the observed data. The models were compared with the observed data (Fig. 5.7, Table 5.5) and even though the observed concentrations have a wide range, the models fit in well with the median values of the observed data. There is a noticeably constant gradual increase in concentration due to evaporation and a slight jump in concentration was observed only when the simulated water is equilibrated with calcite, dolomite and partial pressure.

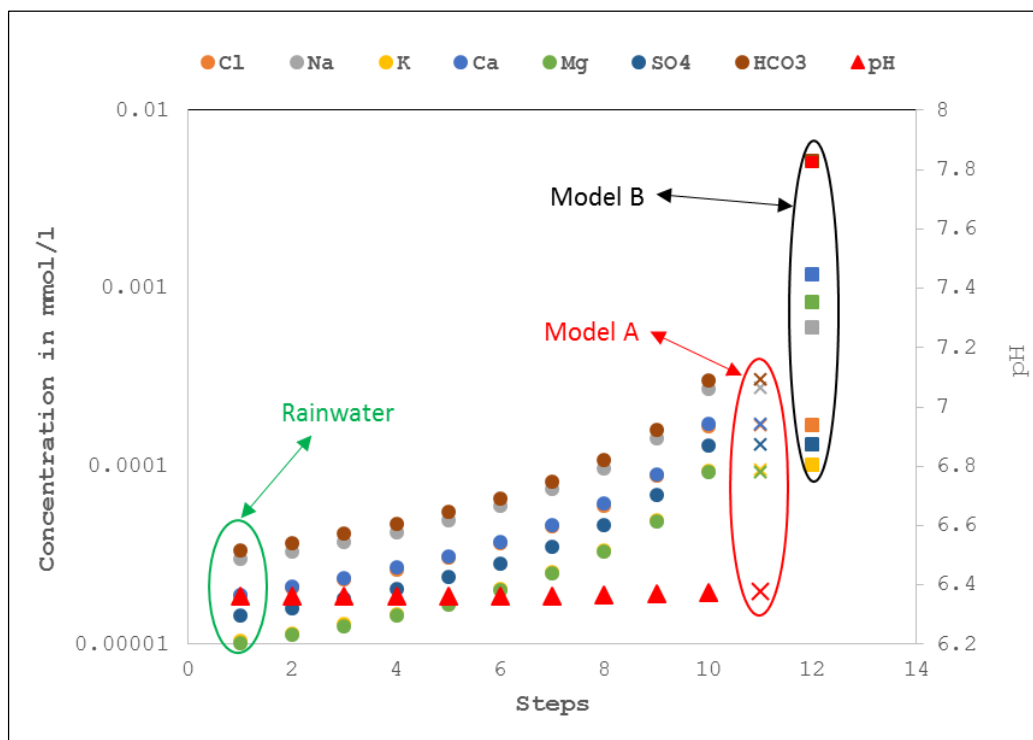


Figure 5-7: A graph showing how the different major ions were changing through the simulations for the two models

Table 5-5: Geochemical model parameters compared with median values for the perched aquifers

Parameters	Perched aquifers in the ephemeral			Perched aquifers in pans/depressions
	Model A	river	Model B	
PH	6.38	7.42	7.82	7.59
Cl ⁻	1.69E-04	1.61E-04	1.69E-04	1.26E-04
Na ⁺	2.74E-04	4.70E-04	6.00E-04	1.87E-04
K ⁺	9.46E-05	2.53E-04	1.02E-04	2.98E-04
Ca ²⁺	1.72E-04	1.99E-04	1.19E-03	1.60E-03
Mg ²⁺	9.25E-05	1.15E-04	8.34E-04	1.15E-03
SO ₄ ²⁻	1.31E-04	6.22E-05	1.31E-04	2.97E-05
HCO ₃ ⁻	3.05E-04	6.57E-04	5.19E-03	4.85E-03
NO ₃ ⁻	2.63E-04	5.40E-05	2.63E-04	7.17E-04
SI Calcite	-3.09	-1.67	0.38	0.40
SI CO ₂ (g)	-2.33	-2.77	-2.48	-2.18
SI Gibbsite	3.49	2.84	3.26	0.30
SI Quartz	0.40	1.04	1.07	1.16
SI Kaolinite	8.61	8.34	9.48	3.70
SI Dolomite	-6.33	-3.41	0.76	0.82
SI Gypsum	-3.23	-3.52	-2.63	-3.18

5.5.4 Stable water isotopes

The hand-dug wells in the pans/depressions hydrotope the perched aquifers have values -9.00 ‰ to -1.30 ‰ and from -61.51‰ to -22.06‰ $\delta^{18}\text{O}$ and $\delta^2\text{H}$ respectively while the regional aquifer have values between -9.39‰ and -6.17‰ for $\delta^{18}\text{O}$ and from -66.5‰ to -48.6‰ for $\delta^2\text{H}$. In the ephemeral river the values from the perched aquifers cover a wide range of isotopic signatures with $\delta^{18}\text{O}$ values from -6.95 ‰ to 0.86 ‰ and $\delta^2\text{H}$ values from -49.1‰ to -7.6‰, while the regional aquifer have narrow range between -9.70 ‰ and -8.81‰ for $\delta^{18}\text{O}$ and from -67.5‰ to -63.28‰ for $\delta^2\text{H}$. It is notable seen that the regional aquifer in the ephemeral river has more depleted values than the regional aquifer in the pans/depressions. All groundwater samples are compiled in $\delta^{18}\text{O}$ versus $\delta^2\text{H}$ space and plotted together with the global meteoric water line (GMWL) as well as the local meteoric water line (LMWL) for the CEB (Fig. 5.7 A and B). Most samples are plotting close but below LMWL which indicates the effects of evaporation. Furthermore, it is observed that in the pans/depressions perched aquifers and the regional aquifer from the same village have values close to one another while in the ephemeral river hand-dug wells and the regional aquifer plot in two distinct fields.

In the pans/depressions the perched aquifers plot on regression line with equation $\delta^2\text{H} = 5.0 \delta^{18}\text{O} - 14.98$ while regional aquifer plot on regression line with equation $\delta^2\text{H} = 5.9 \delta^{18}\text{O} - 10.7$. In the ephemeral river the perched aquifers plot of on a regression line with equation $\delta^2\text{H} = 5.0 \delta^{18}\text{O} - 12.5$ while the regional aquifer plot on a regression line with equation $\delta^2\text{H} = 3.9 \delta^{18}\text{O} - 28.75$. These regression lines intersect the LMWL at (-8.81, -59.02) and (-11.6, -51.8) for perched aquifers and the regional aquifer in the pans/depressions respectively. Whereas in the ephemeral river the perched aquifers intersect the LMWL at (-7.86, -50.9) and at (-10.04, -67.91) for the regional aquifer (Fig. 5.7 A and B). The intersection of the regression line identifies the mean

isotopic composition of the parent/source water. The source/parent water for the regional aquifer is considerably more depleted than in the perched aquifers.

Figure 5.8. C and D shows $\delta^{18}\text{O}$ versus chloride concentrations in the different hydrotopes. No correlation was found in the ephemeral river hydrotope (r^2 is 0.14 and 0.37 for perched aquifers and regional aquifer respectively), however the samples cover a wide range of both isotopic $\delta^{18}\text{O}$ values and chloride content. In the pans/depressions the chloride content is increasing with constant $\delta^{18}\text{O}$ values as the samples plot on the almost horizontal straight line.

The most outstanding difference between the two hydrotopes is that in the pans/depressions the groundwater in both the perched aquifers and the regional aquifer from a village have similar hydrochemical and isotopic compositions whereas in the ephemeral river, the perched aquifers are different from the regional aquifer (Fig. 5.4 – Fig. 5.7).

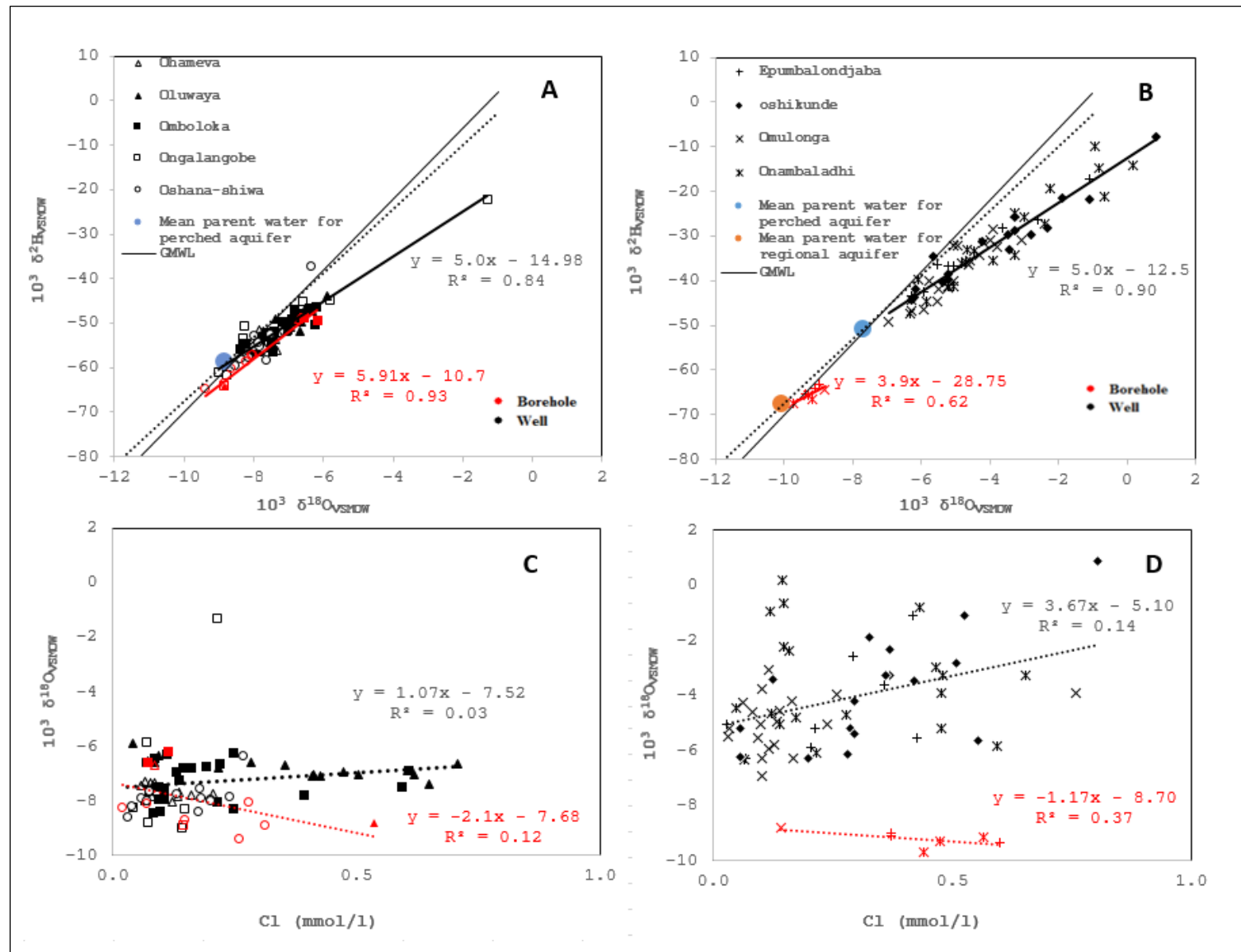


Figure 5-8: Graphs showing the $\delta^{18}O$ values versus δ^2H values and $\delta^{18}O$ versus the Cl concentration. A and C represent pans/depressions while B and D is the ephemeral river

5.6 Discussion

5.6.1 Conceptual model and hydrogeochemical evolution of the groundwater

A clear distinction between the two hydrotopes exists for the perched aquifers, however the regional aquifer in both hydrotopes have similar characteristics. A schematic conceptual model is shown in Fig. 5.9. The conceptual model suggests that about 90% of the rainfall water is evaporated and this results in the chemical composition of groundwater in the ephemeral river. The scattering of data points may be influenced by changes in the degree of the evaporation and the intensity exchange of cations (Post et al., 2017). The main processes controlling groundwater chemistry in this hydrotope are evaporation, mineral dissolution and cation exchange. The groundwater evolves from CaMgHCO_3 to NaHCO_3 along the suggested flow paths. Mineral dissolution increases with increasing depth (from perched aquifers to regional aquifer) as suggested by TDS values and the saturation indices of the hand-dug wells and boreholes. This conceptual model is similar to results obtained in Botswana by Stadler et al. (2010) for Kalahari aquifers in Botswana.

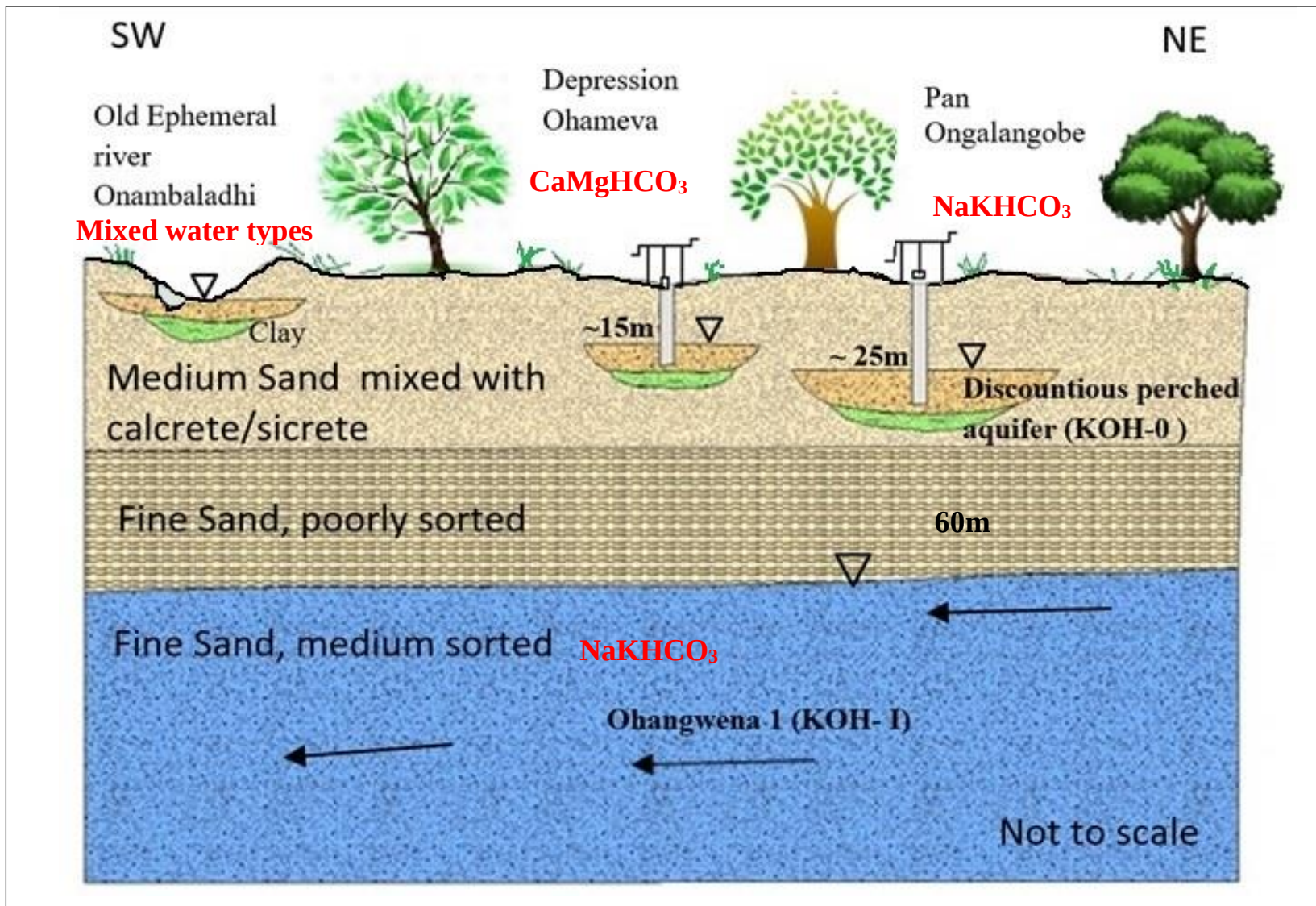


Figure 5-9: A conceptual model of the study area. The depth to water table of both perched aquifers and the regional aquifer increases from Southwest to Northwest

The study suggested that the water in the pans/depressions evolved from CaMgHCO_3 to NaKHCO_3 water type as a result of heterovalent cation exchange processes of calcium and sodium, where by calcium is sourced from calcrete and sandstone matrix dissolution while sodium is from plagioclase weathering. Hamutoko, et al. (2017) attempted to distinguish between cation exchange and silicate weathering in hand-dug wells (KOH-0) using the Jahnke principle (Jahnke, 1999) and concluded that both processes were taking place in same magnitude. On the other hand Schaller (2012) applied the same principle to the regional aquifer KOH-1 and concluded that silicate weathering is the dominant process but not ruling out cation exchange and evaporation processes in the hydrochemical genesis of the groundwater. Thus in this study an index of base exchange (Schoeller, 1965) known as chloro-alkaline indices (CAI) was used to verify the ion exchange between the groundwater and its host environment during residence or travel. The schoeller indices CAI-I and CAI-II were calculated using the following equations and all ions were expressed in meq/l (Liu et al., 2015):

$$CAI - I = \frac{Cl^- - (Na^+ + K^+)}{Cl^-} \dots\dots\dots (5.3)$$

$$CAI - II = \frac{Cl^- - (Na^+ + K^+)}{HCO_3^- + SO_4^{2-} + CO_3^{2-} + NO_3^-} \dots\dots\dots (5.4)$$

When the Schoeller indices (CAI-I and CAI-II) are negative, an exchange of Ca^{2+} or Mg^{2+} in groundwater with Na^+ or K^+ in aquifer materials takes place, Ca^{2+} or Mg^{2+} will be removed from solution and Na^+ or K^+ will be released into the groundwater. Negative value also indicate chloro-alkaline disequilibrium and the reaction is known as cation anion exchange reaction. The host rocks are the primary sources of dissolved solids in the water during this process. In contrast, positive values indicate base exchange reaction. In the present study, all groundwater samples have negative schoeller index values with exceptions of five samples from Omboloka perched aquifer

which have a positive Schoeller index. This means cation–anion exchange reaction dominates in this area in both perched aquifers and regional aquifer and is responsible for the amount of cation in the groundwater. HCO_3^- , which is the dominant anion in the area, is usually derived from CO_2 in the soil zone and dissolution of calcite and dolomite. It is commonly found in recharge zones because of high solubility of calcite and dolomite when it comes in contact with CO_2 rich water (Freeze and Cherry, 1979). Thus, its presence in high amounts suggest that these are recharge areas.

The proposed geochemical models suggest that NaHCO_3 observed in the ephemeral river perched aquifer is a result of evaporative concentration at/near soil surface while in the perched aquifers in the pans and in the regional aquifer it is the result of weathering pedogenic carbonates minerals and sodium-rich silicate minerals by action of dissolved CO_2 in the soil zone. The carbonate system plays a major role in this area. However, it must be noted that these models are not unique and other models using different or additional phases may yield similar results. For instance, using K-feldspar instead of albite in model B and adjusting the stoichiometric coefficient of the equation. Yet the conceptual model remains the same and dissolution of carbonate minerals, weathering of silicates and cation exchange remain the principal processes.

5.6.2 Groundwater recharge mechanisms and rates

All the groundwater samples plot close to the LMWL which indicate that they were recharged in modern climatic conditions or in similar climatic conditions to current climate. But, most samples plot below the LMWL which indicate strong evaporation effect. Though, samples from the perched aquifers from both hydrotopes have regression lines with a slope of 5.0 which typically indicate evaporation in countries with low relative humidity such as Namibia, samples from the open hand-

dug wells in the ephemeral river are more enriched in isotopes than those from pans/depressions. Furthermore samples from hand-dug wells in pans/depressions plot more close to the LMWL than those in the ephemeral river, which could imply different recharge mechanisms for the two hydrotopes. Direct recharge through preferential flow paths and local deep percolation appears to be the major recharge processes in the pans as their plot close to the LMWL while direct recharge through soil matrix (experiencing more evaporation) plays a major role in the ephemeral river as this plot further away from the LMWL. The slopes of the regression lines for the regional aquifer are 5.9 for pans/depressions and 3.9 for ephemeral rivers, respectively. The ephemeral river is affected by evaporation, while the pans/depression shows mixing. This could be mixing of the water affected by evaporation and the water not affected by evaporation. On the other hand, mixing could results from different water sources and recharge processes. Lindenmaier (2014) indicated that KOH-2 which is the deeper Ohangwena regional aquifer have three potential recharge pathways: possible recharge paths; firstly direct infiltration or percolation of the precipitation, secondly, recharge could have resulted from regional lateral recharge originating in the foothills of the Angolan Highlands and thirdly it could be from river bank exfiltration of the Cubango River. These recharge pathways may also be true for KOH-1, but are yet to be proven. Therefore, depleted isotope values in this study reveal that they may be recharged by rainfall infiltrating through preferential paths during large rainfall events or regional lateral recharge originating in the foothills of the Angolan Highlands. The latter fits well, as it is indicated that water still flow in the subsurface of the ephemeral river (Table 5.1) and thus the regional aquifer in this hydrotope is probably recharged through this process.

The water in the regional aquifer has a slightly more depleted source water for pans/depressions - 11.6, -51.8 for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ and -10.04, -67.91 for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ for ephemeral river, respectively,

than the perched aquifers -8.81, -59.02 for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ and -7.86, -50.9 for $\delta^{18}\text{O}$ and $\delta^2\text{H}$. However, because the regression line for the regional aquifer in the pans/depressions has a slope 5.9, which indicates mixing of water sources, therefore the point of intersection will not give the mean parent water. This is also indicated by the calculated mean parent water value which is relatively lower than that of the perched aquifer though they are plotting together. Harrington et al. (2002) showed that depleted isotopes in precipitation are usually associated with very large rainfall events, either of high intensity or long duration. This indicate that recharge to KOH-I (regional aquifer) is limited to larger amount events while small amount events can recharge KOH-0 (perched aquifer) as the mean parent water source is slightly enriched. Then again, the regional aquifer with exception at Omboloka, has depleted isotopic values, though it indicates recharge by large rainfall events, it can also indicate paleo-groundwater. The latter fits well with a study by Geyh (1997) who dated groundwater from KOH-1 with ^{14}C and found groundwater age between 2500 and 20 000 years (Fig. 5.10). Geyh (1997) dated groundwater in the regional aquifer at Omulonga to have an age of 10475 ± 185 , this indicate paleo-groundwater. Unfortunately, the author didn't not date other villages sampled in this study, but dated villages like Ondema which is close to Oshana-shiwa and Omboloka to have an age of 6970 ± 80 , this suggest this are young water as compared to the ephemeral river. Ages from the perched aquifers are yet to be determined. The lack of fractionation of the stable water isotopes as the chloride content increases signifies dissolution as a dominant process in the pans, while in the ephemeral river no trend was established and this indicate more than one geochemical process controls this aquifer.

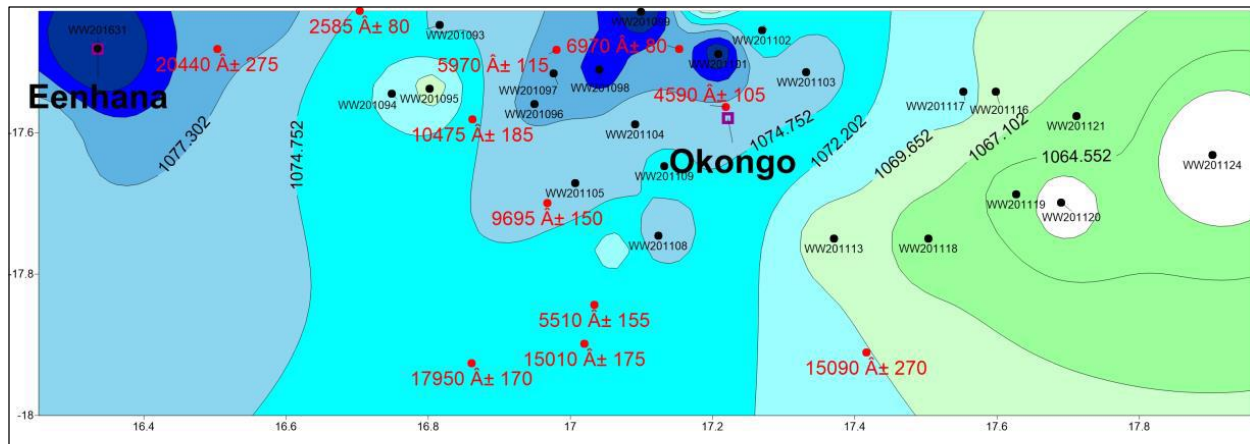


Figure 5-10: Plot of KOH-1 potentiometric surface with groundwater C-14 ages in years. Ages given in red. Source (Ananias, 2015)

Recharge rates are higher in the pans/depressions and range from 36.9 mm/a to 127.7 mm/a and 25.5 mm/a to 162.0 mm/a for perched aquifers and the regional aquifer respectively than in the ephemeral river where recharge rates in perched aquifers changes from 35.5 mm/a to 80 mm/a and 25 mm/a to 87.4 mm/a for the regional aquifer. It's commonly discussed (e.g. De Vries et al., 2000; Xu and Beekman, 2003) that pans/depressions are recharge zones in the Kalahari. Focused, or localized recharge is the dominant processes in these kind of areas according to Scanlon et al (2006), where by water infiltrates through cracks and fractures. Furthermore, pans and depressions are topographically the lowest points in the area and thus surface water flows toward the centre and accumulates there. Additionally, because of the loamy/clay soils in the pans and depressions which are good for agriculture, they are covered in fields which are cultivated every year during the rainy season. Scanlon et al. (2006) discussed that cultivation enhances recharge, in fact in South-western United States changing from natural grasslands and shrublands to cultivated ecosystems have altered systems from discharge (ET) to diffuse recharge of approximately 24 mm per annum. The authors, further emphasised that cultivation increases surface runoff and focusses recharge in endoreic ponds as observed in the Great Plains (N. America) and in Niger (Africa). Thus high recharge rates observed in pans/depressions may have been enhanced by cultivations.

It was also not possible to estimate surface runoff into the wells, but it should be noted as a source of uncertainty when these values are used.

Several authors as discussed in chapter 2 who have worked in the Kalahari concluded that high recharge rates and preferred flow paths are commonly associated with places like pans, areas with shallow calcrete, and areas with less sand cover (Allison and Hughes, 1983; de Vries et al., 2000; Külls, 2000). Therefore our results are in agreement with previous research and recharge rates obtained for the regional aquifers falls in the same ranges. Külls (2000) estimated recharge rates between 1.6 and 4% in North-Western, Namibia using CMB while Van Tonder and Kirchner, 1990 estimated recharge rates between 2.9 to 4.9% in South Africa. Generally recharge in the Kalahari aquifers estimated so far spanned from 0.1 to 25%, but commonly it is less than 10% as summarised in Abiye (2016), Klock (2001), Külls (2000) and Xu & Beekman (2003). But it must be highlighted here that most of the previous study that have recharge rates mainly up to 10 % are usually for the regional aquifer, studies focusing on perched aquifers are not known to the author.

5.6.3 Relationship between KOH-0 and KOH-1

In the ephemeral river hydrotope no mixing/ common origin of the perched aquifer and regional aquifer is suggested by the scatter plots (Fig. 5.5, 5.6 and 5.7). This means the infiltrating water recharges the perched aquifer but does not reach the regional water table. This also suggests that if any contamination is introduced in the perched aquifer, the likelihood of it to reach the regional aquifer is very limited. In the pans and depressions, the overlapping hydrochemistry and isotopic compositions suggests mixing of the aquifers/ groundwater of a common origin. Therefore, pans that act as recharge zones for the perched aquifers might potentially also recharge the regional aquifer. Ananias (2015) concluded that in the areas where the most hand-dug wells are found, there

is a relatively high hydraulic gradient in KOH-1 and this implies that KOH-0 maybe infiltrating into KOH-1. However, the amount of horizontal flow within KOH-1 is much larger than to the vertical flow through the aquitard, and thus the mixing of groundwater in KOH-0 and KOH-1 may be insignificant (Ananias, 2015).

5.7 Conclusion

We investigated the interaction between the perched aquifer KOH-0 and the regional aquifer KOH-1 and developed a conceptual and geochemical models in order to understand recharge mechanisms and geochemical processes in the CEB. Integrated isotopic and hydrochemical tracers provided a comprehensive understanding of the processes of mineralization that underpin geochemical evolution of the groundwater. The main geochemical processes responsible for the observed chemical composition in groundwater are i) strong evaporation, ii) carbonate dissolution and iii) alkali enrichment as a result of silicate weathering and cation exchange. In the ephemeral river rainwater infiltrates through soil matrix to recharge the perched aquifer, but it does not reach the regional aquifer. In contrast, pans/depressions are recharged through infiltration via preferential flow paths. The hydrochemical characteristics of the aquifers, i.e. Ca^{2+} and HCO_3 dominance, confirmed recharge by fast infiltration water or recharge water characterized by a diffuse soil passage. The rainwater is subjected to strong evaporation before and during infiltration. Higher recharge rates are estimated for the pans and depressions in comparison to the ephemeral river.

A hydrochemical and isotopic relationships between the aquifers were established. This helps to improve the understanding of geochemical evolution of the groundwater system in the CEB. The perched aquifers in the ephemeral river have less incommon with the deep groundwater. Thus,

groundwater in the regional aquifer is not threatened by contamination through the perched aquifers. On the other hand, our results suggest an interaction between the two aquifers in the pans/depressions through preferential flow paths although the low permeability and large thickness of the aquitard that is between the perched aquifer and the regional aquifer may limit the magnitude. It is therefore recommended to develop a groundwater flow model to understand this interaction further and also to test if abstracting from either aquifer will affect the other aquifer. The model should also evaluate the effect of land-use changes and climate change effects. Groundwater ages may also shed more light as to the nature of to this interaction.

6 Conclusions

The main goal of this study was to determine groundwater recharge processes and rates as well as assess the groundwater quality for perched aquifers in the Cuvelai-Etosha Basin. Though quantification of groundwater recharge mechanisms and geochemical processes is a vital aspect of IWRM, it's often limited by lack of data. This is also the case for the perched aquifers in the CEB; they are poorly understood aquifers yet they are used as a day to day source of water supply in rural areas. Therefore, in this study hydrochemical and isotopic methods were used to understand groundwater recharge mechanisms and geochemical processes. Firstly, groundwater was characterized with regard to hydrochemical composition and stable isotopes ($\delta^{18}\text{O}$ and $\delta^2\text{H}$), and groundwater quality was assessed. Secondly, the spatio-temporal variations of the groundwater hydrochemical composition and stable water isotopes were determined. Thirdly interaction between the perched aquifer and the regional aquifer was assessed, and finally both, a conceptual and a geochemical model were developed.

Perched aquifers occur as discontinuous aquifers and are very heterogeneous and thus they are very difficult to characterise as a single aquifer. Point data could not be interpolated to the whole catchment and thus a hydrotope approach was adopted for distinct examination. This approach groups different land surfaces according to their natural mosaic structure and each group is treated as one modelling domain. It was concluded that perched aquifers in the CEB occur mainly underneath large pans, depressions and ephemeral river hydrotopes. Hence point data was discussed based on these two hydrotopes. The overview of results obtained in this study is presented in Fig. 6.1. According to WHO recommendations, the water quality in most wells is (theoretically) not permissible for drinking and domestic purposes because of high turbidity, microbiological parameters (e.g. bacteria),

TDS, potassium, fluoride, sulphate, and nitrate concentrations, which are above acceptable values for drinking water. Shallow wells in the ephemeral river generally have a low concentration of minerals, the conceptual model suggests that about 90% of the rainfall water is evaporated and this results in the chemical composition of groundwater in the ephemeral river. The main concern within these wells is high turbidity and microbiological parameters. Deep wells on the other hand, located in pans and depressions have high fluoride and potassium concentrations as a result of the local lithology, while high nitrate concentration originates from manure. Fluoride increases with depth, as it has higher concentrations in the boreholes that are tapping the deeper regional aquifer. In Omusati, sulphate, chloride and TDS are the most problematic substances and these result from dissolution of evaporitic minerals such as gypsum and halite.

A distinct spatial difference between samples from Omusati and Ohangwena regions was observed. The spatial heterogeneity as shown by the TDS, hydrochemical water types, chloride, nitrate and fluoride can be attributed to lithological, climatic and anthropogenic factors. For example, in Ohangwena, deep wells are characterized by two water types; predominantly CaMgHCO_3 and NaKHCO_3 , whereas shallow wells are dominated by mixed water types. In Omusati, CaSO_4 is the dominant water type with CaMgHCO_3 and $\text{NaSO}_4/\text{NaCl}$ types occurring in some places. The dominant geochemical processes responsible for the observed chemical composition in groundwater are strong evaporation, dissolution of carbonate minerals (calcite and dolomite) and evaporitic minerals (gypsum and halite) and silicate weathering and cation exchange. The hydrochemical water types implies that pans in Ohangwena are recharge zones while in Omusati they are discharge zones.

The water stable isotopes ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) signatures suggests that in the ephemeral river rainwater infiltrates through soil matrix to recharge the perched aquifer, but it does not reach the regional

aquifer. In contrast, the pans/depressions are recharged through mixed processes; i) water that is affected by evaporation either before or after infiltration and ii) water that infiltrates through fast preferential flow paths. Interaction with the regional aquifer is also indicated.

Temporal variations in chloride concentration indicate the timing of groundwater recharge; it is observed that recharge is taking place at different times during the rainy season, depending on the rain season. Delay in rain season corresponds to delay in groundwater recharge. For example in 2014 recharge occurred only in June, while in 2015 and 2016 recharge was observed earlier in March. The mean parent isotopic composition for shallow hand-dug wells in the ephemeral river is -7.8‰ for $\delta^{18}\text{O}$ and -51.8‰ for $\delta^2\text{H}$, for deep hand-dug wells in the pans and depressions is -8.7‰ and -58.2‰ for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ as well as -8.6‰ and -57.5‰ for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ for hand-dug wells in Omusati region. High recharge rates are estimated for the pans and depressions in comparison to the ephemeral river as recharge percentage of mean annual rainfall ranges from 7.9% to 17.8% for perched aquifers in ephemeral river and 7.3 % to 25.5% for perched aquifers in pans/depressions, respectively. Because of the limited input data, it is not recommended to take recharge rates as confirmed but rather as a rough first estimate.

The perched aquifers in the ephemeral river have less interaction with the deep groundwater, thus groundwater in the deep regional aquifer is not threatened by groundwater contamination in these hydrotopes. Since Geyh (1997) dated groundwater from the regional aquifer at Omulonga to have age of 10475 ± 185 and from the hydrochemistry and isotopes the all show old groundwater signatures, it can concluded that the water in deep regional aquifer in the ephemeral river is paleo-groundwater. On the other hand, for the pans/depressions, there is a potential interact between the two aquifers although low permeability and large thickness of the aquitard may limit the rate of these processes.

	Ohangwena region			Omusati region	
Hydrotype	Pans/depressions		Ephemeral River	Pans	
Type of Hand-dug wells	Cylindrical-shaped deep wells type 1: Water level 5 - 17 m. b.g.l	Cylindrical-shaped deep wells type 2: Water level 17-30 m. b.g.l	Funnel-shaped Shallow wells: Water level 0-5 m. b.g.l	Funnel-shaped Shallow wells: Water level 0-5 m. b.g.l	Funnel-shaped Shallow wells: Water level 5 -10 m. b.g.l
Villages sampled	Oluwaya, Ohameva, Omboloka	Oshana-shiwa, Okamanya, Ongalangobe	Epumbalondjaba, Omulonga Onambaladhi, Walye-inda	Olumpelengwa, Okakewa	Olumpelengwa, Amarika, Uusathima, Otongo, Onakapanda, Akutsima, Okambata
Geology	Fine sands, clay and calcrete		Medium to coarse grained Sand	Fine sands, clay and calcrete	
Main water types	CaMgHCO ₃	NaKHCO ₃	Mixed Cation-HCO ₃ NaK-mixed Anions	CaMgHCO ₃	CaSO ₄ , NaSO ₄ / NaCl
Substances of concern	Microbiological, K, NO ₃ , F		Turbidity, Microbiology	Turbidity, Microbiology	Turbidity, Salinity, Microbiology, Sulphate
Recharge mechanisms	Direct recharge through preferential flow paths & localised local deep percolation. Recharge only occur from high-intensity or large rainfall events. Mixing of recharge sources is observed.		Direct infiltration through soil matrix	Direct infiltration through soil matrix mixed with preferential flow paths. However this area is rather characterised as discharge areas	
Geochemical processes	Carbonates dissolution, silicate weathering, Evapotranspiration	Cation exchange, silicate weathering, Evapotranspiration	Evapotranspiration, cation exchange	Evapotranspiration, Dissolution of carbonate rocks	Evapotranspiration, Dissolution of evaporites
Temporal variations	During rainy season,: chloride and nitrate declines, Isotope values become depleted During dry season: Chloride and nitrate concentration increases, isotope values become enriched			Chloride and isotope ratios are observed but not following a particular pattern, however TDS increases during dry season	
Recharge rate from Chloride	Median: 17.0 % (85.2 mm/a) Mean: 17.9 % (89.6 mm/a)	Median: 16.8% (84.2 mm/a) Mean:26.6 % (134.7 mm/a/)	Median: 11.57% (52.1 mm/a) Mean:17.04 % (76.7 mm/a)	Not applicable because of other sources of chloride in the area other than rainfall	
Interaction with deep regional aquifers	Possible interaction with the regional aquifer due to overlapping hydrochemical composition and isotopic signatures.		No interaction with the regional aquifer is observed.	It was not analyzed in this project but the regional water level is shallow and thus it sometimes difficult to differentiate between perched and regional aquifer	

Figure 6-1: The figure shows an overview of the sites sampled and results obtained in the study.

7 Recommendations

- This study is the first of its kind to look at spatial and temporal patterns in perched aquifers at a local scale in Namibia and thus the results have important implications for future research. The data generated and methodologies developed here can be used in areas with similar hydrological and hydrogeological setting and thus also form as baseline and guidance for future research.
- At the beginning of this project, there were no piezometers in the perched aquifers and only in October 2016 five monitoring boreholes were drilled and thus the water level fluctuation data is very limited. Therefore it is recommended, to establish long term monitoring stations for water levels, water quality and stable isotopes.
- Currently, nitrate contamination is associated with anthropogenic sources (manure) and therefore proper planning of better infrastructure and protection zones will be required to avoid further pollution.
- Natural contaminants such as fluoride, TDS, sulphates etc. would require treatment for the water to be usable.
- Furthermore, it is usually recommended that more than one method is applied to estimate groundwater recharge, however with relatively limited data, it was not possible to use further methods. Therefore quantification of groundwater recharge could be improved by;
 - A soil water balance model (Diffuse recharge) in the ephemeral river and
 - Hydrographs (preferential paths) in the pans and depressions.
- It is recommended to develop groundwater flow model for understanding the interaction of perched and regional aquifers. The model should also evaluate the effect of land-use changes

and climate change effects as well as estimate safe abstractions rates for the perched aquifers.

The data generated in this research can be used to constrain and verify these models.

- Strong evaporation limits groundwater recharge, thus communities should be encouraged to harvest rain water e.g. in cisterns and use harvested water during rainy season, to prevent over-exploitation of the perched aquifers.
- Education on basic water usage and protection will also be an advantage i.e. the local communities should be trained/ made aware of the limited resource and how much water can be abstracted.

On-going projects

Currently there are two on-going MSc projects within the SASSCAL task 007 that will compliment these results include the determination of groundwater ages for perched aquifers and regional aquifer and delineation of the extend of perched aquifers using geophysics. Groundwater ages may also shed more light on the interaction between perched and regional aquifers. Ceramic and bone-char based filters are currently tested at household level to determine if they are feasible in removing fluoride and microbial contaminants and accepted by local communities.

8 References

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9 Appendices

Village	Well_type	Lat	Long
Akutsima	Omusati	-18.32000	14.95778
Amarika central wellfield	Omusati	-18.48111	15.35306
Amarika north wellfield	Omusati	-18.38917	15.28917
Amarika Southwellfield	Omusati	-18.52528	15.34917
Okakewa I	Omusati	-18.64639	15.45083
Okakewa II	Omusati	-18.64833	15.45472
Okakombe	Omusati	-18.20500	14.94444
Okambata I	Omusati	-18.35667	14.84306
Okambata II	Omusati	-18.34889	14.85306
Okambata III	Omusati	-18.35528	14.845
Olumpelengwa central	Omusati	-18.62652	15.03611
Olumpelengwa deep	Omusati	-18.66333	15.13
Olumpelengwa shallow	Omusati	-18.58972	14.94222
Onakapanda	Omusati	-18.39122	15.17239
Onakapanda I	Omusati	-18.39222	15.17139
Onakatili I	Omusati	-18.38194	15.045
Onakatili II	Omusati	-18.41000	15.04361
Onambandje	Omusati	-18.39444	15.08694
Otongo I	Omusati	-18.39417	15.10056
Otongo II	Omusati	-18.49806	15.27333
Uusathima I	Omusati	-18.54750	14.88056
Uusathima II	Omusati	-18.53778	14.87417
Ohameva I	Ohangwena_Deep well	-17.58411	17.09300
Ohameva II	Ohangwena_Deep well	-17.58311	17.09400
Okamanya	Ohangwena_Deep well	-17.53117	17.20073
Okamanya handpump	Ohangwena_Deep well	-17.53152	17.20070
Oluwaya	Ohangwena_Deep well	-17.53908	17.05647
Oluwaya field	Ohangwena_Deep well	-17.53808	17.05747
Oluwaya handpumb	Ohangwena_Deep well	-17.53747	17.05842
Omboloka dune	Ohangwena_Deep well	-17.40878	17.13767
Omboloka Pan	Ohangwena_Deep well	-17.40678	17.13072
Ongalangobe	Ohangwena_Deep well	-17.49347	17.26575
Ongalangobe I	Ohangwena_Deep well	-17.49447	17.26375
Ongalangobe II	Ohangwena_Deep well	-17.49347	17.26475
Oshana-shiwa	Ohangwena_Deep well	-17.51525	17.24986
Oshana-shiwa handpump	Ohangwena_Deep well	-17.51438	17.25073
Epumbalondjaba	Ohangwena_Shallow well	-17.63208	16.80992
Omulonga I	Ohangwena_Shallow well	-17.55889	16.89528

Appendix A: Location of sampling sites

Omulonga II	Ohangwena_Shallow well	-17.56572	16.88900
Onambaladhi I	Ohangwena_Shallow well	-17.71669	16.77308
Onambaladhi II	Ohangwena_Shallow well	-17.71711	16.77228
Onambaladhi III	Ohangwena_Shallow well	-17.71611	16.77128
Oshikunde I	Ohangwena_Shallow well	-17.55364	16.74981
Oshikunde II	Ohangwena_Shallow well	-17.55058	16.74911
Walye inda	Ohangwena_Shallow well	-17.66661	16.81269
Walye inda field	Ohangwena_Shallow well	-17.66561	16.81169

Appendix B: Raw hydrochemical and isotopic data collected in this study

Village	No	Sampling date	Water level [m]	Temp [°C]	O ₂ -content [mg/l]	ORP [mV]	pH	EC [μS/cm]	HC O ₃ ⁻ [mg/l]	Cl ⁻ [mg/l]	F ⁻ [mg/l]	SO ₄ ²⁻ [mg/l]	NO ₃ ⁻ [mg/l]	Na ⁺ [mg/l]	K ⁺ [mg/l]	Mg ²⁺ [mg/l]	Ca ²⁺ [mg/l]	SiO ₂ [mg/l]	Balance [%]	δ ¹⁸ O [‰]	δ ² H [‰]
Akustima	JT02-37	Sep-14	walk in	20.2		-1	7.35	2530	24	26	1.1	1721	2.3	22	22	40	700		-1	-6.33	-44.9
Akustima	JT03-14	Mar-15	2 - 3	21.6		-334	7.63	3420	386	43	0.954	3200	14.7							-4.23	-32
Akutsima	JT01-02	Jun-14	walk in	18.5		-78	7.19	2030	25	4	0.6	1198	0.6	24	41	39	688		-18	-5.46	-35.3
Amarika	JT08-14	Oct-16	6	26.7		79.1	7.46	14420	1168	5584	0.63	3503	90.3	5070	35.5	247	252	104	1	-5.05	-46.3
Amarika central wellfield	JT01-17	Jun-14	5	15.6		225	7.75	526	221	21	0.3	<1	0.9	76	13	6.8	26		13	-3.1	-25.1
Amarika central wellfield	JT02-24	Sep-14	walk in	21.7		138	8.18	2148	989	218	0.4	2	2.9	373	24	47	23		0	-2.49	-33
Amarika central wellfield	JT03-08	Mar-15	5	24.4		132	7.01	2750	249	1393	0.233	54	47.2							-6.66	-50.6
Amarika central wellfield	JT05-07	Nov-15		21.1		-283	7.89	2430	1080	553	0.345	174	0.10	653	18.4	42.7	74.8	85.8	-1	-3.76	-35.5
Amarika central wellfield	JT07-21	May-16		17.7		28	7.93	222	382	342	0.029	26.6	1.82	124	22.8	36.4	151	68.7	0	-5.2	-34.7
Amarika north wellfield	JT01-18	Jun-14	5	17.2		236	7.44	1338	167	186	0.2	15	6.4	31	8.6	25	126		-4	-5.86	-48.7
Amarika north wellfield	JT02-23	Sep-14	walk in	14.1		146	7.51	1607	420	297	0.4	26	2.2	41	8.5	37	256		-1	-4.77	-42.5

Appendix B: Raw hydrochemical and isotopic data collected in this study

Village	No	Sampling date	Water level [m]	Temp [°C]	O ₂ -content [mg/l]	OR P [mV]	pH	EC [µS/cm]	HC O ₃ ⁻ [mg/l]	Cl ⁻ [mg/l]	F ⁻ [mg/l]	SO ₄ ²⁻ [mg/l]	NO ₃ ⁻ [mg/l]	Na ⁺ [mg/l]	K ⁺ [mg/l]	Mg ²⁺ [mg/l]	Ca ²⁺ [mg/l]	SiO ₂ [mg/l]	Balance [%]	δ ¹⁸ O [‰]	δ ² H [‰]
Amarika north wellfield	JT03-07	Mar-15	4	22.9		153	7.16	2174	342	42	0.338	9	3.45							-5.27	-42.2
Amarika north wellfield	JT05-06	Nov-15		20.6		-319	7.83	1827	441	443	0.382	309	0.043	469	11.5	21.9	71.5	76.4	0	-5.13	-36.8
Amarika north wellfield	JT07-20	May-16		19.7		-272	7.18	2210	357	8.53	0.163	1.75	0.047	18.6	22.2	14.3	62	60.9	-4	-5.74	-35.3
Amarika South wellfield	JT01-16	Jun-14	about 3.5	18.9		221	6.6	146	56	9	0.2	94	0.8	8.5	8.2	5.4	54		-4	-3.49	-27.2
Between Onambaladhi and Walye-inda	JT02-14	Sep-14	walk in	18.1		14	6.3	182.6	13	19	0.4	50	2.4	39	6.2	1.9	6.1		0	6.73	9.2
Between Onambaladhi and Walye-inda	W02-02	Mar-14	walk in	30.7	8.27		5.67	196	1.8	28	0.2	25	2.2	32	4.6	0.8	2		3	-2.68	-20.7
Elundu	JT06-22/ET01-01	Mar-16		32.1		28.6	8.74	89.3												-6.3	-48.1
Epumbalodjaba	JT04-25	Aug-15	walk in	26.2		25.9	6.41	181.1												-4.94	-36
Epumbalon djaba	JT02-10	Sep-14	walk in	18.4		147	5.68	155.5	7.6	7.5	0.1	26	8.3	8.2	15	3.2	7.1		5	-5.22	-36.6
Epumbalon djaba	JT03-22	Mar-15	walk in	34.9		149	5	183.4	14	15.1	0.078	15	456							-5.53	-36.4
Epumbalon djaba	JT05-20	Nov-15		35.4		46.2	9.28	138.3	58.6	14.8	0.114	19.5	2.35	14.2	16.8	3.53	9.49		0	-1.1	-17.1

Appendix B: Raw hydrochemical and isotopic data collected in this study

Village	No	Sampling date	Water level [m]	Temp [°C]	O ₂ -content [mg/l]	OR P [mV]	pH	EC [µS/cm]	HC O ₃ ⁻ [mg/l]	Cl ⁻ [mg/l]	F ⁻ [mg/l]	SO ₄ ²⁻ [mg/l]	NO ₃ ⁻ [mg/l]	Na ⁺ [mg/l]	K ⁺ [mg/l]	Mg ²⁺ [mg/l]	Ca ²⁺ [mg/l]	SiO ₂ [mg/l]	Balance [%]	δ ¹⁸ O [‰]	δ ² H [‰]
Epumbalon djaba	JT06-16	Mar-16		25.8		131.2	8.3	99.8	48.4	10.4	0.093	2.7	0.327	10.1	10.9	3.39	8.37	69	10	-2.6	-26.4
Epumbalon djaba	JT07-03	May-16		20.6		133.2	7.71	144	20.9	12.7	0.091	20.2	37.1	13.4	14.3	4.4	10.3	74.9	3	-3.63	-28.3
Epumbalon djaba	JT08-24	Oct-16	walk-in				5.58	302	47.7	12.6	0.399	18.6	96.3	26.4	31.9	7.95	12.5		2	-5.65	-45.2
Epumbalon djaba	W02-013	Mar-14	walk in	32.4	10.8		7.97	215.1	18	1	0.1	10	5.5	4.1	13	2.4	5.8		0	-5.04	-36.8
Epumbalon djaba	W02-216	Jun-14		24.4	5.75		5.81	170	21	7.24	0.065	13.8	33.2	6.6	14.2	3.04	7.07	68.6	-5	-5.91	-42.4
Epumbalon djaba	W04-018	Jun-15		20.5	4.24		4.76	163	21.7	2.4	0.073	14.8	26.5	2.6	2.6	2.64	6.48	78	-3	-6.29	-43.4
Epumbalon djaba borehole	W02-218	Jun-14		24.4	7.6		9.04	2142	605	13.2	4.7	20.2	1.2	288	7.7	0.5	1.56	49.1	8	-9.1	-64
Epumbalon djaba borehole	W04-020	Jun-15		23	8.22		8.76	2102	648	21.2	4.59	18.3	1.4	285	6.8	0.475	1.45	47.9	3	-9.36	-65.4
Epumbalon djaba surface water	JT02-20	Sep-14																		13.59	45
Epumbalon djaba surface water	JT04-26	Aug-15							25.5											21.33	41
Epumbalon djaba surface water	JT06-17	Mar-16		26.4		105.4	7.95	523												4.38	3.1
Epumbalon djaba surface water	W02-014	Mar-14																		-0.22	-16.5

Appendix B: Raw hydrochemical and isotopic data collected in this study

Village	No	Sampling date	Water level [m]	Temp [°C]	O ₂ -content [mg/l]	ORP [mV]	pH	EC [μS/cm]	HC O ₃ ⁻ [mg/l]	Cl ⁻ [mg/l]	F ⁻ [mg/l]	SO ₄ ²⁻ [mg/l]	NO ₃ ⁻ [mg/l]	Na ⁺ [mg/l]	K ⁺ [mg/l]	Mg ²⁺ [mg/l]	Ca ²⁺ [mg/l]	SiO ₂ [mg/l]	Balance [%]	δ ¹⁸ O [‰]	δ ² H [‰]
Epumbalon djaba surface water	W02-217	Jun-14																		8.22	22.1
Epumbalon djaba surface water	W04-019	Jun-15																		13.57	49.3
Ohameva	JT02-09	Sep-14	21.15	25.5		223	7.8	508	238	2	2.9	3	13	1.2	6.6	32	64		-1	-7.43	-52.8
Ohameva	JT03-27	Mar-15	21.5	26.5		27	7.68	542	232	7.32	2.54	1	742							-7.71	-51.8
Ohameva	JT04-15	Aug-15	14.1	23.5		85.2	7.96	577	295	4.78	2.5	4.7	62.1	4.3	21.8	29.3	73.2	221	5	-7.71	-55.4
Ohameva	JT07-09	May-16	13.53	25.4		164.7	8.01	407	293	2.84	2.95	2.68	65.8	1.3	9.9	29.8	62	109	-3	-7.86	-56.6
Ohameva	W02-024	Mar-14	2.9	26	5.21		7.96	518	242	2.3	2.4	2.8	9.1	0.7	6.8	26	59		4	-7.3	-52.3
Ohameva	W02-22	Jun-14		24.8	6.62		7.69	605	285	3.06	2.92	2.26	53.8	1.5	7	29.2	64.2	221	0	-7.36	-53.7
Ohameva	JT05-18	Nov-15	14.2	27		77.3	7.64	407	325	4.32	2.4	2.25	45.6	4.4	12.4	27.5	67.3		-2	-8.02	-55.5
Ohameva	W01-075	Nov-13	21.24	26.1	6.3		7.6	562	292	2.95	2.77	2.01	46.9	1.3	6.7	29.1	65.6	95.4	1	-7.47	-52.7
Ohameva 1	JT08-5	Oct-16	13.92	29.8		68.4	7.14	390	295	2.73	2.87	2	59	1.5	10.9	31.3	65.7	123	1	-7.33	-56.1
Ohameva 2	JT08-6	Oct-16	15.48	26		177.3	7.37	396	316	2.99	2.38	1.91	35.5	4.7	13	27.2	67.5	118	1	-7.47	-55.9
Ohameva I	JT06-2	Mar-16		26.2		151.5	7.81	407	330	4.71	2.06	2.03	43.3	3.1	10.9	28.1	72.3	109	0	-7.85	-51.6

Appendix B: Raw hydrochemical and isotopic data collected in this study

Village	No	Sampling date	Water level [m]	Temp [°C]	O ₂ -content [mg/l]	ORP [mV]	pH	EC [µS/cm]	HC O ₃ ⁻ [mg/l]	Cl ⁻ [mg/l]	F ⁻ [mg/l]	SO ₄ ²⁻ [mg/l]	NO ₃ ⁻ [mg/l]	Na ⁺ [mg/l]	K ⁺ [mg/l]	Mg ²⁺ [mg/l]	Ca ²⁺ [mg/l]	SiO ₂ [mg/l]	Balance [%]	δ ¹⁸ O [‰]	δ ² H [‰]
Ohameva I	W04-021	Jun-15		24.8	3.83		4.45	628	314	5.67	2.55	1.99	71.2	3.4	2.8	28.8	75.5	27	-2	-7.8	-56.3
Oidimba surface water	W02-017	Mar-14																		0.52	-9.4
Okakewa I	JT01-19	Jun-14	walk in	23.2		228	8.21	232	75	13	0.2	8	1	15	7.6	4.7	19		-5	-2.54	-28.8
Okakewa II	JT01-20	Jun-14	walk in	22.6		229	8.85	278	91	2.6	0.2	9	0.8	17	8.1	7.2	39		-28	-1.65	-25.3
Okakombe	JT01-01	Jun-14	1	16.8		-75	7.2	2220	202	46	0.1	2174	1	50	43	50	778		-6	-3.64	-27.6
Okakombe	JT03-15	Mar-15	walk in	28.1		-383	7.02	5240	935	4771	0.199	3150	195							-4.58	-33
Okakombe	JT02-38	Sep-14	walk in	19.3		-288	7.22	3970	64	134	0.1	1669	0.9	79	22	57	651		-2	-3.46	-33.5
Okakombe	JT04-11	Aug-15	walk in						61.8											-0.15	-21.4
Okamanya	JT03-32	Mar-15	17.3	26.2		180	7.79	664	330	21	1.59	0	68.1							-7.48	-51.9
Okamanya	JT05-14	Nov-15	19.1	25.2		77.6	7.49	505	316	10.9	1.53	1.71	106	15	31.1	22.8	73		-2	-8.09	-55.8
Okamanya	W02-29	Jun-14		24.4	3.29		7.65	754	422	17.9	2.04	2.03	34.4	8.6	34.7	29.5	86	102	-1	-6.99	-50.2
Okamanya	W04-027	Jun-15																		-6.64	-47.2
Okamanya	JT06-03	Mar-16	18.21	26.6		22.2	7.66	263	190	7.19	0.444	1.97	33.3	2.6	21.1	21.1	49.1	49.1	11	-6.28	-39.3
Okamanya	JT08-9	Oct-16	19.7	26.7		141.2	7.32	488	321	9.3	1.3	1.58	98.5	19.3	29.2	20.9	76.1	103	-1	-7.59	-57.6

Appendix B: Raw hydrochemical and isotopic data collected in this study

Village	No	Sampling date	Water level [m]	Temp [°C]	O ₂ -content [mg/l]	ORP [mV]	pH	EC [μS/cm]	HC O ₃ ⁻ [mg/l]	Cl ⁻ [mg/l]	F ⁻ [mg/l]	SO ₄ ²⁻ [mg/l]	NO ₃ ⁻ [mg/l]	Na ⁺ [mg/l]	K ⁺ [mg/l]	Mg ²⁺ [mg/l]	Ca ²⁺ [mg/l]	SiO ₂ [mg/l]	Balance [%]	δ ¹⁸ O [‰]	δ ² H [‰]
Okamanya	W01-105	Nov-13		25.1	3.91		7.4	779	331	14.8	1.78	1.72	29	2.7	34.5	27.3	83.4	83.6	7	-7.64	-54.1
Okamanya	W02-004	Mar-14		25.3	1.34		7.73	722	357	5.5	1.6	5.9	3.8	9.4	38	27	79		2	-7.32	-52
Okamanya Hp	JT02-04	Sep-14	17.15	24.7		173	7.38	621	265	14	0.8	3	2.2	3.4	14	22	90		-7	-7.42	-49.9
Okamanya Hp	JT03-31	Mar-15	17.75	27.4		52	7.24	734	254	21.9	0.769	0	573							-8.25	-55.5
Okamanya Hp	JT04-19	Aug-15	walk in	25.8		21.5	7.76	728	365	15.7	0.887	3.21	221	2.1	26.3	23.9	97.4	102	-15	-8.07	-56.1
Okamanya Hp	JT05-13	Nov-15		25.4		3.7	7.65	539	325	14.9	0.869	3.75	120	10.8	24.6	22	93.3		-2	-8.23	-55
Okamanya HP	JT06-02	Mar-16	17.37	28.7		60	7.63	523	325	15.2	0.887	2.31	213	2.1	28.4	23.2	91.1	100	-12	-8.76	-56.1
Okamanya Hp	JT07-05	May-16		26.3		48.2	7.72	513	325	13.6	0.836	2.17	118	10.5	25.6	22.1	87.7	93.9	-3	-8.04	-56.1
Okamanya HP	JT08-8	Oct-16	20.45	27.9		7.9	7.13	514	328	13.4	0.779	2.04	115	11.9	27	22.5	92	98.5	0	-7.73	-57.2
Okamanya Hp	W01-103	Nov-13		25.7	4.53		7.4	832	325	19.4	0.885	2.17	146	2.3	27.3	25	99.3	80.3	-3	-7.95	-56.7
Okamanya Hp	W02-003	Mar-14		26.1	4.35		7.26	820	268	8.6	0.7	3.3	35	9.3	28	24	96		2	-7.96	-54.7
Okamanya Hp	W02-28	Jun-14		26	4.92		7.24	801	319	17.3	0.947	2.3	139	9.8	26.8	24.9	96.3	104	-1	-7.96	-55.8
Okamanya Hp	W04-026	Jun-15		25.3	5.47		7.42	785	325	15.5	0.827	2.17	214	11	26.1	23.6	95.1	101	-4	-8.1	-56.5
Okamanya I	JT06-04	Mar-16	7.9	26.2		148	7.79	490	338	2	1.6	1.95	75.9	13.9	32.6	23.7	73.7	99.6	1	-8.17	-54.7

Appendix B: Raw hydrochemical and isotopic data collected in this study

Village	No	Sampling date	Water level [m]	Temp [°C]	O ₂ -content [mg/l]	ORP [mV]	pH	EC [μS/cm]	HC O ₃ ⁻ [mg/l]	Cl ⁻ [mg/l]	F ⁻ [mg/l]	SO ₄ ²⁻ [mg/l]	NO ₃ ⁻ [mg/l]	Na ⁺ [mg/l]	K ⁺ [mg/l]	Mg ²⁺ [mg/l]	Ca ²⁺ [mg/l]	SiO ₂ [mg/l]	Balance [%]	δ ¹⁸ O [‰]	δ ² H [‰]
Okamanya pond	W02-005	Mar-14																		-21.23	-91.8
Okambata	JT08-22	Oct-16	5	28.7		-203	6.72	2156	186	61.6	3.67	1918	0.078	78.9	17.6	113	618	108	-2	-7.18	-50.2
Okambata II	JT01-04	Jun-14	walk in	18.1		-21	7.36	2540	390	11	0.5	1355	0.8	16	60	32	893		-15	-2.41	-18.9
Okambata I	JT01-03	Jun-14	walk in	17.8		-100	7.67	2360	160	3.8	0.5	2145	0.6	36	52	77	768		0	-5.94	-42.3
Okambata I	JT02-36	Sep-14	walk in	21.6		-210	7.33	3430	55	28	1.4	1517	3.7	26	18	42	624		-3	-4.14	-34.8
Okambata I	JT03-21	Mar-15	2 - 3	20.4		-366	7.01	3250	426	259	1.58	2250	4.36							-7.56	-47.7
Okambata I	JT04-09	Aug-15	walk in	21.7		-313	7.42	3530	349	92.1	3.44	2201	0.55	22	27.4	196	618	108.7	-8	-7.48	-52.4
Okambata I	JT05-10	Nov-15		24.8		-315	7.45	2560	299	93	3.37	2185	0.072	120	27.5	186	590	104	-4	-7.62	-51.6
Okambata I	JT07-25	May-16		18		-380	7.67	3300	754	101	2.68	2439	0.328	104	64.2	181	884	117	-1	-3.34	-25.6
Okambata II	JT01-05	Jun-14	walk in	16.8		-26	7.48	2000	188	5.9	0.4	2174	4.1	21	43	43	767		-8	-5.8	-38.5
Okambata II	JT02-35	Sep-14	walk in	16.9		-72	7.07	2730												-6.03	-42.6
Okambata II	JT03-13	Mar-15	2 - 3	19.8		-380	6.93	3440	882	1.16	1.01	2250	21.2							-6.65	-45.9
Okambata II	JT04-10	Aug-15	walk in	21.8		-245	7.59	2730	154	37.8	3.66	1755	7.85	44.5	16.4	83.6	618	99.8	-1	-7.33	-50
Okambata II	JT05-11	Nov-15		26.9		-242	7.53	2076	169	48.2	3.67	1812	6.87	62.3	16.6	97	605	101	-2	-7.49	-49.7

Appendix B: Raw hydrochemical and isotopic data collected in this study

Village	No	Sampling date	Water level [m]	Temp [°C]	O ₂ -content [mg/l]	OR P [mV]	pH	EC [μS/cm]	HC O ₃ ⁻ [mg/l]	Cl ⁻ [mg/l]	F ⁻ [mg/l]	SO ₄ ²⁻ [mg/l]	NO ₃ ⁻ [mg/l]	Na ⁺ [mg/l]	K ⁺ [mg/l]	Mg ²⁺ [mg/l]	Ca ²⁺ [mg/l]	SiO ₂ [mg/l]	Balance [%]	δ ¹⁸ O [‰]	δ ² H [‰]
Okambata II	JT07-26	May-16		20.4		-330	7.63	222	195	47.8	3.39	1662	0.06	54.3	15.8	82.7	569	90	-3	-7.81	-51.1
Olumpeleng wa	JT08-18	Oct-16	6.4	21.4		107.6	7.89	7470	825	1591	2.34	2275	607	2018	89.2	278	111	82.1	1	-6.47	-53.8
Olumpeleng wa 2	JT08-19	Oct-16	4	22.6		99.7	6.98	546	439	1.86	0.806	91.4	0.018	2.6	3.4	53.6	77.7		-4	-7.18	-48.9
Olumpeleng wa central	JT02-28	Sep-14	walk in	17.6		-8	7.74	2104	142	57	1.8	213	6.2	32	5.9	36	75		-4	-7.47	-50.7
Olumpeleng wa deep	JT01-10	Jun-14	5	18.2		175	8.01	7520	481	1006	1.4	2281	103	1623	210	194	79		6	-6.89	-53.8
Olumpeleng wa deep	JT02-29	Sep-14	walk in	15.4		-14	8.63	10320	862	1847	1.6	2726	316	2414	100	309	59		5	-3.54	-38.4
Olumpeleng wa deep	JT03-04	Mar-15	walk in	23.5		80	9.05	7070	521	2084	0.465	2550	2.6							-1.37	-19.9
Olumpeleng wa deep	JT04-03	Aug-15	6.3	15		215.9	8.06	9970	798	1653	2.33	2356	614	2062	91.2	276	102	78.9	0	-7.07	-53.3
Olumpeleng wa deep	JT05-03	Nov-15		25.5		61.9	7.95	7370	788	1604	2.33	2371	615	2013	90.8	270	107	80.5	0	-7.36	-53.9
Olumpeleng wa deep	JT07-17	May-16		18.5		-322	7.35	4790	796	1597	2.68	2386	610	1963	81.3	247	105	83.5	-2	-7.34	-54.8
Olumpeleng wa shallow	JT01-12	Jun-14	3	20.2		135	7.43	626	356	2.8	0.7	<1	4.5	4.7	2	47	66		-6	-6.6	-45.2
Olumpeleng wa shallow	JT02-27	Sep-14	walk in	31.9		-46	7.9	630	256	2.5	0.8	70	17	4.4	9.9	57	73		-5	-6.04	-42
Olumpeleng wa shallow	JT03-03	Mar-15	walk in	33.9		199	7.71	203.6	88	7.69	0.343	13	0.843							-5.86	-43

Appendix B: Raw hydrochemical and isotopic data collected in this study

Village	No	Sampling date	Water level [m]	Temp [°C]	O ₂ -content [mg/l]	ORP [mV]	pH	EC [μS/cm]	HC O ₃ ⁻ [mg/l]	Cl ⁻ [mg/l]	F ⁻ [mg/l]	SO ₄ ²⁻ [mg/l]	NO ₃ ⁻ [mg/l]	Na ⁺ [mg/l]	K ⁺ [mg/l]	Mg ²⁺ [mg/l]	Ca ²⁺ [mg/l]	SiO ₂ [mg/l]	Balance [%]	δ ¹⁸ O [‰]	δ ² H [‰]
Olumpeleng wa shallow	JT04-04	Aug-15	walk in	15.7		142.7	8.05	586	375	3.56	0.72	47	8.21	2.9	6.1	42.4	67.6	61.2	-2	-5.57	-31.3
Olumpeleng wa shallow	JT05-04	Nov-15		31.1		63.7	8.05	510	421	2.77	0.784	61.2	4.06	3	5.2	49.4	71.6	55.4	-3	-6.61	-40.4
Olumpeleng wa shalow	JT07-18	May-16		21.3		79.8	7.78	104.8	257	1.42	0.795	39.2	3.63	3.9	3.9	29.5	42.1	59.1	-4	-6.51	-39.2
Oluwaya	JT08-13	Oct-16	11.84	24.9		89.9	7.14	591	304	12.5	1.79	4.17	191	34	29.1	25.9	82.4	117	-1	-6.68	-52
Oluwaya	W02-25	Jun-14		24.4	6.86		7.63	888	282	21.9	2.04	4.86	231	14.5	10.3	26.8	27	214	-35	-7.02	-51.5
Oluwaya field	JT02-08	Sep-14	9.8	22.5		201	7.84	548	258	1.4	4.5	6	10	4.3	24	41	48		-2	-5.9	-43.9
Oluwaya field	W01-078	Nov-13	10.99	25	5.8		7.51	1031	276	21.4	1.73	4.94	296	25.4	23.5	32.6	24	92.5	-29	-6.88	-49.5
Oluwaya field	W02-022	Mar-14	10	25.1	3.33		7.91	526	263	2.5	3.3	1	5.2	3.8	20	31	42		5	-6.52	-46.8
Oluwaya field	W02-23	Jun-14		22.2	5.64		7.98	603	303	3.34	4.36	4.92	46.6	3.4	2.7	38.6	49.7	24	-2	-6.32	-47.4
Oluwaya Hp	JT02-07	Sep-14	10.72	24.9		195	7.64	857	228	10	1.7	6	55	25	23	32	101		-2	-6.6	-48.7
Oluwaya Hp	JT03-28	Mar-15	10.55	26		27	7.51	867	319	23	1.51	2	2222							-7.38	-49.1
Oluwaya Hp	JT04-16	Aug-15	2.5	24.8		85.1	7.93	898	388	17.9	1.74	6.72	224	29.5	27.2	30	102	27	-6	-7.04	-51.1
Oluwaya Hp	JT05-17	Nov-15	10.84	26.2		67.9	7.69	624	296	15.1	1.77	4.93	217	29	24.9	27.3	90.5		-2	-7.09	-50.3
Oluwaya Hp	JT06-10	Mar-16	13.8	26.2		213.7	7.72	602	290	14.5	1.8	4.69	205	27.5	24.7	26.7	90.5	25	-1	-7.07	-51.9

Appendix B: Raw hydrochemical and isotopic data collected in this study

Village	No	Sampling date	Water level [m]	Temp [°C]	O ₂ -content [mg/l]	ORP [mV]	pH	EC [μS/cm]	HC O ₃ ⁻ [mg/l]	Cl ⁻ [mg/l]	F ⁻ [mg/l]	SO ₄ ²⁻ [mg/l]	NO ₃ ⁻ [mg/l]	Na ⁺ [mg/l]	K ⁺ [mg/l]	Mg ²⁺ [mg/l]	Ca ²⁺ [mg/l]	SiO ₂ [mg/l]	Balance [%]	δ ¹⁸ O [‰]	δ ² H [‰]
Oluwaya Hp	JT07-08	May-16	2.25	23.3		160.9	8.08	604	290	14.6	1.81	4.58	203	27	24.5	25.5	86.2	105	-3	-7.01	-50.7
Oluwaya Hp	W01-081	Nov-13	10.47	25.5	5.7		7.7	616	319	3.02	3.97	4.36	57.6	9.6	22.2	38.1	48.8	90.3	0	-6.58	-48.1
Oluwaya Hp	W02-023	Mar-14	10.2	25.4	5.69		7.51	986	234	7.7	1.4	5.9	64	25	24	29	102		3	-6.78	-49.4
Oluwaya Hp	W02-24	Jun-14		23.9	5.55		7.52	1027	268	25.1	1.75	4.49	286	21.2	20.2	32.7	27	210	-29	-6.64	-49.8
Oluwaya Hp	W04-022	Jun-15		24.3	5.53		7.35	909	291	16.8	1.73	4.47	220	26.4	23.8	28.1	96.8	25	0	-6.95	-50.9
Omboloka 1	JT08-10	Oct-16	8.15	24.2		108.2	6.41	428	378	3.3	0.427	2.9	20.5	0.9	3.8	15.1	105	84	-1	-7.48	-56.2
Omboloka 2	JT08-11	Oct-16																			
Omboloka Borehole	W04-023	Jun-15		21.1	7.14		7.9	575	310	2.46	2.01	2.62	55.2	10.1	21	30.1	59.3	99.8	2	-6.57	-48.6
Omboloka Dune	JT02-06	Sep-14	6.65	24.1		230	7.48	513	223	6.7	2	5	15	0.9	2.7	31	68		-1	-6.72	-49.1
Omboloka Dune	JT03-30	Mar-15	7.43	25.5		138	7.49	519	243	21.5	1.81	0	489							-6.84	-46.9
Omboloka Dune	JT04-18	Aug-15	7.86	23.8		72.6	7.95	500	324	5.05	2.09	4.25	56.6	0.7	3	29.1	68.8	101	-5	-6.78	-48.8
Omboloka Dune	JT05-16	Nov-15	8.29	24.9		84.5	7.82	373	281	4.59	1.95	3.15	51.6	0.9	2.7	27.8	63.9		-1	-6.94	-49.1
Omboloka Dune	JT06-09	Mar-16	2.02	27.4		29.7	7.78	371	296	4.75	2.06	3.42	38.1	0.7	3.1	27.8	66.5	100	-1	-7.22	-49.7
Omboloka Dune	JT07-07	May-16	8.39	24.8		147.3	7.91	367	275	5.19	2.01	3.36	53.8	0.8	3.1	26.4	63.6	95.2	-2	-6.79	-49.5

Appendix B: Raw hydrochemical and isotopic data collected in this study

Village	No	Sampling date	Water level [m]	Temp [°C]	O ₂ -content [mg/l]	ORP [mV]	pH	EC [μS/cm]	HC O ₃ ⁻ [mg/l]	Cl ⁻ [mg/l]	F ⁻ [mg/l]	SO ₄ ²⁻ [mg/l]	NO ₃ ⁻ [mg/l]	Na ⁺ [mg/l]	K ⁺ [mg/l]	Mg ²⁺ [mg/l]	Ca ²⁺ [mg/l]	SiO ₂ [mg/l]	Balance [%]	δ ¹⁸ O [‰]	δ ² H [‰]
Omboloka Dune	JT08-12	Oct-16	8.6	23.7		95.8	7.03	374	277	3.82	1.92	2.68	52.1	0.7	2.8	27.2	65.6	107	0	-6.27	-50
Omboloka Dune	W01-087	Nov-13	7.7	25.9	2.95		7.5	570	281	7.68	1.98	3.54	59.8	1.8	3.8	29.2	68.3	81	0	-6.6	-47.6
Omboloka Dune	W02-002	Mar-14	6.85	25.3	2.89		7.21	602	263	2.6	0.5	4.2	2.5	1	3.7	16	73		5	-7.62	-52.1
Omboloka Dune	W02-27	Jun-14		24	4.17		7.55	593	269	8.71	2.1	4.6	65	1.2	3.3	28.4	67.9	102	0	-6.22	-46.3
Omboloka Dune	W04-024	Jun-15		25	5.29		7.53	542	274	5.69	2.1	3.42	57.1	0.9	2.8	28.3	67	101	0	-6.75	-49.3
Omboloka Pan	JT02-05	Sep-14	5.6	24.4		220	7.2	593	334	3.3	0.6	2	3.8	0.8	2.9	21	107		0	-7.91	-55.8
Omboloka Pan	JT03-29	Mar-15	7.6	26.3		130	7.16	603	335	8.68	0.471	0	232							-8.24	-54.4
Omboloka Pan	JT04-17	Aug-15	7.74	24.5		87.7	7.73	587	278	3.67	0.553	4.03	19.8	0.8	3.4	17.1	22	83.8	-33	-7.53	-54.3
Omboloka Pan	JT05-15	Nov-15	8.13	25.3		80.7	7.52	429	384	3.69	0.519	2.86	18.2	1	3.1	15.9	103		-2	-7.82	-53.5
Omboloka Pan	JT06-05	Mar-16	7.8	26.1		140.7	7.65	421	378	3.41	0.497	2.84	18.3	0.6	3.2	16.1	104	81.8	0	-8.35	-54.4
Omboloka pan	JT07-06	May-16	8.4	23.4		139.7	7.69	431	416	2.27	0.65	2.43	6.39	0.8	3.1	26.9	89.2	81.9	-2	-7.97	-55.8
Omboloka Pan	W01-084	Nov-13	6.61	25.6	3.06		7.1	649	404	7.51	1.17	2.06	10.3	1.9	7.1	18.8	108	67.5	1	-8.03	-55.8
Omboloka Pan	W02-001	Mar-14	7.8	26.6	2.72		7.4	567	268	3	1.8	6.4	21	1.1	3.6	28	71		4	-6.41	-46.4
Omboloka Pan	W02-26	Jun-14		25	3.04		7.16	682	408	3.68	0.664	2.18	13.1	1	3.4	19.7	107	87.7	0	-7.92	-56.4

Appendix B: Raw hydrochemical and isotopic data collected in this study

Village	No	Sampling date	Water level [m]	Temp [°C]	O ₂ -content [mg/l]	ORP [mV]	pH	EC [μS/cm]	HC O ₃ ⁻ [mg/l]	Cl ⁻ [mg/l]	F ⁻ [mg/l]	SO ₄ ²⁻ [mg/l]	NO ₃ ⁻ [mg/l]	Na ⁺ [mg/l]	K ⁺ [mg/l]	Mg ²⁺ [mg/l]	Ca ²⁺ [mg/l]	SiO ₂ [mg/l]	Balance [%]	δ ¹⁸ O [‰]	δ ² H [‰]
Omboloka Pan	W04-025	Jun-15		25.2	4.47		7.14	623	390	3.63	0.485	2.72	17.7	0.9	3.9	16.6	111	82.2	0	-7.89	-55.7
Omboloka pan1	JT06-06	Mar-16	7.62	25.3		29.3	7.67	443	423	2.87	0.621	2.37	3.38	0.9	3.9	28	94	85.6	0	-8.4	-55.8
Omboloka pan2	JT06-07	Mar-16	9	25.7		217.3	7.76	521	366	13.9	2.01	2.39	90.9	2.2	7	57.8	59.4	108	0	-7.75	-52.9
Omboloka pan3	JT06-08	Mar-16	8.3	26.1		141.2	7.66	523	353	21	2.26	2.65	101	6	21.6	45.6	63.4	22	-3	-7.45	-51.6
Omulonga	JT05-25	Nov-15	walk in	35.5		69.1	7.3	402	165	26.9	0.072	26.7	39.8	22.2	54.6	15.5	27.8		4	-3.9	-28.4
Omulonga 1	JT08-23	Oct-16	walk in	31.7		59.6	5.68	118.5	79.1	6.3	0.113	13.7	0.083	4.7	19.7	4.66	14.7		2	-3.6	-25.9
Omulonga I	JT02-21	Sep-14	walk in	27		210	7.21	92.2	14	3.3	0.1	24	4.6	3.4	10	2.7	8.3		7	-5.54	-44.5
Omulonga I	JT03-25	Mar-15	walk in	31		61	8.13	83	47	8.49	0.049	5	197							-5.06	-40.2
Omulonga I	JT04-27	Aug-15	walk in	27.2		88.2	7.47	219.5	25.8	5.9	0.062	7.16	25.5	3.4	13.4	3.74	2.9		-10	-6.27	-46.9
Omulonga I	JT05-23	Nov-15	walk in	34.4		99.2	6.59	87.5	40.4	3.57	0.061	6.03	12.2	3.3	10.5	3.11	10.8		5	-6.27	-44.4
Omulonga I	JT06-19	Mar-16	walk in	26.2		108.4	8.39	97.9	74.8	2.95	0.156	4.49	0.187	2.1	8.3	4.65	17	44.8	4	-4.63	-36.3
Omulonga I	JT07-11	May-16	walk in	25.5		99.2	8.05	130.8	68.9	4.54	0.034	8.26	0.158	3.2	11.2	3.05	11.5	53.7	-7	-5.78	-40.1
Omulonga I	W02-020	Mar-14	walk in	33.7	20		10.4	258	81	1.2	0.1	<1	<0.5	6.7	30	3.8	8.3		-2	-5.22	-41.5

Appendix B: Raw hydrochemical and isotopic data collected in this study

Village	No	Sampling date	Water level [m]	Temp [°C]	O ₂ -content [mg/l]	ORP [mV]	pH	EC [μS/cm]	HC O ₃ ⁻ [mg/l]	Cl ⁻ [mg/l]	F ⁻ [mg/l]	SO ₄ ²⁻ [mg/l]	NO ₃ ⁻ [mg/l]	Na ⁺ [mg/l]	K ⁺ [mg/l]	Mg ²⁺ [mg/l]	Ca ²⁺ [mg/l]	SiO ₂ [mg/l]	Balance [%]	δ ¹⁸ O [‰]	δ ² H [‰]
Omulonga I	W02-133	Jun-14	walk in	20.6	4.88		6.31	96.7	30.5	3.63	0.032	5.2	3.98	1.9	8.6	1.95	7.2	63.7	3	-6.95	-49.1
Omulonga I	W04-030	Jun-15	walk in	22	8.04		6.6	96.2	24.1	4.09	0.009	4.94	21.4	2.4	8.8	2.32	7.72	52	-3	-3.09	-31.1
Omulonga II	JT02-22	Sep-14	walk in	23.3		20	7.76	135	30	2.2	0.1	2	5.7	2.2	14	4.6	21		-4	-4.28	-34.2
Omulonga II	JT03-26	Mar-15	walk in	29.1		87	7.8	81.4	34	9.14	0.05	1	192							-3.98	-30.9
Omulonga II	JT04-28	Aug-15	walk in	24.2		131.2	7.34	97.5	25.5	5.8	0.039	4.71	14.3	3.3	2.8	2.65	8.85		-2	-4.2	-31.4
Omulonga II	JT05-22	Nov-15	walk in	32.1		76.2	6.62	101.8	82.5	3.54	0.034	3.12	0.029	2.3	12.6	3.88	10.5		-9	-5.05	-32.2
Omulonga II	JT06-18	Mar-16	walk in	25.6		22.1	7.56	54.5	39.4	3.57	0.107	2.7	0.188	2	6.2	2.77	9.09	42.8	7	-3.79	-32.4
Omulonga II	W02-021	Mar-14	walk in	32.8	5.5		7.2	71	25	1.1	0.1	<1	2.1	0.8	5.4	2.2	7.3		-2	-5.49	-41.9
Omulonga II	W02-134	Jun-14	walk in	15	5.32		6.67	180	35.9	4.9	0.013	5.69	19.4	2.1	13.1	3.4	10.7	51.8	3	-4.56	-35.5
Omulonga II	W04-031	Jun-15	walk in	24.3	18.9		8.96	107.7	57.7	4.15	0.037	5.22	1.35	2.3	9.7	3.3	2.1	63.4	-5	-5.93	-46.5
Omulonga III	JT07-10	May-16	walk in	16.2		147	7.76	85.1	22.6	4.74	0.031	5.24	27.3	2.7	9.8	3.06	10.1	51.9	3	-4.93	-32.2
Onakapanda	JT02-32	Sep-14	walk in	19.3		1	7.52	5710	218	534	3.1	2807	14	591	44	291	614		-3	-6.74	-51.5
Onakapanda	JT03-09	Mar-15	3	21.5		-331	7.29	3650	310	602	0.752	2200	4.34							-4.41	-29.4

Appendix B: Raw hydrochemical and isotopic data collected in this study

Village	No	Sampling date	Water level [m]	Temp [°C]	O ₂ -content [mg/l]	ORP [mV]	pH	EC [μS/cm]	HC O ₃ ⁻ [mg/l]	Cl ⁻ [mg/l]	F ⁻ [mg/l]	SO ₄ ²⁻ [mg/l]	NO ₃ ⁻ [mg/l]	Na ⁺ [mg/l]	K ⁺ [mg/l]	Mg ²⁺ [mg/l]	Ca ²⁺ [mg/l]	SiO ₂ [mg/l]	Balance [%]	δ ¹⁸ O [‰]	δ ² H [‰]
Onakapanda	JT04-06	Aug-15	walk in	16.5		150.3	7.62	5800	318	526	3.51	2816	67.4	616	40.9	268	613	79.7	0	-7.19	-53.9
Onakapanda	JT05-08	Nov-15		24.6		64.8	7.69	4300	298	517	3.72	2885	52	617	41.1	289	600		1	-7.2	-51.8
Onakapanda	JT07-22	May-16		16.6		58.8	7.89	4540	340	529	3.63	2731	75.1	612	42.9	265	555	84.8	-1	-6.97	-51.2
Onakapanda I	JT01-09	Jun-14	walk in	17.1		130	7.78	2370	20	28	0.4	2179	0.7	45	21	31	776		-5	-3.67	-31
Onakatili	JT04-08	Aug-15	walk in	24		-294	7.52	2980												-6.92	-48.3
Onakatili	JT05-12	Nov-15		25.4		81.8	7.32	2098	243	48.9	3.01	1630	2.35	45.7	30.6	86.2	567	99.5	-2	-7.36	-49.3
Onakatili	JT07-24	May-16		18.6		-373	7.5	2410	540	59	3.31	1640	0.159	44.4	47.9	88.8	710	100	2	-6.96	-47.6
Onakatili I	JT01-06	Jun-14	walk in	18		-184	7.51	5870	464	17	0.5	2287	Interference	41	133	173	1033		-11	1.32	-13.3
Onakatili I	JT02-34	Sep-14	walk in	23.6		-358	7.27	3240	257	52	2	2009	1.9	45	85	104	696		1	5.34	-42
Onakatili I	JT03-2	Mar-15	2 - 3	22.2		-376	7.06	3270	516	6081	1.95	2150	2.97							-7.02	-46.8
Onakatili II	JT01-07	Jun-14	walk in	20		-23	7.13	2910	367	25	1.5	1360	1.1	48	74	94	732		-14	6.57	-47.6
Onakatsili	JT08-21	Oct-16	3	26.2		-404	7	2590	905	61	2.8	2000	0.245	50.8	50.1	104	895	112	-2	6.12	-47
Onambaladh1	W02-009	Mar-14	walk in																	-3.58	-29.8
Onambaladh1	W02-010	Mar-14	walk in																	-2.09	-19.9

Appendix B: Raw hydrochemical and isotopic data collected in this study

Village	No	Sampling date	Water level [m]	Temp [°C]	O ₂ -content [mg/l]	ORP [mV]	pH	EC [μS/cm]	HC O ₃ ⁻ [mg/l]	Cl ⁻ [mg/l]	F ⁻ [mg/l]	SO ₄ ²⁻ [mg/l]	NO ₃ ⁻ [mg/l]	Na ⁺ [mg/l]	K ⁺ [mg/l]	Mg ²⁺ [mg/l]	Ca ²⁺ [mg/l]	SiO ₂ [mg/l]	Balance [%]	δ ¹⁸ O [‰]	δ ² H [‰]
Onambaladhi	JT05-19	Nov-15	walk in	35		26	9.36	86.5	84.3	5.27	0.318	1.63	0.028	18.1	5.6	2.24	8.27		-2	-0.66	-21.1
Onambaladhi	JT06-13	Mar-16	walk in	24.8		140.8	6.85	164.7	49	16.5	0.182	18.5	19.1	17.3	18.3	5.2	2.1	45.3	-6	-2.99	-25.9
Onambaladhi	JT06-21	Mar-16	walk in	24.1		219	8.5	46.5	34	4.24	0.161	0.729	0.321	8.5	3.6	1.27	3.57	43.8	3	-0.94	-9.9
Onambaladhi	JT08-1	Oct-16	walk-in	28.8		87.5	7.42	62.4	48.2	5.64	0.169	0.81	0.187	11.5	6.1	1.48	5.35		3	-2.39	-27.2
Onambaladhi 2	JT08-2	Oct-16	walk-in	34		69.3	7.96	149.7	43.2	23.2	0.381	23	0.108	32.6	11.7	1.12	3.39		3	-3.29	-34.3
Onambaladhi Borehole	W04-021	Jun-15		20.3	6.13		8.41	1073	583	15.6	4.02	19.6	0.028	258	5.4	0.263	1.13	45.5	4	-9.71	-67.5
Onambaladhi hole	W04-015	Jun-15																		-7.55	-51.4
Onambaladhi I	JT02-15	Sep-14	walk in	18.9		161	6.64	102.3	13	2.3	0.2	34	3.5	2	8.6	2.8	7.6		0	-6.34	-47.3
Onambaladhi I	JT03-18	Mar-15	walk in	30.6		217	8.3	109.9	37	16.9	0.235	7	67.6							-5.22	-41.3
Onambaladhi I	JT04-22	Aug-15	walk in	17.9		98.8	8.39	107.5	36	9.81	0.245	10.8	1.16	14.9	9.8	3.13	7.79		16	-4.71	-35.8
Onambaladhi I	W02-006	Mar-14	walk in	25.1	4.34		6.8	233	60	17	0.2	5	0.9	17	18	3.9	9		-2	-3.28	-24.9
Onambaladhi I	W02-22	Jun-14		17	4.2		6.66	178	34.9	21	0.195	8.2	7.21	13.7	2.2	2.31	6.05	59.1	-12	-5.83	-44.7
Onambaladhi I	W04-013	Jun-15		17.9	5.09		5.42	106.4	14.5	7.63	0.218	10.6	24.6	21.9	6.1	1.22	4.17	71.8	13	-6.07	-39.7
Onambaladhi II	JT02-16	Sep-14	walk in	21.7		154	6.8	173.5	36	4.9	0.2	22	2.5	18	14	1.9	5.5		-2	-5.05	-41.2

Appendix B: Raw hydrochemical and isotopic data collected in this study

Village	No	Sampling date	Water level [m]	Temp [°C]	O ₂ -content [mg/l]	ORP [mV]	pH	EC [μS/cm]	HC O ₃ ⁻ [mg/l]	Cl ⁻ [mg/l]	F ⁻ [mg/l]	SO ₄ ²⁻ [mg/l]	NO ₃ ⁻ [mg/l]	Na ⁺ [mg/l]	K ⁺ [mg/l]	Mg ²⁺ [mg/l]	Ca ²⁺ [mg/l]	SiO ₂ [mg/l]	Balance [%]	δ ¹⁸ O [‰]	δ ² H [‰]
Onambaladhi II	JT03-19	Mar-15	walk in	29.3		37	9.8	157.1	67	15.3	0.202	2	96.2							-0.82	-14.8
Onambaladhi II	JT04-21	Aug-15	walk in	16.6		91	8.87	83.7	40.2	5.16	0.243	1.93	2.2	2.7	5.5	2.55	9.67		3	0.17	-14.1
Onambaladhi II	W02-007	Mar-14	walk in	26.2	9.6		6.7	185	38	1.7	0.1	30	5.5	9.6	19	4.5	10		2	-4.47	-33.5
Onambaladhi II	W02-213	Jun-14		20	7.86		6.67	85.7	21.9	6.13	0.154	9.84	0.478	16.2	2	0.455	0.85	71.7	5	-4.81	-36.1
Onambaladhi II	W02-221	Jun-14		20	8.81		6.78	207	48.4	16.9	0.23	16.7	7.67	16.3	18.3	3.56	9.51	40.3	5	-3.91	-35.6
Onambaladhi II	W04-014	Jun-15		17.4	8.62		5.62	52.1	22	4.33	0.142	3.37	0.606	7.1	2.5	0.833	2.85	53.3	1	-4.66	-32.9
Onambaladhi III	JT07-01	May-16		18.8		143.5	7.84	54.5	51.6	5.2	0.159	0.099	0.035	8.8	5	1.76	5.67	48.2	-3	-2.26	-19.5
Onambaladhi Pond	W02-008	Mar-14																	-6	-4.19	-34.2
Onambandje	JT01-08	Jun-14	walk in	22.6		-210	7.27	2630	117	17	1.1	1145	0.5	33	70	43	710		-19	-6.56	-45.6
Onambandje	JT02-33	Sep-14	walk in	27.6		-339	7.13	3180	198	101	2.1	1680	4.2	74	51	84	708		-5	-7.5	-52.7
Onambandje	JT03-10	Mar-15	2	21.8		-348	7.04	3200	225	392	2.03	1800	2.44							-7.09	-45.8
Onambandje	JT04-07	Aug-15	walk in	22.8		-280	7.5	3280	355	136	2.75	1792	1.49	101	48.7	97.1	666	82.5	0	-7.55	-50.6
Onambandje	JT05-09	Nov-15		26.8		-172	7.71	2420	277	141	2.75	1859	0.121	106	47.8	94.8	636	80.1	-3	-7.12	-48.1

Appendix B: Raw hydrochemical and isotopic data collected in this study

Village	No	Sampling date	Water level [m]	Temp [°C]	O ₂ -content [mg/l]	ORP [mV]	pH	EC [μS/cm]	HC O ₃ ⁻ [mg/l]	Cl ⁻ [mg/l]	F ⁻ [mg/l]	SO ₄ ²⁻ [mg/l]	NO ₃ ⁻ [mg/l]	Na ⁺ [mg/l]	K ⁺ [mg/l]	Mg ²⁺ [mg/l]	Ca ²⁺ [mg/l]	SiO ₂ [mg/l]	Balance [%]	δ ¹⁸ O [‰]	δ ² H [‰]
Onambandje	JT07-23	May-16		19.2		-269	7.76	2360	265	128	2.7	1712	0.107	94	45.6	85.4	601	72.3	-2	-7.1	-46.5
Onambandje	JT08-20	Oct-16		23.2		-224	6.74	2380	272	146	2.64	1899	0.037	117	55.2	100	675	78.2	0	-6.77	-49.3
Ongalangobe	JT02-03	Sep-14	25.2	26.4		138	7.64	530	277	1.4	0.4	<1	2.9	30	73	13	31		0	-8.26	-50.6
Ongalangobe	W02-026	Mar-14	24.6	26.3	2.31		7.61	536	275	5.2	0.3	<1	1.6	29	76	10	26		4	-8.31	-53.5
Ongalangobe	W02-099	Jun-14		22.9	5.4		7.68	499	298	7.61	0.363	2.24	3.09	44.9	8.7	9.99	43.9	93.6	0	-1.3	-22.1
Ongalangobe Borehole	W01-090	Nov-13					7.6	481	298	6.94	0.353	2.16	3.05	44.3	8.2	10.1	43.2	69.6	-1		
Ongalangobe borehole	W02-025	Mar-14					8.4	490	259	5.1	0.3	1	1.1	44	8	9.6	41		5		
Ongalangobe I	W01-092	Nov-13	26.35	27	1.64		7.5	802	500	5.05	0.516	2.14	0.083	46.8	24	16.5	40.8	82.9	-17	-9	-61.2
Ongalangobe I	W02-100	Jun-14		26.6	3.63		7.61	489	279	2.41	0.332	1.26	0.568	26	65.5	9.48	26.5	69.1	2	-6.6	-45.2
Ongalangobe II	W01-094	Nov-13	28.55	26.9	1.78		8.2	283	741	2.5	0.785	2.34	0.394	240	76.6	1.55	6.75	70.1	2	-8.78	-61.5
Ongalangobe II	W02-101	Jun-14		25.6	5.28		8.05	299	783	2.48	0.802	2.65	1.067	247	76.4	1.6	6.21	92.7	0	-5.82	-44.8
Oshana shiwa	JT04-20	Aug-15	18.2	24.3		73.7	8.04	760	45.3	7.07	2.97	4.2	215	67.1	36.9	29.7	47.2	108	30	-7.93	-54.9
Oshana shiwa	JT06-01	Mar-16	20.38	27.5		217.4	7.71	478	461	1.06	2.59	1.07	0.493	81.8	32.2	19.7	33.4	103	-1	-8.56	-59.4

Appendix B: Raw hydrochemical and isotopic data collected in this study

Village	No	Sampling date	Water level [m]	Temp [°C]	O ₂ -content [mg/l]	ORP [mV]	pH	EC [μS/cm]	HC O ₃ ⁻ [mg/l]	Cl ⁻ [mg/l]	F ⁻ [mg/l]	SO ₄ ²⁻ [mg/l]	NO ₃ ⁻ [mg/l]	Na ⁺ [mg/l]	K ⁺ [mg/l]	Mg ²⁺ [mg/l]	Ca ²⁺ [mg/l]	SiO ₂ [mg/l]	Balance [%]	δ ¹⁸ O [‰]	δ ² H [‰]
Oshana shiwa	W01-097	Nov-13		26.3	1.4		7.9	722	422	4.59	2.7	1.76	33.6	74	37.1	22.4	34.6	85.9	0	-7.74	-55.7
Oshana shiwa	W02-028	Mar-14	18	26.1	5.15		7.61	884	280	2.4	2.4	4	46	75	40	28	41		3	-8	-55.2
Oshana shiwa	W02-21	Jun-14		23.5	6.19		7.72	868	345	8.47	2.94	3.14	170	69.3	36	30.2	47.8	22	0	-7.83	-55.2
Oshana shiwa	W04-028	Jun-15		22.5	3.4		7.74	830	359	6.38	2.94	2.6	215	62.5	34.3	29	45.8	109	-8	-7.89	-54.3
Oshana shiwa borehole	W01-099	Nov-13		26.1	2.82		7.6	913	343	9.87	2.99	2.7	195	72	38.7	31.9	48.5	93.4	-1	-8.04	-57.2
Oshana shiwa borehole	W02-029	Mar-14		27.4	5.75		7.62	596	325	2.4	2.4	1.1	2.5	58	32	17	29		5	-8.08	-56.9
Oshana shiwa borehole	W02-098	Jun-14		24.7	6.19		8	598	376	0.666	2.82	1.09	4.25	58.7	31.1	18.4	32.7	106	1	-8.22	-58.7
Oshana shiwa borehole	W04-029	Jun-15		21.3	4.21		8.6	493	294	9.15	0.699	3.93	3.66	92.4	13.6	5.49	6.93	30.3	-1	-9.39	-64.6
Oshana shiwa	JT02-02	Sep-14	18.28	24.6			7.69	799	280	6.3	2.8	5	38	74	36	30	43		0	-7.52	-52.4
Oshana shiwa	JT03-34	Mar-15	17.6	25.6		25	7.71	651	256	9.49	1.97	0	987							-6.36	-37.2
Oshana shiwa	JT05-21	Nov-15	18.13	26.9		60.6	7.93	542	367	7.08	2.96	2.71	121	63.3	35	29.5	44.3		-1	-8	-52.7
Oshana shiwa	JT07-04	May-16	20.65	25.6		142.2	8.15	476	459	1.31	2.61	0.931	0.066	79.1	31.1	18.5	32.2	97.6	-2	-8.18	-57.8
Oshana shiwa	JT08-7	Oct-16	20.65	26.3		-154	7.31	509	487	2.67	2.54	0.6	0.042	89	33.7	19.3	32.8	104	-2	-7.65	-58.2

Appendix B: Raw hydrochemical and isotopic data collected in this study

Village	No	Sampling date	Water level [m]	Temp [°C]	O ₂ -content [mg/l]	OR P [mV]	pH	EC [μS/cm]	HC O ₃ ⁻ [mg/l]	Cl ⁻ [mg/l]	F ⁻ [mg/l]	SO ₄ ²⁻ [mg/l]	NO ₃ ⁻ [mg/l]	Na ⁺ [mg/l]	K ⁺ [mg/l]	Mg ²⁺ [mg/l]	Ca ²⁺ [mg/l]	SiO ₂ [mg/l]	Balance [%]	δ ¹⁸ O [‰]	δ ² H [‰]
Oshana shiwa hand pump	JT03-33	Mar-15	20.75	27.6		138	7.85	568	301	6.2	2.38	0	27.5							-8.38	-57.9
Oshana shiwa hand pump	JT02-01	Sep-14	21.02	26.1			7.9	558	307	2	2.7	2	1.2	62	30	20	29		-1	-7.88	-54.7
Oshikunde	JT08-4	Oct-16	walk in	34.6		63.4	8.34	180.3	115	11.6	0.139	8.91	0.149	34.4	18.7	2.81	9.62		6	-1.88	-21.5
Oshikunde I	JT02-17	Sep-14	walk in	26.1		107	9.19	196.9	60	18	0.1	13	4.5	25	14	3	21		-5	-2.81	-29.6
Oshikunde I	JT03-16	Mar-15	walk in	24.3		22	7.32	195.5	82	28.5	0.109	1	44.8							0.86	-7.6
Oshikunde I	JT04-21	Aug-15	walk in	25.3		29.2	8.58	271	48.7	13.1	0.098	23.8	46.3	29.6	24.7	3.19	16.8		11	-3.27	-28.8
Oshikunde I	JT05-26	Nov-15		37.6		56.5	8.84	139.3	98.5	12.8	0.131	5.14	0.135	27.2	16.6	2.15	8.19		2	-3.28	-25.9
Oshikunde I	JT06-20	Mar-16		25.5		-8.3	6.95	145.5	97.2	13.1	0.407	4.6	0.214	28	13.8	2.84	2.2	35.4	-4	-2.32	-28
Oshikunde I	JT07-12	May-16		13.6		-287	7.87	1683	111	13	0.103	13.5	33.3	29.3	28.6	4.1	16.5	68.4	3	-3.11	-27.6
Oshikunde I	W02-015	Mar-14	walk in	32.3	10.5		8.67	215	40	4.4	0.1	<1	1.1	9.8	8	1.6	6.1		-1	-3.44	-33.1
Oshikunde I	W02-219	Jun-14		21.4	15.2		8.7	262	76.2	18.6	0.082	5.23	10.6	29.5	2.5	2.7	2.9	71.4	-9	-1.1	-21.7
Oshikunde I	W04-010	Jun-15		17.4	8.39		7.61	296	90.3	14.9	0.088	14.2	32.9	30.7	29.7	2.81	13.8	54.3	5	-3.49	-29.6
Oshikunde II	JT02-18	Sep-14	walk in	26.2		156	6.4	221.9	35	2	0.1	6	3.2	18	6.2	1.8	7.6		-7	-5.21	-39.8
Oshikunde II	JT03-17	Mar-15	walk in	22.5		214	6.43	133	57	19.6	0.081	0	109							-5.65	-34.6

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Village	No	Sampling date	Water level [m]	Temp [°C]	O ₂ -content [mg/l]	ORP [mV]	pH	EC [μS/cm]	HC O ₃ ⁻ [mg/l]	Cl ⁻ [mg/l]	F ⁻ [mg/l]	SO ₄ ²⁻ [mg/l]	NO ₃ ⁻ [mg/l]	Na ⁺ [mg/l]	K ⁺ [mg/l]	Mg ²⁺ [mg/l]	Ca ²⁺ [mg/l]	SiO ₂ [mg/l]	Balance [%]	δ ¹⁸ O [‰]	δ ² H [‰]
Oshikunde II	JT04-13	Aug-15	walk in	25.9		28.7	7.55	146.3	92.1	10.2	0.143	2.8	6.83	23.6	7.9	2.62	2.9		-11	-5.21	-38.4
Oshikunde II	JT05-27	Nov-15		36.6		96	7.81	112	72.6	10.5	0.165	4.64	0.15	27.4	8	2.33	9.94		13	-4.21	-31.3
Oshikunde II	JT06-21	Mar-16		26.1		35.4	6.81	215	70.1	10.5	0.22	7.19	0.32	28.7	8.3	2.23	9.73	72.4	14	-5.37	-40.5
Oshikunde II	JT07-13	May-16	4.85	13.2		76.9	7.96	2290	71.5	10.6	0.163	8.17	1.41	30.3	9.5	1.71	6.98	67.9	10	-4.77	-35.6
Oshikunde II	W02-016	Mar-14	walk in	28.2	6.48		5.71	94.6	70	11	0.1	20	1.7	15	27	3.9	13		-1	-6.22	-43.9
Oshikunde II	W02-130	Jun-14		24.4	8.84		6.35	109	31.4	7	0.066	0.989	4.58	14.5	5.6	1.53	6.41	79.8	20	-6.29	-44.2
Oshikunde II	W04-02	Jun-15		23.9	6.39		6.76	142	35.6	9.91	0.093	5.94	21.8	20.6	5.7	1.61	7.65	85.8	7	-6.14	-42
Oshuuli Deep	JT03-24	Mar-15	2.1	26.2		82	7.82	863	487	21.8	0.329	0	217							-2.43	-1.3
Oshuuli Deep	W02-132	Jun-14		19.1	2.67		7.14	833	293	26.2	0.189	41.5	76.8	17.1	132.5	20.5	46.8	76.5	3	-5.33	-41.4
Oshuuli shallow	JT02-19	Sep-14	walk in	22.5		25	8.48	2370	766	9	1.2	18	5.4	485	38	1.8	8.4		-16	-5.05	-42.2
Oshuuli shallow	JT03-23	Mar-15	walk in	24.6		99	6.89	601	185	26.8	0.164	53	82							-6.24	-41.4
Oshuuli shallow	JT04-14	Aug-15	walk in	25.9		54.6	7.54	564	310	17.5	0.213	29.1	150	14.2	82.6	13.6	31.5		3	-6.15	-43.8
Oshuuli shallow	JT05-24	Nov-15		38.2		70.8	7.58	328	149	14.1	0.219	20.3	49.9	15.2	66.4	9.41	24.4			-5.76	-40.4
Oshuuli shallow	W02-018	Mar-14	walk in	23.8	2.17		7.03	585	251	6	0.1	<1	<0.5	8.2	101	14	33		-4	-5.44	-40.5

Appendix B: Raw hydrochemical and isotopic data collected in this study

Village	No	Sampling date	Water level [m]	Temp [°C]	O ₂ -content [mg/l]	OR P [mV]	pH	EC [μS/cm]	HC O ₃ ⁻ [mg/l]	Cl ⁻ [mg/l]	F ⁻ [mg/l]	SO ₄ ²⁻ [mg/l]	NO ₃ ⁻ [mg/l]	Na ⁺ [mg/l]	K ⁺ [mg/l]	Mg ²⁺ [mg/l]	Ca ²⁺ [mg/l]	SiO ₂ [mg/l]	Balance [%]	δ ¹⁸ O [‰]	δ ² H [‰]
Oshuuli shallow	W02-131	Jun-14		22.4	3.66		8.25	2470	1544	4.65	1.5	2.8	43.4	620	47.6	2.86	10.2	90.8	5	-5.52	-44
Oshuuli shallow	W04-032	Jun-15		28.6	10.4		7.1	675	106	20.9	0.245	32	164	16.8	95.2	15.7	35.7	85.3	5	-6.27	-45
Otongo	JT05-05	Nov-15		29.9		-324	7.29	4990	423	1078	0.389	2357	0.108	832	68	149	695	106	-1	-4.88	31.5
Otongo	JT07-19	May-16		15.2		-109	7.64	396	336	1055	0.452	2210	0.535	768	58.6	141	660	108	-1	-5.12	29.9
Otongo	JT08-15	Oct-16	2	28.6		70.8	6.63	6920												-4.73	34.4
Otongo I	JT01-14	Jun-14	1.5	16.2		25	8.56	5130	198	557	0.1	1737	1.5	449	167	85	946		-16	4.88	19
Otongo I	JT02-25	Sep-14	walk in	14.1		-336	7.55	5250	290	783	0.3	2226	4	625	57	23	797		-2	-1.29	15.5
Otongo I	JT03-05	Mar-15	walk in	31.1		-39	7.61	4710	253	1368	0.265	2550	5.73							-3.13	22.3
Otongo I	JT04-05	Aug-15	walk in	16.8		-250	7.61	5880	443	831	0.39	2139	3.41	686	64.4	135	689	101		-4.42	27.4
Otongo II	JT01-15	Jun-14	walk in	17.9		-157	7.62	5740	288	641	0.2	2084	1.1	704	151	107	759		-9	-2.73	19.1
Otongo II	JT02-26	Sep-14	walk in	19.4		-368	7.45	2450	659	2143	0.4	3780	1.5	2169	232	286	920		-5	-4	29.3
Otongo II	JT03-06	Mar-15	walk in	33.8		-366	7.43	10830	418	5673	0.499	2900	18.9							-2.46	14.9
Uusathima	JT05-01	Nov-15		29.6		-5.4	7.86	2177	108	221	3.78	1570	22.5	19.8	69.8	43.1	676	104	-2	-6.76	43.2
Uusathima	JT05-02	Nov-15		29.3		-322	7.61	1569	268	19.6	1.98	1164	16.2	8.9	10.7	25.1	522		-2	-5.38	30.3
Uusathima	JT07-16	May-16		16.5		67.1	8.31	321	123	24.8	2.16	1351	0.089	12.4	17.6	18.7	555	53.4	-2	5.94	-38

Appendix B: Raw hydrochemical and isotopic data collected in this study

Village	No	Sampling date	Water level [m]	Temp [°C]	O ₂ -content [mg/l]	OR P [mV]	pH	EC [μS/cm]	HC O ₃ ⁻ [mg/l]	Cl ⁻ [mg/l]	F ⁻ [mg/l]	SO ₄ ²⁻ [mg/l]	NO ₃ ⁻ [mg/l]	Na ⁺ [mg/l]	K ⁺ [mg/l]	Mg ²⁺ [mg/l]	Ca ²⁺ [mg/l]	SiO ₂ [mg/l]	Balance [%]	δ ¹⁸ O [‰]	δ ² H [‰]
Uusathima	JT07-15	May-16		17.8		66.4	8.09	7240	185	237	3.67	1603	0.192	22.5	72.7	44	672	196	-5	-6.02	-39.1
Uusathima 1	JT08-16	Oct-16	5.25	20.5		93.1	6.64	2870	104	539	3.65	1620	71.3	47.2	74.2	63.8	887	106	2	-6	-42.9
Uusathima I	JT02-30	Sep-14	walk in	16.1		-156	7.61	3190	77	322	3.5	1555	2	19	77	42	803		-3	-6.78	-44.7
Uusathima I	JT03-01	Mar-15	walk in	26.7		183	8.5	355	47	21.7	0.236	175	1.71							-4.42	-35.4
Uusathima I	JT04-01	Aug-15	4.77	15.5		139.7	8.03	2770	89.7	140	3.92	1552	27.8	19.2	68.4	43.7	654	96.6	1	-6.54	-40.7
Uusathima II	JT01-13	Jun-14	4	14.5		-99	7.15	2070	402	9	1.6	1366	<0.5	8.4	13	32	702		-2	-5.33	-31.7
Uusathima II	JT02-31	Sep-14	walk in	16.2		-313	7.13	2590	210	10	2.2	1762	2.7	9.6	21	43	721		2	-5.85	-37.3
Uusathima II	JT03-02	Mar-15	walk in	26.5		130	7.61	696	57	19.9	0.19	25	1.29							-5.92	-46
Uusathima II	JT04-02	Aug-15	4.3	21.5		-263	7.63	2280	269	15.9	2.05	1317	1.27	6.3	9.9	24	618	75.8	2	-5.41	-29.9
Uusathima III	JT07-14	May-16		13.9		19.4	8.19	1649	260	11.7	1.86	1429	0.122	7.2	12.4	22.3	622	67.9	-2	-6.49	-42.1
Uusathima R	JT08-17	Oct-16	5.05	20.7		139.4	7.02	1718	85.9	40	2.58	1473	8.65	16.9	28.1	23	603	71.5	0	-5.42	-39.2
Uusathima recharging water	JT06-23	Mar-16		25.3		21.6	7.5	190	27.1	13.7	0.28	78.3	1.85	9.2	2.8	2.52	33.6	2.6	-3	-7.97	-46.3
Uusathima surface water pond	JT06-24	Mar-16		27		20.6	7.45	150.4	33	13.9	0.217	54.7	1.71	8.8	2.8	2.51	25	2.7	-5	-7.21	-45.4

Appendix B: Raw hydrochemical and isotopic data collected in this study

Village	No	Sampling date	Water level [m]	Temp [°C]	O ₂ -content [mg/l]	ORP [mV]	pH	EC [μS/cm]	HC O ₃ ⁻ [mg/l]	Cl ⁻ [mg/l]	F ⁻ [mg/l]	SO ₄ ²⁻ [mg/l]	NO ₃ ⁻ [mg/l]	Na ⁺ [mg/l]	K ⁺ [mg/l]	Mg ²⁺ [mg/l]	Ca ²⁺ [mg/l]	SiO ₂ [mg/l]	Balance [%]	δ ¹⁸ O [‰]	δ ² H [‰]
Uusathima well 1 recharged	JT06-25	Mar-16		27		142.2	7.9	296.4	25.8	15.8	0.157	151	2.23	10.6	3	2.86	65.5	3.4	0	-7.14	-45.8
Uusathima well 2 not-recharged	JT06-26	Mar-16		24.7		183.8	7.48	1592	58.8	74.7	0.494	2195	1.04	7.3	25	14.6	575	32.7	-33	-6.28	-44.2
Walye-Inda	JT07-02	May-16		19.5		133.9	7.37	217.1	60.5	14.3	0.157	15.3	0.345	18.6	14.4	2.53	7.3	58.7	1	-4.3	-34.4
Walye-inda	JT08-3	Oct-16	walk in	33		85.2	7.27	119	45.1	15.3	0.248	15.3	0.145	22.2	11.4	1.04	2.95		0	-4.65	-39.2
Walye-inda	JT02-13	Sep-14	walk in	22.1		38	6.41	216.3	28	2.5	0.2	24	2.8	21	2	1.8	6.2		-6	-5.34	-40.1
Walye-inda	JT03-21	Mar-15	walk in	36		40	6.8	250	216	23.9	0.236	0	265							-3.78	-30.3
Walye-inda	JT04-24	Aug-15	walk in	23.8		141.3	7.35	183.6		16.6	0.257	15.1	6.37	25.2	15.4	2.34	8.04			-3.76	-30.8
Walye-inda	JT06-15	Mar-16		24.7		210	8.56	296												-1.87	-26.3
Walye-inda	W04-017	Jun-15		23.6	5.3		5.47	143.7	40.7	14.1	0.246	9.83	10.8	17	2	1.19	4.36	66	-14	-4.53	-33.7
Walye-inda field	JT02-21	Sep-14	walk in	19.4		177	7.29	89.8	25	2.8	0.3	7	0.6	10	6.4	2.7	3.6		-5	-3.21	-32.2
Walye-inda field	JT03-20	Mar-15	walk in	34.5		217	7.8	87.4	20	10.9	0.304	13	138							-3.79	-31.2
Walye-inda field	JT04-23	Aug-15	walk in	25.2		69.3	7.77	210.9	51.1	6.76	0.551	7.66	4.99	24.8	5.4	2.78	4.8		13		
Walye-inda field	JT06-14	Mar-16				25.5	8.18	90	84.2	7.45	0.345	4.14	0.404	20.5	6.9	3.33	6.23	97.2	-1	-3.18	-29.6
Walye-inda field	W02-021	Mar-14	walk in	32.2	7.36		6.2	65.1	15	0.8	0.1	17	0.9	6.9	5.4	1.6	2.5		-1	-5.96	-42.6

Appendix B: Raw hydrochemical and isotopic data collected in this study

Village	No	Sampling date	Water level [m]	Temp [°C]	O ₂ -content [mg/l]	ORP [mV]	pH	EC [μS/cm]	HC O ₃ ⁻ [mg/l]	Cl ⁻ [mg/l]	F ⁻ [mg/l]	SO ₄ ²⁻ [mg/l]	NO ₃ ⁻ [mg/l]	Na ⁺ [mg/l]	K ⁺ [mg/l]	Mg ²⁺ [mg/l]	Ca ²⁺ [mg/l]	SiO ₂ [mg/l]	Balance [%]	δ ¹⁸ O [‰]	δ ² H [‰]
Walye-inda field	W02-214	Jun-14		20.1	9.49		6.95	100.1	29.5	6.01	0.221	5.41	0.557	21.8	5.3	2.07	3.58	79.1	29	-4.74	-40.3
Walye-inda field	W04-016	Jun-15		24.4	4.66		5.96	133.5	57	9.7	0.608	9.46	6.16	27.7	5.4	3.21	7	137	12	-5.15	-41.3



Test method details

All methods are based on Standard methods for the Examination of Water and Wastewater, 22th ed. 2012 (US Standard methods) unless otherwise stated

Test Method No.: W 022
AWWA 4500-H⁺ B

Title: Electrometric pH Measurement

1. Definition of term

At a given temperature the intensity of the acidic or basic character of a solution is indicated by pH or hydrogen ion activity.

2. Principle

The basic principle of electrometric pH measurement is determination of the activity of the hydrogen ions by potentiometric measurements using a glass electrode and a reference electrode. The electromotive force (emf) produced in the glass electrode system varies linearly with pH. This linear relationship is described by plotting the measured emf against the pH of different buffers. Sample pH is determined by extrapolation.

Test Method No.: W 007
AWWA 2510 B

Title: Electrical Conductivity Measurement

1. Definition

Conductivity, k , is a measure of the ability of an aqueous solution to carry an electric current. This ability depends on the presence of ions, on their total concentration, mobility, and valence; and on the temperature of measurement. Solutions of most inorganic compounds are relatively good conductors. Conversely, molecules of organic compounds that do not dissociate in aqueous solution conduct a current very poorly, if at all.

Test Method No.: W 027
AWWA 2130 B

Title: Turbidity - Nephelometric Method

1. Definition of term

Turbidity is an expression of the optical property that causes light to be scattered and absorbed

Appendix C: Analytical methods used at Analytical Laboratory Services as prepared by the laboratory.

rather than transmitted with no change in direction or flux level through the samples.

2. Principle

This method is based on a comparison of the intensity of light scattered by the sample under defined conditions with the intensity of light scattered by a standard reference suspension under the same conditions. The higher the intensity of scattered light, the higher the turbidity.

Test Method No.: W 006

Title: Colour - Photometric Method

AWWA Pt-Co-2120 B

1. Definition of term

The term “colour” is used here to mean true colour, that is, the colour of water from which the turbidity has been removed. The term “apparent colour” includes not only colour due to substances in solution, but also that due to suspended matter. Apparent colour is determined on the original sample without filtration or centrifugation.

2. Principle

Colour is determined by visual comparison of the sample with known concentrations of coloured solutions. The platinum-cobalt method of measuring colour is the standard method, the unit of colour being that produced by 1mg platinum/l in the form of the chloroplatinate ion.

Test Method No.: W 019

Title: Oxidation/Reduction Potential Measurement

AWWA 2580 B

1. Principle

Electrometric measurements are made by potentiometric determination of electron activity (or intensity) with an inert indicator electrode and a suitable reference electrode.

Test Method No.: W 025

Title: Total Dissolved Solids dried at 180°C

AWWA 2540 C

1. Definition of term

“Dissolved solids” is the portion of solids that passes through a filter of 2.0µm (or smaller) nominal pore size under specified conditions. Dissolved solids may include organic and inorganic matter.

2. Principle

A well-mixed sample is filtered through a standard glass fiber filter, and the filtrate, evaporated to dryness in a weighed dish and dried to constant weight at 180°C. The increase in dish weight represents the total dissolved solids

Test Method No.: W 026

Title: Total Suspended Solids dried at 103-105°C

AWWA 2540 D

1. Definition of term

“Suspended solids” is the portion retained on the filter.

2. Principle

A well-mixed sample is filtered through a weighed standard glass-fiber filter and the residue retained on the filter is dried to a constant weight at 103 to 105°C. The increase in weight of the filter represents the total suspended solids.

Test Method No.: W 001

Title: Alkalinity – Titration Method

AWWA 2320 B

1. Definition

Alkalinity of a water is its acid-neutralising capacity. It is the sum of all the titratable bases. Alkalinity is a measure of an aggregate property of water and can be interpreted in terms of specific substances only when the chemical composition of the sample is known.

Total alkalinity is the term used for the quantity measured by titration to pH of 4.9, 4.6, 4.5 or 4.3 depending on the type of sample using a mixed bromocresol green-methyl red indicator. The total alkalinity includes all carbonate, bicarbonate and hydroxide alkalinity. Phenolphthalein alkalinity is the term used for the quantity measured by titration to pH 8.3 using phenolphthalein or metacresol purple indicator and registers the total hydroxide and one half of the carbonate present.

2. Principle

When alkalinity is due entirely to carbonate or bicarbonate content, the pH at the equivalence point of the titration is determined by the concentration of carbon dioxide at that stage. CO₂ concentration depends, in turn, on the total carbonate species originally present and any losses that may have occurred during titration.

Test Method No.: W 004

Title: Chloride – Argentometric Method

AWWA 4500-Cl B

1. Principle

In a neutral or slightly alkaline solution, potassium chromate can indicate the end point of the silver nitrate titration of chloride. Silver chloride is precipitated quantitatively before red silver chromate is formed.

Test Method No.: W 008

Title: Fluoride - Ion-Selective Electrode Method

AWWA 4500-F C

1. Principle

The fluoride electrode measures the ion activity of fluoride in solution rather than concentration. Fluoride ion activity depends on the solution total ionic strength and pH, and on fluoride complexing species. Adding an appropriate buffer provides a nearly uniform background, adjusts

Appendix C: Analytical methods used at Analytical Laboratory Services as prepared by the laboratory.

the pH, and breaks up complexes so that, in effect, the electrode measures concentration.

Test Method No.: W 024
AWWA 4500-SO₄ E

Title: Sulphate - Turbidimetric Method

1. Principle

Sulphate ion is precipitated in an acetic acid medium with barium chloride so as to form barium sulphate crystals of uniform size. Light absorbance of the barium sulphate suspension is measured by a turbidimeter and the sulphate concentration is determined by comparison of the reading with a standard curve.

Test Method No.: W 015
AWWA 4500-NO₂ B

Title: Nitrite - Photometric Method

1. Principle

Nitrite is determined through formation of a reddish purple azo dye produced at pH 2.0 to 2.5 by coupling diazotized sulfanilamide with N-(1-naphtyl)-ethylenediamine dihydrochloride (NED dihydrochloride).

Test Method No.: W 016
(Spectroquant)

Title: Nitrate - Photometric Method

1. Principle

In concentrated sulphuric acid nitrate ions react with a benzoic acid derivative to form a red nitro compound that is determined photometrically

Test Method No.: W 028 Title: Nitrate in seawater - Photometric Method

Principle (Spectroquant)

In concentrated sulphuric acid, in the presence of chloride nitrate ions react with resorcinol to form a red-violet indophenol dye that is determined photometrically.

Test Method No.: W 023
AWWA 4500-Si D

Title: Molybdosilicate –Photometric Method

1. Principle

Ammonium molybdate at pH approximately 1.2 reacts with silica and any phosphate present to produce heteropoly acids. Oxalic acid is added to destroy the molybdophosphoric acid but not the molybdosilicic acid. The intensity of the yellow colour is proportional to the concentration of “molybdate-reactive” silica.

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Test Method No.: W 010
AWWA 2340 B

Title: Hardness, total – C alculatation

1. Definition

Total hardness is defined as the sum of the calcium and magnesium concentrations, both expressed as calcium carbonate, in milligrams per liter.

2. Discussion

Hardness by calculation, is applicable to all waters and yields the higher accuracy. If a mineral analysis is performed, hardness by calculation can be reported.

Test Method No.: W 020

Title: Reactive Phosphate HR – Photometric

1. Definition of term Method (Hach)

Phosphates that respond to colorimetric tests without preliminary hydrolysis or oxidative digestion of the sample are termed 'reactive phosphorous'. While reactive phosphorous is largely a measure of orthophosphate, a small fraction of any condensed phosphate.

present usually is hydrolyzed unavoidably in the procedure. Reactive phosphorous occurs in both dissolved and suspended form

2. Principle

In a dilute orthophosphate solution, ammonium molybdate reacts under acid conditions to form a heteropoly acid, molybdophosphoric acid. In the presence of vanadium, yellow vanadomolybdophosphoric acid is formed. The intensity of the yellow colour is proportional to phosphate concentration.

Test Method No.: W 021
AWWA 4500-P B+C

Title: Total Phosphorus – Persulphate Method

1. Definition of term

Total phosphorous includes reactive, acid-hydrolyzable and organic phosphorous. Because phosphorous may occur in combination with organic matter, a digestion method to determine total phosphorous must be able to oxidize organic matter effectively to release phosphorous as orthophosphate.

2. Principle

The sample is first digested and then the liberated orthophosphate determined photometrically (see above).

Test Method No.: W 011 Title: Total Nitrogen – Photometric Method (Spectroquant), The digestion is analogous to EN ISO 11905-1

1. Definition of term

The test method determines total nitrogen by oxidation of all nitrogenous compounds to nitrate.

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Ammonia, nitrate, and nitrite must be determined individually so that “organic nitrogen” can be obtained by difference. Kjeldahl nitrogen is total nitrogen minus ‘oxidised nitrogen’, namely nitrate and nitrite.

2. Principle

Organic and inorganic nitrogen compounds are transformed into nitrate according to Koroleff’s method by treatment with an oxidizing agent in a thermoreactor. In concentrated sulphuric acid, this nitrate reacts with a benzoic acid derivative to form a red nitro compound that is determined photometrically.

Test Method No.: W 013

Title: Ammonia – Photometric method

1. Principle (Spectroquant)

Colorimetry of blue 2,2 ‘-isopropyl-5,5’-methyl-indophenol (Berthelot’s reaction)

Following adjustment to pH 13, ammonia reacts with hypochlorite to monochloramine, which in turn forms a blue indophenol dye in a catalysed 2-stage reaction with thymol

Test Method No.: W 018

Title: Absorbed Oxygen – I odometric Method

SANS 5220:2005

1. Definition of term

The method is an empirical measure of both organic and inorganic matter that can be oxidized by an acidified permanganate solution over a period of 4h at 27°C.

2. Principle

The permanganate is partially reduced by the oxidisable material present in the sample. The remainder of the permanganate is titrated with sodium thiosulphate and the oxygen absorption value calculated from the amount of permanganate reduced.

Test Method No.: W 005

Title: COD - Closed Reflux - Photometric Method

AWWA 5220 D

1. Definition of term

The chemical oxygen demand (COD) is used as a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant.

2. Principle

Most types of organic matter are oxidized by a boiling mixture of chromic and sulphuric acids. A sample is refluxed in strongly acid solution with a known excess of potassium dichromate. After digestion, the oxygen consumed is measured against standards at 600 nm with a spectrophotometer.

Test Method No.: W 002

Title: 5-Day BOD Test

AWWA 5210 B

Appendix C: Analytical methods used at Analytical Laboratory Services as prepared by the laboratory.

1. Definition of term

The BOD test measures the biodegradable organic carbon and, under certain conditions, the oxidizable nitrogen present in the waste.

2. Principle

The method consists of filling with sample, to overflowing, an air-tight bottle and incubating it at 20°C temperature for 5 d in the dark. Dissolved oxygen is measured initially and after incubation and the BOD is computed from the difference between the initial and the final DO.

Test Method No.: W 009 Title: Oil and Grease Partition-Gravimetric Method AWWA 5520 B

1. Principle

In the determination of oil and grease, an absolute quantity of a specific substance is not measured. Rather, groups of substances with similar physical characteristics are determined quantitatively on the basis of their common solubility in an organic extracting solvent. “Oil and grease” is defined as any material recovered as a substance soluble in the solvent.

2. Application

Following method is suitable for biological lipids and mineral hydrocarbons. It also may be suitable for most industrial wastewater or treated effluents containing these materials, although sample complexity may result in either low or high results because of lack of analytical specificity.

Test Method No.: W029 Title: Chlorine reactive cyanides without distillation, Photometric Method (Riedel-deHaën)

1. Definition of term

Cyanide compounds that are amenable to chlorination include free cyanide as well as those complex cyanides that are potentially dissociable.

2. Principle

This test is based on the addition of chloramine-T and subsequent colour complex formation with barbituric acid. Only those metal cyanides and metal cyano-complexes react which are destroyed by hypochlorite, free cyanide and thiocyanate (albeit at a reduced speed) are converted to CNCl; the chlorine cyanide in turn reacts with pyridine splitting the pyridine ring into glutacone dialdehyde. Glutacondialdehyde condenses with 1,3-dimethyl-barbituric acid and forms a violet polymethine dye.

Test Method No.: W030 Title: Dissolved Sulphide Methylene Blue Method – Photometric Method (Spectroquant)

1. Definition of term

Dissolved sulphide is that remaining after suspended solids have been removed by flocculation

Appendix C: Analytical methods used at Analytical Laboratory Services as prepared by the laboratory.

and settling. For samples that are entirely free from suspended solids dissolved sulphide equals total sulphide.

2. Principle

The methylene blue method is based on the reaction of sulphide, ferric chloride and dimethyl-p-phenylenediamine to produce methylene blue. Ammonium phosphate is added after colour development to remove ferric chloride colour

Test Method No.: W031
AWWA 4500 B

Titel: Sulphite iodometric Method

1. Principle

An acidified sample containing sulphite is titrated with a standardised potassium iodide-iodate titrant. Free iodine, liberated by the iodide-iodate reagent, reacts with SO_3^{2-} . The titration endpoint is signalled by the blue colour resulting from the first excess of iodine reacting with a starch indicator

Test Method No.: W032 Titel: Consecutive iodometric determination of Br^- and I^-

1. Principle

Bromide and iodide ions can be determined successively in one water sample using a method developed by p. Höfer. Hypochlorite ions are used to oxidise bromide ions to bromate ions and iodide ions to iodate ions. The excess hypochlorite ions are destroyed by formic acid.

Subsequently, iodide ions added at pH 3 to 4 are oxidised to iodine by the iodate ions. In this solution, following the addition of hydrochloric acid and adjustment of pH to less than 1, the bromide ions are then detected analogously.

Direct determination of bromide ions is possible in a range between 0.01 and 15 mg/L and determination of iodide ions in a range between 0.005 and 5 mg/L of the water sample.

Test Method No.: W033

Titel: Metals by Plasma Emission Spectroscopy

For dissolved metals (such as ground waters) samples should be filtered through 0.45µm into a HNO_3 preserve bottle.

For dissolved metals that are not field filtered and acidified, samples will be filtered on receipt from an unpreserved sample container and then acidified.

For total recoverable metals (such as surface waters) samples should be placed unfiltered into a HNO_3 preserved bottle.

For total recoverable metals that are not field preserved, a sub-sample will be taken from the unpreserved bottle on receipt and acidified with HNO_3 .

Appendix D: Analytical methods used at BGR hydrochemistry laboratory as prepared by the laboratory.

IC and ICP-OES

The determination of the concentrations of major and minor ions was done using a DIONEX ICS-3000 ion chromatograph (Cl, Br, F, NO₃, NO₂, NO₂, SO₄) a SPECTRO ARCOS ICP-OES (Na, K, Ca, Mg, P, Fe, Mn, Al, Si, PO₄) and a UNICAM UV 300 photometer (NH₄). Commercial standard solutions are used for daily calibration and limits of quantitation are determined by 10-point calibration according to the DIN 32645 standard. Determination of HCO₃ and CO₃ concentrations was done on a SCHOTT Titroline Alpha Plus automatic titration system according to a modified DIN 38409-H7-2 standard by evaluation of titration curve shapes for the identification and quantitation of these species. The contribution of PO₄ to alkalinity was estimated from ICP-OES concentration data.

ICP-MS

The concentration of uranium and trace elements was measured using AGILENT 7500 ICP-MS. Precision is estimated based on results of daily check standard measurements according to the DIN ISO 11352:2013-03 standard, and accuracy from proficiency testing results and daily measurement of standard solutions.

Isotopes - Picarro

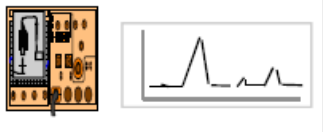
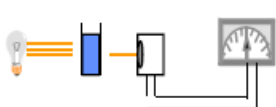
The stable water isotope (¹⁸O and ²H) abundances were determined using a PICARRO L2120-i cavity ring-down laser spectrometer. The accuracy based on independently measured control standards is better than 0.2‰ and 0.8‰ for δ¹⁸O and δ²H, respectively.

All water samples were shipped to Germany and analyzed at the isotope laboratory of the BGR in Hannover for δ²H and δ¹⁸O simultaneously using a Picarro L2120-i cavity ring down (CRD) laser spectrometer after vaporization. The samples were measured at least four times and the reported value is the mean value. All values are given in delta notation in per mill (‰) vs. VSMOW. For a representation of delta values in Tables and Figures we follow recommendations given by Coplen et al. (2011). Raw data were checked for organic contamination using the software Chemcorrect (unaltered software settings) and corrected for memory effects (Van Geldern et al., 2012), drift, and normalized to the VSMOW/SLAP scale. External reproducibility, defined as standard deviation of a quality check standard during all runs, was better than 0.20 ‰ and 0.8 ‰ for δ¹⁸O and δ²H, respectively.

Coplen TB 2011. Guidelines and recommended terms for expression of stable isotope-ratio and gas-ratio measurement results. Rapid Commun. Mass Spectrom. 25: 2538-2560. DOI: 10.1002/rcm.5129.

Van Geldern R, Barth JAC 2012. Optimization of instrument setup and post-run corrections for oxygen and hydrogen stable isotope measurements of water by isotope ratio infrared spectroscopy (IRIS). Limnol. Oceanogr: Methods 10, 1024-1036 (2012). DOI: 10.4319

Appendix D: Analytical methods used at BGR hydrochemistry laboratory as prepared by the laboratory.

BGR - B 2.3 Stand 09 / 15	Hinweise zur Probenahme	zu bestimmende Verbindung	Analysenverfahren	
 500 ml	Hauptbestandteile Probe sollte klar sein ! Kühl aufbewahren. Flasche möglichst ohne Restluft verschließen ! Nach Möglichkeit sofort im Labor abliefern	HCO₃ CO₃	Potentiometrische Titration	
		F, NO₂, Br Cl NO₃ SO₄	Ionen - chromatographie	
		K , Na Mg, Ca Cl, S	ICP - OES	
	Verschmutzungsindikatoren . Bestimmung innerhalb 24 Std. - kühl lagern (4°C)	NH₄	Photometrie	
 100 ml	Spurenelemente 100 ml Probe filtrieren - 0,45µm (0,1µm für Sonderuntersuchungen) und mit 1 ml HNO ₃ am Entnahmeort ansäuern !	Spuren z.B. Ag Al Ba Be Cd Cr Cu Fe Li Mn Ni Pb Sc V Zn As	ICP - OES ICP - MS	
 100 ml	Summenparameter TIC, TOC, TNb. Für DOC-Best Probe über 0,45µm filtrieren.	TIC: gesamter anorg. Kohlenstoff TOC: gesamter org. Kohlenstoff TNb: gesamter gebundener Stickstoff DOC: gelöster org. Kohlenstoff NPOC: :nicht ausblabarer org. C	TIC/TOC/TNb-Analysator Katal. Verbrennung im O ₂ -Strom CO ₂ -Detektion im IR-Detektor NO-Detektion im CL-Detektor	