DIGBY WELLS
ENVIRONMENTAL

To:	Jade Greve	**Date:**	30 June 2022
From:	Digby Wells Environmental	**Proj #:**	AFT7220
RE:	**Isotope Analysis Results**		

Dear Jade,

This memo provides feedback on the isotope results for the five (5) samples collected at the AfriTin's Tin Mine between 19 and 25 January 2022. The isotope samples were collected to trace links between the water located in the K5 pit with surrounding groundwater locations. The five water samples represent groundwater (BH8, BH10, BH12), pit water (K5) and rainwater (Rain 2), the locations of which are presented in Figure 7.

The Mine is situated in Uis (within the Erongo Region, Namibia), which is approximately 200 km north of Swakopmund. The project area is classified as a hot desert climate (BWh) based on the Köppen-Geiger classification system. The BWh classification characterises areas where evaporation and transpiration exceed precipitation with hot to exceptionally hot (over 40°C) periods of the year. The annual rainfall for the project area ranges between ~2 - 592 mm, with an average of 88 mm per year (National Centers for Environmental Prediction, 2022) (Environmental Compliance Consultancy, 2021). Chloride method estimates from the rainwater sample indicate approximately 0.7% of rainfall contributes to recharge of the groundwater aquifer.

Stable isotopes of oxygen (^{18}O) and hydrogen (^{2}H) can be used as environmental tracers. The composition of stable isotopes in natural waters can change based on physical, chemical, and biological processes that occur within the hydrological cycle as a result of isotope fractionation.

Tritium is a radioactive isotope of hydrogen which has been applied in age determinations of groundwater.

1. Methodology

Two samples were collected from each site, 1 x 1 l sample for the tritium analysis and 1 x 40 ml sample for the stable hydrogen ($\delta^{2}H$) and oxygen ($\delta^{18}O$) analysis. No additives or preservatives were added to the samples. The samples were submitted to Ithemba Laboratories in South Africa for Analysis. In addition to the isotope samples, the groundwater and pit water locations were sampled and analysed for the major cation and anions to determine the hydrochemistry characteristics for the site.

Stable isotopes are reported in δ(‰) values with respect to a common international reference system to allow for comparison to other results obtained from different laboratories. The

Standard Mean Ocean Water (SMOW) reference standard corresponds to a hypothetical water having both oxygen and hydrogen isotopic ratios equal to the mean isotopic ratios of ocean water. The SMOW reference is a theoretical reference and therefore cannot be used to calibrate laboratory measurements. To assist with the intercalibration of laboratories, a water sample was prepared to have an isotopic composition as close to the SNOW theoretical reference. This reference standard is referred to as Vienna-SNOW (V-SMOW). There is a reported difference of 0.02‰ ($\delta^{18}O$) and 0.2‰ ($\delta^{2}H$) in the V-SMOW reference standard compared to the SNOW reference standard (International Atomic Energy Agency, 1981).

The reference standard used in this report to determine the isotopic ratios is the Standard Mean Ocean Water (SMOW).

1.1. Hydrochemistry

The Piper Diagram is particularly useful for identifying groundwater facies and groups samples with a similar water chemistry. The Expanded Durov Diagram improves on the Piper Diagram by displaying important hydrochemical processes, such as ion exchange, simple dissolution and mixing of waters with different qualities.

The STIFF Diagram graphically displays the water quality which creates distinctive signatures for water samples which can be used to show potential links between sources and receptors.

1.2. Isotope Interpretation

Stable isotopes can be used to determine the origin of groundwaters based on their abundance and variations, which can be subdivided into four categories:

- Meteoric waters are derived directly from precipitation or from fresh surface waters via recharge and the isotope composition of these waters generally matches the composition of the local precipitation.

  In arid areas, groundwater is likely to be more enriched in the heavy isotopes relative to precipitation (International Atomic Energy Agency, 1981). Groundwater aquifers in desert areas are exposed to little irregular precipitation and are therefore less likely to be flushed by recharge so there are increased chances for groundwaters with paleowater characteristics to be present (International Atomic Energy Agency, 1981);
- Paleowater represents meteoric waters which have originated in the distant past especially if there have been climatic changes in the area (International Atomic Energy Agency, 1981);
- Geothermal waters are derived from aquifers which have been exposed to temperatures of more than 80 C which results in a change of isotope composition (International Atomic Energy Agency, 1981); and
- Formation waters represent saline groundwater which are typically located at great depths in sedimentary aquifers (International Atomic Energy Agency, 1981).

1.2.1. Meteoric Waters

A relationship between the stable isotopic ratios of $\delta^{2}H$ and $\delta^{18}O$ in meteoric waters was described in 1961 and defined the Global Meteoric Water Line (GMWL) (Craig, 1961). The GMWL is defined as:

$$\delta 2H = 8 \times \ \delta 18O + 10$$

Since 1961, IAEA in co-operation with the World Meteorological Organization (WMO) have been undertaking a worldwide survey of the heavy oxygen ($\delta^{18}O$) and hydrogen ($\delta^{2}H$ and ^{3}H) isotopes in precipitation to determine temporal and spatial variations within these stable isotopes. Initial assessments of the isotope database indicated that the distribution of heavy isotopes can be influenced by latitude, altitude, distance to the coast, intensity of precipitation and surface air temperature (International Atomic Energy Agency, 1992).

A Local Meteoric Water Line (LMWL) was calculated using the isotope in precipitation statistics from the Windhoek Station, which is the nearest station to the Uis Tin Mine. The Windhoek Station analysed rainfall samples between January 1961 and December 2001, resulting in 141 $\delta^{18}O$ results, 97 $\delta^{2}H$ results and 122 $\delta^{3}H$ results. The LMWL statistics for this dataset are provided in Table 1 and were used to calculate the LMWL trend lines using the function:

$$y = ax + b$$

Table 1: LMWL Windhoek Statistics (International Atomic Energy Agency, 2022)

Regression Type	a	b	Std Error	R^2	N
LSR[1]	7.14 ± 0.19	7.95 ± 0.91	7.08	0.94	93
RMA[2]	7.36 ± 0.19	8.59 ± 0.91	7.08	0.94	93
PWLSR[3]	7.30 ± 0.17	9.36 ± 1.00	5.67	0.96	87

A later study by Putman et al (2019) assessed variations in Local Meteoric Water Lines (LMWL) compiled using the isotope dataset by the International Atomic Energy Agency (IAEA). From this study seasonal trends (Figure 1) were identified (Putman, Fiorella, Bowen, & Cai, 2019). Arid regions of the Köppen-Geiger classification are categorized as B: hot/dry – hot/humid which have a range in $\delta^{18}O$ of between -9‰ - 9‰ and $\delta^{2}H$ of between -40‰ - 10‰.

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[1] LSR – Least Squares Regression Method.
[2] RMA – Reduced Major Axis Regression Method.
[3] PWLSR – Penalised Weighted Least Squares Regression Method.

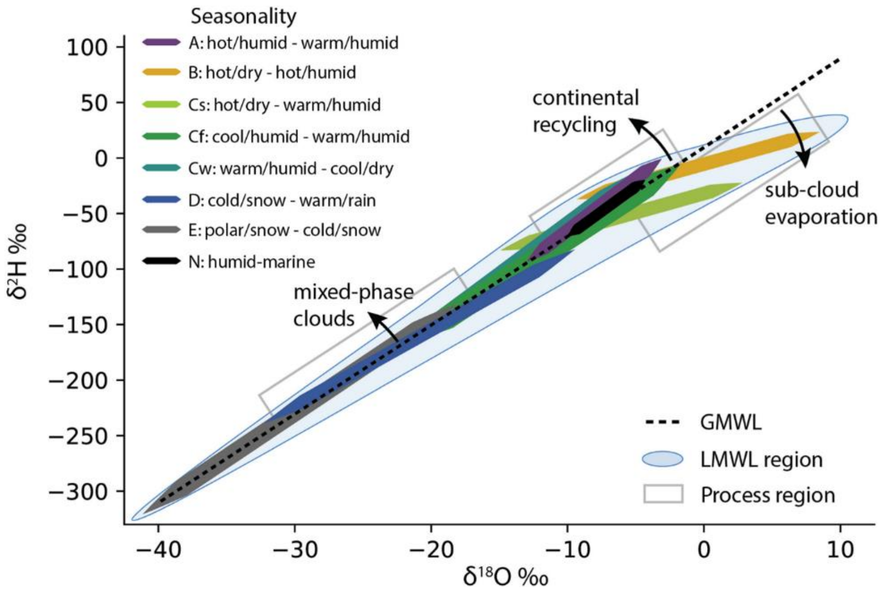

Figure 1: Seasonality of LMWL around the GMWL (Putman, Fiorella, Bowen, & Cai, 2019)

1.2.2. Paleowater

Paleowater is groundwater which originates from water cycles under different environmental conditions to the present day. Paleowater characteristics can follow similar enrichment processes to meteoric water especially if related to evaporitic period or marine transgressions. The dating of dissolved inorganic carbon (DIC) becomes important to identify paleowater and understand the methods of recharge (International Atomic Energy Agency, 1981).

Tritium is the only radioactive isotope of hydrogen with a half-life of 12.43 years. During the 1950’s and 1960’s large quantities of tritium were introduced into the hydrological cycle because of atmospheric thermonuclear testing and therefore tritium is used as an environmental tracer for water originating from this period (Solomon & Cook, 2000). Waters which are derived exclusively from precipitation before 1953 would have a maximum tritium concentration of 0.1-0.4 TU. Higher tritium values in water indicate that some water has been derived from precipitation after 1953 (Kendall & Doctor, 2003).

2. Results

2.1. Groundwater Levels

The water level in the K5 pit (774 mamsl) is currently lower than the surrounding groundwater levels measured in the water supply boreholes (which ranges between 778 – 800 mamsl. Groundwater will therefore flow towards the pit along fractures and groundwater flow paths (Figure 2).

2.2. Hydrochemistry

Water Quality samples were taken from the groundwater boreholes (BH8, BH10 and BH12) as well as the K5 pit. There were a total of five (5) groundwater samples collected per borehole as part of the hydrogeological water supply assessment. One sample was collected from the K5 for comparison.

Based on the Piper (Figure 3) and Expanded Durov (Figure 4) Diagrams the groundwater samples for BH8, BH10 and BH12 indicate a sodium-chloride water type which typically indicates groundwater with a long residence time or stagnant (slow moving) groundwater with little to no recharge. The K5 pit sample has a similar hydrochemistry to the groundwater samples as displayed on the Piper and Expanded Durov Diagrams.

The STIFF Diagrams (Figure 5) for the groundwater samples display a similar signature to each other and confirms the dominance of the sodium and chloride ions. The K5 pit water sample has a similar signature to the groundwater samples but with higher salt concentrations because of evaporation.

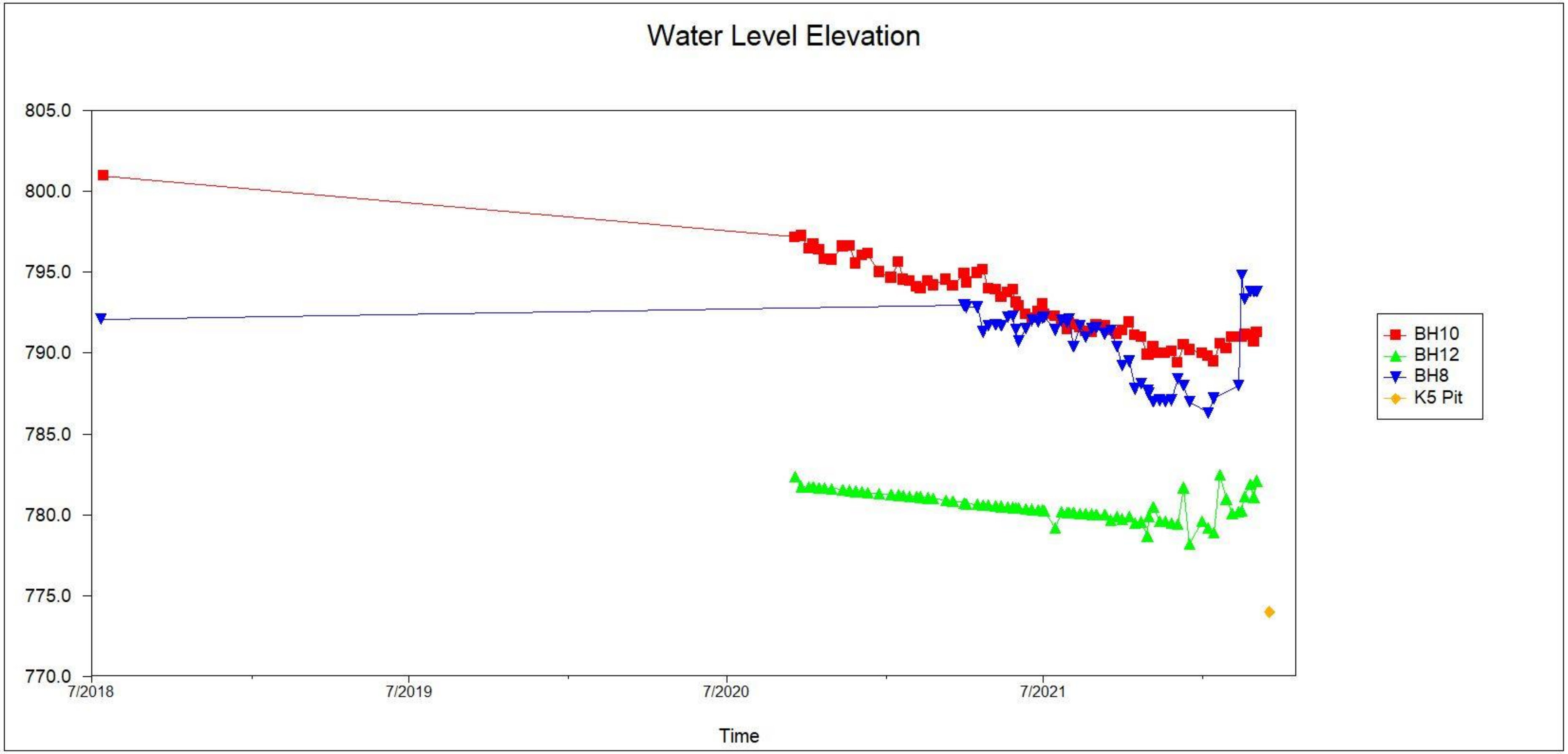

Figure 2: Groundwater Elevations

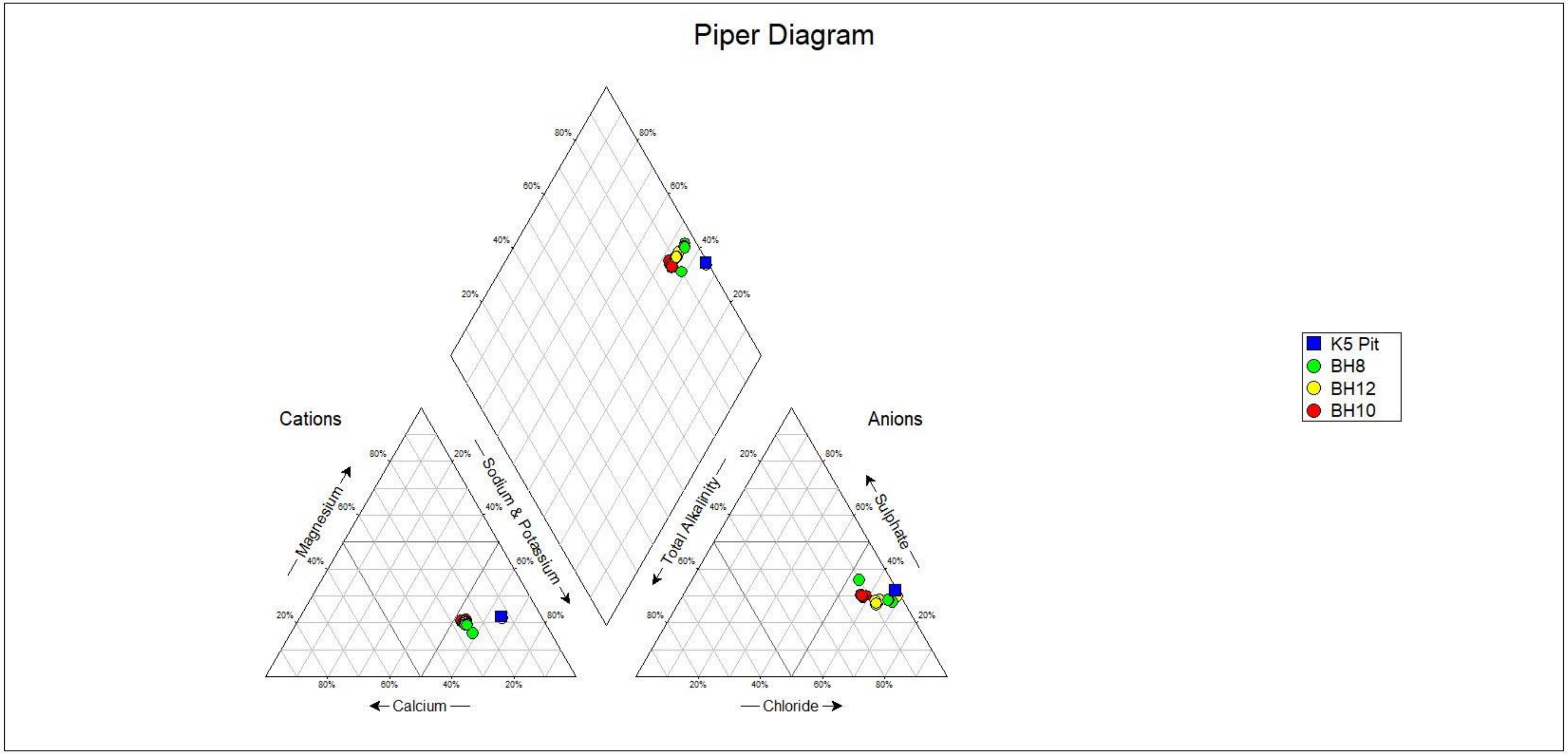

Figure 3: Piper Diagram

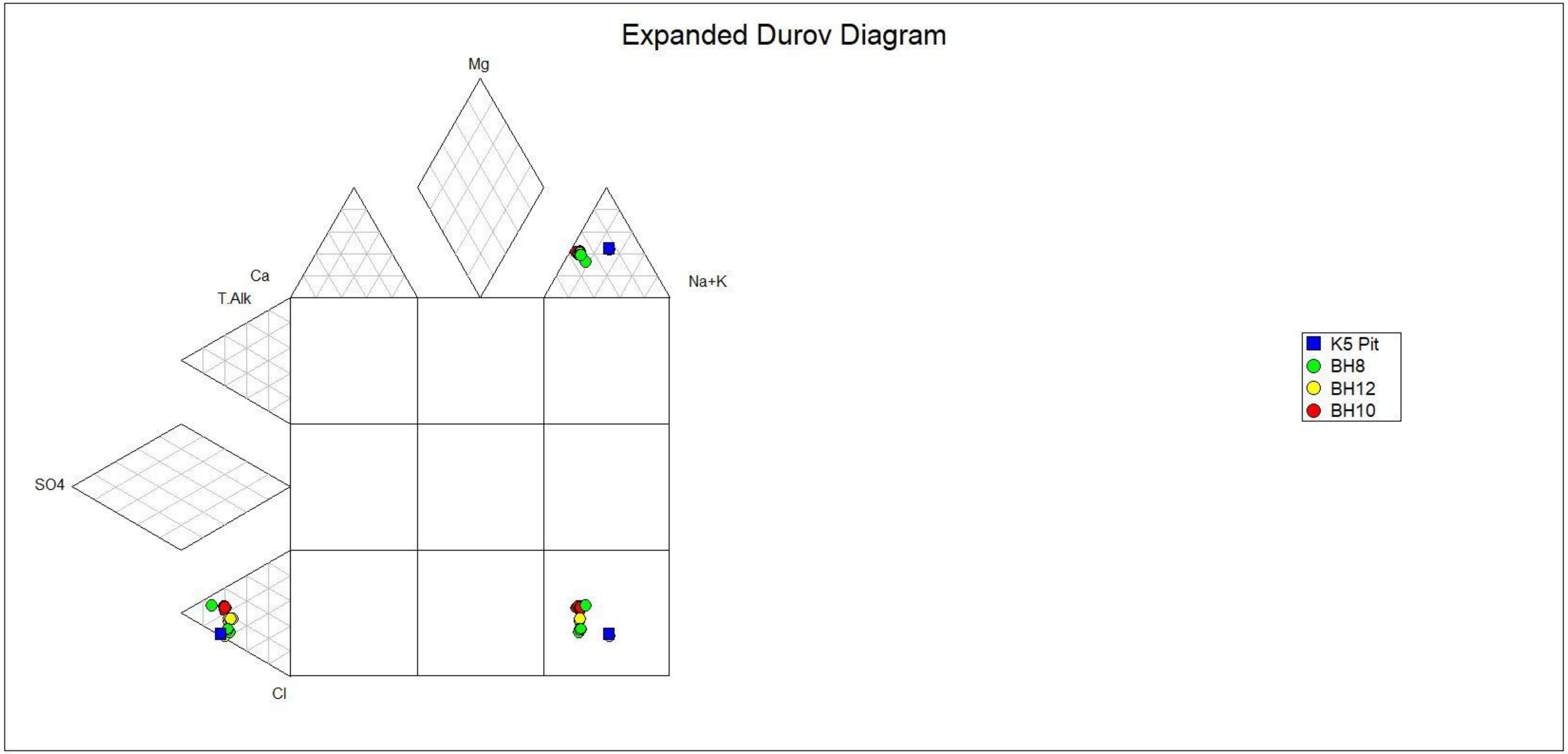

Figure 4: Expanded Durov

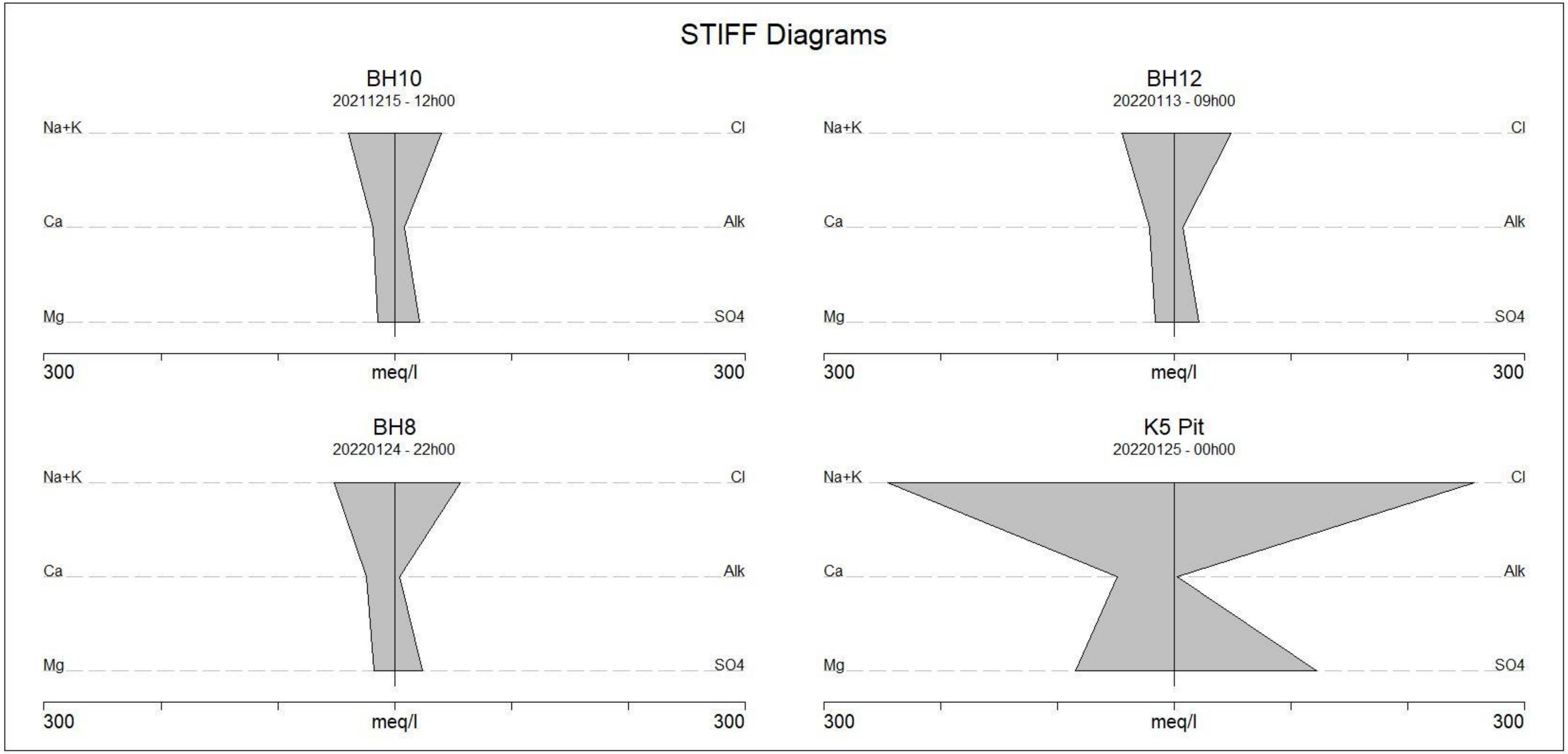

Figure 5: STIFF Diagram

2.3. Stable Isotopes

The Isotope results are provided in Table 2. A sample showing a negative δ value is depleted in heavier isotopes, and a sample with a positive δ value is enriched in heavier isotopes in respect to the SMOW. A more/ less positive versus more/less negative is used to describe the difference between two isotope values.

Table 2: Isotope Results

Sample ID	Sample Date	$\delta^{2}H$ ‰	TU	$\delta^{18}O$ ‰
K5	25/01/2022	+31.9	1.4 ± 0.3	+9.25
BH8	25/01/2022	-35.8	1.2 ± 0.3	-4.90
BH10	25/01/2022	-42.5	0.6 ± 0.3	-5.89
BH12	25/01/2022	-38.6	1.2 ± 0.3	-5.31
Rain 2	19/01/2022	-55.5	3.3 ± 0.4	-8.76

The rainwater sample has isotopic ratios of $\delta^{18}O$ and $\delta^{2}H$ as -8.8‰ and -55.5‰ respectively. This sample plots near the lower range of $\delta^{18}O$ and $\delta^{2}H$ for arid climates and is more positive in the $\delta^{2}H$ isotope and more negative in the $\delta^{18}O$ isotope as compared to the GMWL (Figure 6). The LMWL calculated using the LSR, RMA and PWLSR statistics (International Atomic Energy Agency, 2022) are also provided on Figure 6 and show a better fit to the collected rainwater sample.

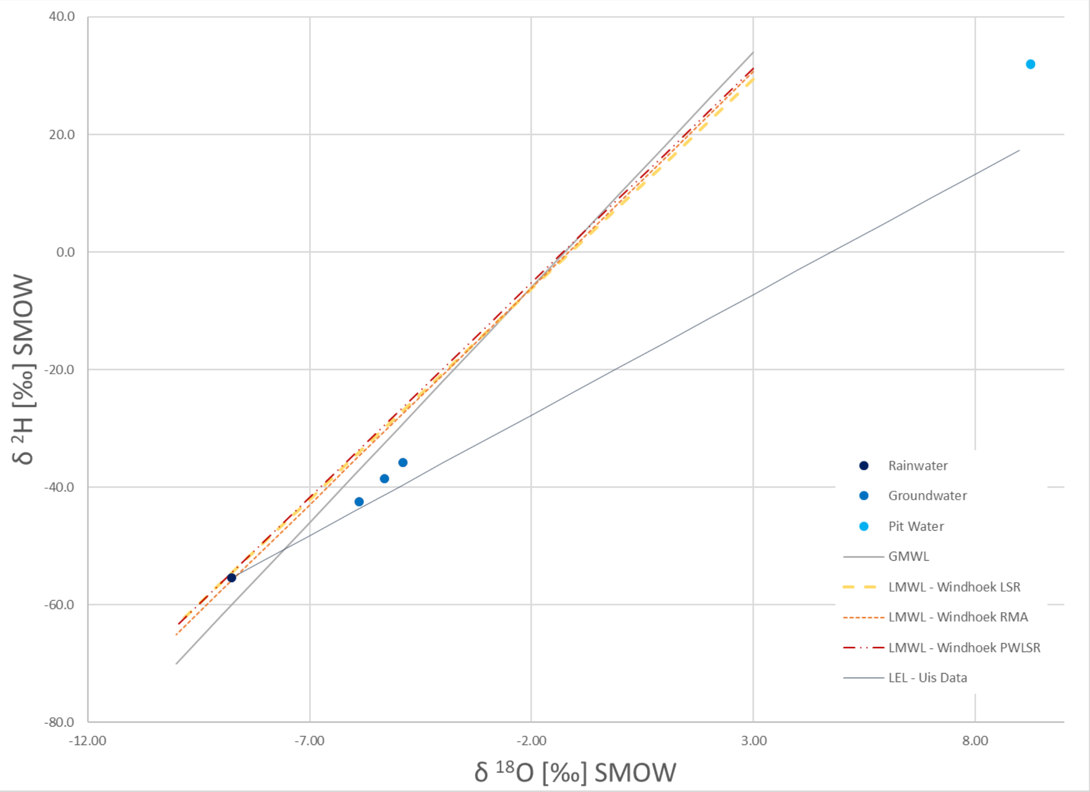

Figure 6: Isotope Results Compared to Meteoric Data

The Pit Water sample (K5) has the highest values of $\delta^{18}O$ and $\delta^{2}H$ compared to the rainwater and groundwater samples. Lakes and surface water bodies which lose water by evaporation are characterised by an enrichment in the heavy isotopes (International Atomic Energy Agency, 1981) because of the isotopic fractionation which occurs between the liquid and gaseous phases of water during the evaporation process. The enrichment of the heavy isotopes occurs along Local Evaporation Lines (LEL) which deviate from the meteoric water line with lower slopes. Based on the rain and pit water samples the slope of the evaporation line calculates to 4.1 using the following function:

$$S = \frac{[h(\delta a - \delta w) + \epsilon]2H}{[h(\delta a - \delta w) + \epsilon]18O}[4]$$

The dominant isotopic fraction in evaporation is kinetic fractionation, which is an irreversible process, where the product of the process is continuously removed. In an evaporation process the effect is not only dependent on temperature but also the relative humidity (h) of the atmosphere. The effect of humidity is important for the interpretation of the LEL slope as the smaller the humidity is the higher the change in δ^{18} O and δ^{2} H values will be. The calculated

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[4] Where h represents a humidity of 43% (World Weather Online, 2022);
Δa represents the respective isotope in atmosphere vapor (assumed to be represented by the precipitation isotopes);
Δw represents the respective isotope in surface water; and
ϵ (Total isotope fractionaction) calculated using the hydrocalculator (Skrzypek, et al., 2015).

LEL for the Uis data is indicative as the calculation based on average temperature and humidity values for Uis in January[5].

The three groundwater samples (BH8, BH10 and BH12) indicate similar results for the stable isotopes with a range in $\delta^{18}O$ of between -5.9‰ – -4.9‰ and a range in $\delta^{2}H$ of between -42.5‰ – -35.8‰. The groundwater samples are more positive in $\delta^{18}O$ and $\delta^{2}H$ compared to the rainwater sample and plot below the GMWL and LMWL and within the arid climate range of the seasonality trend.

The groundwater samples can be representative of meteoric water which has been enriched in the heavier isotopes because of evaporation. The lower slopes of evaporation lines for the groundwater samples are often linked to diffusive evaporation from soil water and fractionation occurring before percolation takes place.

There is the potential for paleowater or mixing of paleowater to be present but additional $^{13}C/^{14}C$ isotopic assessments would be required to determine this and would likely be limited to ages less than 20 000 - 25 000 years (International Atomic Energy Agency, 1981). The tritium results will provide more information as to the recent age of the water samples.

2.4. Tritium

The tritium results are provided in Table 2. The rain sample indicates a tritium value of 3.3 ± 0.4 TU which is in the range expected for rainfall with 1 TU being indicative of high precipitation in oceanic regions and 10 TU representing arid inland areas (Phillips & Castro, 2014).

The K5 pit sample has a similar tritium value (1.4 ± 0.3 TU) to BH8 and BH12 (1.2 ± 0.3 TU), all higher than 0.1-0.4 TU, indicating that these waters are recent and have been derived from precipitation after 1953. These sample locations have had a similar exposure to precipitation from the 1950s.

The sample collected from BH10 has a lower tritium value of 0.6 ± 0.3 TU compared to the other samples indicating that the source of water was predominately recharged prior to 1953 (old water) with less recharge post 1950’s when compared to BH8 and BH12. This could indicate BH10 is drawing from a deeper fracture system in comparison to BH8 and BH12 even though the main water strike is shallower or that the fracture system is not recharged as easily as the fractures supplying BH8 and BH12.

3. Conclusion

Based on the groundwater levels, hydrochemistry and isotope results provided in Section 2, groundwater is a contributing source to the K5 pit. The groundwater levels indicate that groundwater flow will be towards the K5 pit. The aquifer and the pit water quality show a similar hydrochemistry, however the isotope results indicate that the pit water has been concentrated because of evaporative processes.

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[5] Slight variations in temperature and humidity can affect the slope of the LEL line.

The tritium results indicate that K5 may have a similar source to the aquifer supplying BH8 and BH12 (all recent waters). The aquifer supplying BH10 however was predominantly recharged before the 1950's with less recharge after 1950 when compared to BH8 and BH12 indicating that the aquifer supplying BH10 may be a deeper aquifer of old water, or the fracture system is not recharged as often as BH8 and BH12.

- It is recommended to check the tritium isotopes for all the water supply boreholes to determine if there are any other boreholes which may be drawing water from a deeper or less recharged aquifer; and
- It is also recommended to monitor the tritium isotopes within the water supply boreholes on an annual basis to determine if there are any changes to the aquifer supplying the boreholes (determine if a deeper or less recharged aquifer becomes a more dominant source to the boreholes).

Regards,

Megan Edwards

Hydrogeologist

Levi Ochieng

Principal Geochemist

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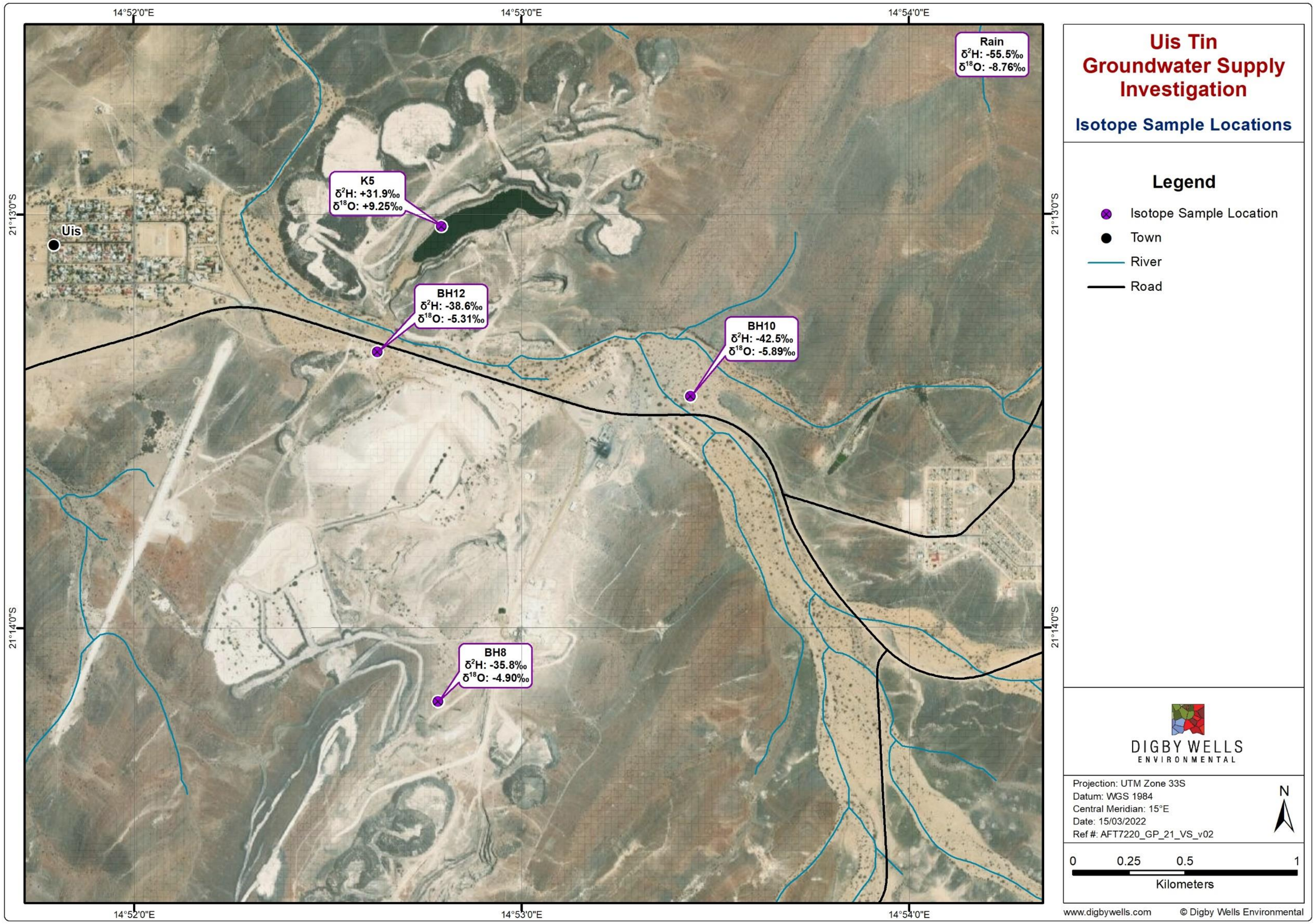

Figure 7: Isotope Sample Locations