

APPENDIX 3

STABLE ISOTOPES IN WATER OF THE  
RÖSSING MINING AREA  
AND SURROUNDS

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## EXECUTIVE SUMMARY

Stable isotope analysis data are reported of water samples collected from the Rössing mining area, from the adjacent gorges, from boreholes and pools in the Khan and Swakop rivers and from boreholes on the small-holdings along the Swakop river near Swakopmund.

<sup>18</sup>O and deuterium analysis could clearly distinguish water from the tailings dam at the mine due to its evaporative nature. Water in the gorges leading into the Khan river was different from that found in the river, reflecting local recharge. No indications of water from the mine operations adding to that in the Khan river could be found. There were small differences in stable isotope levels in the lower and upper parts of both the Khan and the Swakop rivers to enable water types to be distinguished, probably as separate recharge events.

Water from boreholes on the small-holdings along the Swakop river has the general characteristics of Swakop river water subject to some evaporative enrichment.

Nitrogen isotope analysis was done on some water samples and indicated a wide range of values. At this stage no clear isotopic signal of nitrate from the mining operations is evident that can be used for the identification of this nitrogen source in other parts of the water system here.

## 1. INTRODUCTION

The naturally occurring stable isotopes hydrogen (H), deuterium (D), oxygen-16 (<sup>16</sup>O), oxygen-18 (<sup>18</sup>O) have become useful tools in hydrological studies. The main applications of environmental isotopes can be summarised as follows:

- to provide a signature to a particular water type
- to identify the occurrence of mixing two or more water types
- to identify likely sources of constituents of the water
- to indicate evaporative conditions.

In the context of the Rössing EIA where issues such as these are relevant, a survey of isotope contents of various water sources was done, more or less on the same samples collected for chemistry and uranium isotopes (see report by Oschadleus and Vogel).

## 2. STABLE ISOTOPE HYDROLOGY

Since isotope ratio variations in nature are quite small (only a few percent) it has become customary to express these ratios (<sup>18</sup>O/<sup>16</sup>O, D/H or <sup>15</sup>N/<sup>14</sup>N) as positive or negative deviations of the ratio (R) from a standard. The relative difference is designated by δ (normally expressed in parts per thousand, permililitre ‰).

$$\delta_x = \frac{R_x - R_{std}}{R_{std}} * 1000$$

Where R is the particular isotopic ratio for the sample and standard. The standard used for oxygen and hydrogen is SMOW (Standard Mean Ocean Water) and for nitrogen AIR (atmospheric nitrogen).

The isotope ratios of natural compounds may change as a consequence of the history and processes to which such compounds have been submitted in the environment. The mass differences between isotopes of the same element produces small differences in their chemical and physical behaviour which in turn establish slightly different isotopic compositions (isotope fractionations), among co-existing chemical compounds or phases.

### 2.1 Stable isotopes of oxygen and hydrogen in the hydrological cycle

The most important physical process causing variation of isotopic composition in

natural waters is vapour-liquid fractionation during evaporation and condensation. The vapour pressure of water containing the light isotopes ( $^1\text{H}$  and  $^{16}\text{O}$ ) is greater than that of water containing the heavier isotopes ( $\text{D}$  and  $^{18}\text{O}$ ). When liquid water and water vapour are in equilibrium, the vapour is isotopically lighter with respect to both  $\text{D}/\text{H}$  and  $^{18}\text{O}/^{16}\text{O}$  than the liquid, and hence water vapour in the atmosphere is isotopically lighter than water in the ocean. Water vapour which evaporates from the ocean is depleted by 10-15‰ in  $^{18}\text{O}$  and by 80-120‰ in  $\text{D}$  with respect to SMOW (Standard Mean Ocean Water).

When water vapour condenses to form rain, fractionation takes place in the reverse direction, with the liquid being isotopically heavier than the vapour. The fractionation during evaporation is thus largely reversed during condensation and the first rain to fall from water vapour over the ocean would have an isotopic composition of about -3 ‰. If this rain again forms a vapour,  $^{18}\text{O}$  will be selectively removed from the vapour phase and the  $\delta^{18}\text{O}$  of the vapour will become progressively more negative as the rain continues to fall. By this process rainfall becomes progressively lighter in both  $\delta\text{D}$  and  $\delta^{18}\text{O}$  as it occurs further from the ocean source. The  $\delta\text{D}$  and  $\delta^{18}\text{O}$  values in precipitation generally plot close to a straight line (the *Meteoric Water Line*) with equation:

$$\delta\text{D} = 8 * \delta^{18}\text{O} + 10$$

The slope (8) is a general constant determined by the physical properties of the isotopes. The intercept (10), also called the d-excess, is a general one applicable to most of the world's composite set of samples. Local d-excess variations between +5 and +15 are known and are due to specific meteorological conditions. Water with an isotopic composition falling on the MWL is almost certain to have originated from the atmosphere and to be unaffected by other isotopic processes, i.e. pure rainwater.

Evaporation from *open* water surfaces causes deviations from the meteoric water line. Because of the higher mobility of the lighter molecules containing  $^1\text{H}$  and  $^{16}\text{O}$  these tend to pre-dominate in the vapour removed from an open water body subject to evaporation. This results in enrichment of the heavier isotopes in the water remaining. The ratio of *evaporative* enrichment of the two isotope pairs is different from that of *condensation* and the relation holding the MWL does not hold any more. This leads to the conclusion that deviations from the MWL are, in general caused by evaporation and that the slope of the  $\delta\text{D}/\delta^{18}\text{O}$  plot for evaporative water is 4-6. Using this slope the original stable isotope content of the water prior to evaporation, can be estimated by extrapolation of the evaporation line (EVL) towards the MWL. The data of this project provide good examples of this feature. Isotope enrichment is limited to cases of evaporation from open water surfaces, such as lakes, pools, etc. High evaporation through soils or through plant transpiration will not produce isotope enrichment, but will certainly cause increased salinity of the remaining water.

Isotopes of oxygen and hydrogen are, in many cases, ideal geochemical tracers of underground water because their concentrations are not subject to changes by interaction with the aquifer material. Once underground and removed from zones of evaporation, the isotope ratios are conservative and only affected by mixing. When precipitation infiltrates to feed ground water, mixing in the unsaturated zone smooths the isotopic variations depending on residence times and quantities involved. Depending on the input values water types can be followed by their isotope signal.

Analyses of  $\delta\text{D}$  and  $\delta^{18}\text{O}$  can be used to identify the probable source of an underground water. If the isotopic composition of an underground water plots close to the meteoric water line in a position similar to that of present-day precipitation in the same region, the water is almost certainly meteoric. Although the isotopic composition of precipitation at a particular location is approximately constant, it varies from season to season and from one rainstorm to another, but is generally on the MWL.

## 2.2 Nitrogen isotopes to trace nitrate in water

$^{14}\text{N}$  and  $^{15}\text{N}$  are the two stable isotopes of nitrogen occurring in nature. Most nitrogen occurs as  $^{14}\text{N}$  with only 0.37 % of atmospheric nitrogen present as  $^{15}\text{N}$ . The small difference in the atomic masses of the two isotopes leads to isotopic fractionation in natural systems. Variations of the isotopic ratio of a nitrogen compound can be due to:

- physical fractionation (diffusion, evaporation and sublimation);
- chemical equilibrium fractionation (equilibrium reactions);
- chemical kinetic fractionation (non-equilibrium reactions); and
- the isotopic ratio of the source material.

Variations in natural abundance of stable nitrogen isotopes can semi-quantitatively differentiate agronomic from organic waste sources of nitrate in ground water. As a general rule, manufactured (inorganic) fertilizer materials tend to have  $\delta^{15}\text{N}$  values close to natural atmospheric abundance (ie.  $\delta^{15}\text{N}$  is close to zero). This is so because the ultimate source of most fertilizers is atmospheric nitrogen. Organic matter in soils is typically enriched in  $^{15}\text{N}$  and nitrate derived from soils generally gives  $\delta^{15}\text{N}$  of +3 to +10. Animal and human wastes have been found to be slightly to highly enriched in  $^{15}\text{N}$  as a result of biochemical fractionation and subsequent ammonia volatilization of the waste. Nitrate derived from animal and human wastes typically give  $\delta^{15}\text{N}$  values of +7 to +25. Therefore isotope data was thought to be useful to this study in differentiating between nitrogen naturally occurring in the soil, nitrogen derived from inorganic fertilizers and possible nitrate contamination from the mining operations.

### 3. SAMPLING FOR ISOTOPES IN THE PROJECT AREA

Oxygen isotope analyses were done on a number of the samples that have been collected for chemical analysis in the project area between October 1996 and February 1997. Some sources were sampled both before and after the flood of February/March 1997 in order to observe flood influences. Depending on the variations encountered,  $^{18}\text{O}$  analysis was followed by deuterium analysis, in order to better define the causes for the oxygen isotope variations. Samples collected from the mining area are shown in Figure 1 (from the report on uranium by Oschadleus and Vogel). The data are presented in Table 1 sorted by river valley and approximate location where they occurred (upper, lower or mining area).

A scrutiny of the available chemical analyses of the water samples showed that comparatively high nitrate values are found in some of them. A few of these samples were analyzed for the  $^{15}\text{N}$  content of the nitrogen. The results are presented in Table 2.

## 4. RESULTS

### 4.1 Oxygen and hydrogen isotope variations in the Rössing mine area

Within the general area of the Rössing mine and the immediate stretch of the Khan river (Figure 1) there are some large  $^{18}\text{O}$  variations indicating the influence of evaporation. All of these variations follow a typical evaporation line intersecting the meteoric water line at an  $\delta^{18}\text{O}$  of about -7 ‰ which appears to be typical for the area. (Figure 2)

The two samples from the tailings dam are the most evaporated and follow an EVL up to  $\delta^{18}\text{O}$  close to zero. This is characteristic of water where significant water loss by evaporation has occurred, thereby setting a clear evaporative marker in the water that can be followed. It is often found in drainage water from mining operations.

Less developed evaporative signals are visible in the samples from Panner and Pinnacle trenches. All of these lie on the evaporation line and could therefore be either evaporated to a lesser extent than the dam samples referred to above or mixtures of these with less evaporated water. It is of importance that water from the base of Pinnacle Gorge, which could be "draining" the area containing the tailings dam is no more enriched than Panner Gorge. It suggests that the  $\delta^{18}\text{O}$  values in the range of -3 ‰ could be the general value of these smaller sources, distinct from the flood water that is much more depleted in both isotopes. Earlier measurements of rainfall in Windhoek has shown that some evaporative enrichment of rainfall occurs in this arid region and deviations from the MWL are likely in areas with little rain.

Borehole K at the junction of the Khan river is on a mixing line between Khan river water and the water draining this gorge.

Borehole 1.9 drains a separate uranium outcrop on the south bank of the Khan river (Figure 1). This showed more evaporation in November ( $\delta^{18}\text{O}=-1.85$ ) compared to February after the floods ( $\delta^{18}\text{O}<-3.4$ ‰). The latest samples or on the EV line closer to the MW line. It is likely that in this case there was some dilution of the borehole water by fresher flood water or local rain water, whichever the case may be. In both cases one is dealing with a quicker flow of water towards the borehole.

The two production boreholes (numbers 2 and 8) have very negative isotope values somewhat lower than the recent flood water (Figure 2). This suggests that they are not significantly affected by any evaporated water and are likely direct flood water as judged by the location on the MWL. They differ from the most recent flood water and probably represent a long term average of the floods and would be expected to be more consistent water sources. They do not show any contribution from the above mentioned evaporated water types.

### 4.2 Oxygen and hydrogen isotope variations in the Khan river valley

In the main river valleys (Khan and Swakop) some samples were sampled more than once and indicated little change of isotope composition, i.e. stable water sources. Overall there seems to be some patterning of  $^{18}\text{O}$  and deuterium values (Figure 3).

In the Upper Khan river valley (the area upstream of the Dome Gorge confluence) borehole Tr0 indicated a constant  $^{18}\text{O}$  value between November 1996 and March 1997 in spite of the occurrence of the February/March floods which had somewhat different isotope composition. It is therefore not influenced by flood water immediately. It rather responds over the long-term to the effects of the flood water in the river. The Vergenoeg spring has lower  $\delta^{18}\text{O}$  and is probably fed from another source. The two flood water samples indicate the variability that may occur in rain, though both are directly on the MWL (figure 3).

Water from the Khan Mine Gorge where three samples were obtained, shows indications of evaporated water somewhat different from the rest of the water system since they are located somewhat above the general evaporated line of the entire system here. Borehole J could be a local evaporated source, or the remains of past mining operations, similar to the tailings dam in the Pinnacle Gorge. Further downstream, the isotope signal is not dissimilar from that in Pinnacle and Panner gorges. The -4 and -3 values of  $^{18}\text{O}$  here are likely to reflect this particular rainfall, and recharge situation.

The close clustering of isotope composition of the boreholes in the Lower Khan River valley Tr5 and the group 1.10 to 1.12 suggests a very uniform water source in spite of a considerable distance (12.5 km) between the two groups. This is likely to be an aggregate of flood waters over some time, or a single flood that recharged all of this river bed. There no sign of water from the mining operations in the Lower Khan

river. Within the precision of this approach (probably <10%), any water from the mining operations, with much higher  $\delta^{18}\text{O}$  and  $\delta\text{D}$ , would have caused that of Tr5 to be higher than Tr0, which is not the case (Figure 3).

#### 4.2 Oxygen and hydrogen isotope variations in the Swakop river valley

The isotope pattern in the Swakop river valley is somewhat different from that of the Khan river valley (Figure 4). There are a few samples with high  $^{18}\text{O}$  (>-2 ‰), well on an evaporation line. These are probably due to some local evaporation from pools of standing water (Goanikontes, Southberg and Swakop road crossing). The Goanikontes pool was considerably different in March, on the mixing line towards water addition with isotope make-up similar to Haigamkab, for instance. This is probably due to mixing with, or displacement by flood water.

The other upper Swakop ground waters (Haigamkab, Horebis and WW21950) are all close to the same  $\delta^{18}\text{O}$  of -6‰ as in the upper Khan, but higher than the lower Khan value (figure 3) and only marginally below the MWL. These are then the unadulterated river waters recharged locally and can, as a group be slightly above or below the MWL.

Borehole water from the farms along the Lower Swakop river shows a variety of isotope values reflecting various degrees of evaporative isotope enrichment (Figure 4). The isotope values of water from these farm boreholes scatter more than is found in other boreholes in river beds of both rivers. Evaporation starting at an initial  $\delta^{18}\text{O}$  of about -8 ‰ evaporating to various extents with some large scatter of isotope values around this line, can explain all the isotope variations. The possibility of other water sources contributing some water cannot be excluded at this stage. There are no isotope local rainfall data or borehole waters away from the river available to use as likely end-members for such mixture evaluation.

The borehole at Palmenhorst, just below the junction of Khan and Swakop rivers has isotope values just on the MWL and represents unevaporated (single event?) flood water somewhat higher than the average values represented by the clustering found elsewhere in these rivers.

#### 4.3 Nitrogen isotope data

Nitrate is quite common in water sources in the area. In 1970 and 1974 a number of analyses of borehole water were done in the context of the CSIR water quality mapping of the country. This concentrated on the farms towards the east of the study area and indicated a range of high nitrate concentrations with an average of 41 mgN/l. The question arises to what extent the Rössing mining activities contribute to the occurrence in local ground water.

Samples for nitrogen isotope analysis were selected on the basis of their availability at this stage of the investigation and the sample size available. Data are shown in Table 2.

The results obtained to date are not definitive. No samples directly from the present mining area have yet been analyzed to establish the likely contamination signal from mining activities. As mentioned above, the  $^{15}\text{N}$  value of explosive derived nitrate would be expected to be close to zero (with respect to the AIR standard). The source nearest to the abandoned Khan Mine is in fact the lowest of all. The other samples all have high  $\delta^{15}\text{N}$ : more than one would expect from natural sources, (denitrification of organic matter in the soil). The values obtained suggest either that most of the nitrate is derived from the bacterial decay of animal or human wastes or that the natural nitrate content of the water is being reduced by denitrification thereby causing higher nitrogen isotope concentrations.

These influences would have to be established with more care before the technique can be used as tracer of nitrate in the area. Such a test would involve re-sampling specific boreholes and analysing for dissolved oxygen and Eh at the same time. Collection of wash water in the actual mining operation would also be required.

A possibility that will have to be borne in mind is that some nitrate could spread through the air as a result of the explosions causing nitrogen oxides to be distributed in the air. This nitrogen would then precipitate as fog, rain or dust eventually. One would then have to seek contaminated or uncontaminated water not by their location in the river system, but in relation to the prevailing winds.

## 5. CONCLUSIONS

- Water in the Rössing tailings dam shows a high hydrogen and oxygen isotope enrichment signal which can be used for water tracing.
- Water in the Panner, Pinnacle and Dome Gorges shows isotope enrichments different from that of the Khan river water, reflecting local recharge of rain water there. Water at the lower end of Pinnacle Gorge, in which the Rössing mine tailings dam is situated, does not show abnormally high isotope enrichment, compared to that found in the other parallel gorges.
- There is no indication that substantial amounts (>10%) of isotopically enriched water from the mining operations contributes to the water in the Khan river.
- The water types in the Khan river above and below the mining area appear to present different recharge events.
- The water types in the Swakop river above and below its confluence with the Khan appear to present different recharge events.

- Water from the farms along the Swakop river near Swakopmund generally show the isotope signal of the Swakop river subject to some evaporation effects. Possible contributions from other sources cannot be quantified as yet.
- Nitrogen isotope analysis could not distinguish between natural and possible mine produced nitrate in any of the ground waters.

**Table 1:  $^{18}\text{O}$  and deuterium results from the Rössing mining area, and the Khan and Swakop river valleys**

Sample number	Sample name	Date	$\delta^{18}\text{O}$ (‰SMOW)	$\delta\text{D}$ (‰SMOW)
<b>UPPER KHAN RIVER VALLEY</b>				
G4056	Vergenoeg Spring	10-Oct-96	-7.48	-46.8
S4670	Khan riv flood water	12-Feb-97	-5.68	-34.4
S4673	Khan riv flood water	21-Jan-97	-6.59	-44.9
G4195	Transect 0	10-Mar-97	-6.21	-44.4
G4062	Transect 0	06-Nov-96	-6.43	-43.1
<b>MINE AREA</b>				
G4207	Borehole K	10-Mar-97	-4.91	-35.6
G4197	SRK Tailings Dam GW seepage	12-Mar-97	-0.46	-16.6
G4194	Tailings Dam surface seepage	12-Mar-97	-0.57	-16.5
G4206	Pinnacle Trench	12-Mar-97	-3.20	-29.0
G4208	Panner Trench	12-Mar-97	-2.84	-30.0
G4064	Borehole 1.9	11-Nov-96	-1.85	-23.0
G4190	Borehole 1.9	05-Feb-97	-3.41	-31.3
G4235	Borehole 1.9	21-Feb-97	-3.82	-34.6
G4061	Production Borehole 2	06-Nov-96	-7.19	-47.6
G4055	Production borehole 8	09-Oct-96	-6.96	-43.7
<b>KHAN MINE GORGE</b>				
G4239	Borehole J	21-Feb-97	-0.60	-23.6
G4238	Khan Mine Well	21-Feb-97	-4.10	-32.5
G4236	Khan Mine Spring	21-Feb-97	-4.04	-30.4
<b>LOWER KHAN RIVER VALLEY</b>				
G4196	Transect 5	10-Mar-97	-6.96	-48.5
G4060	Transect 5	06-Nov-96	-7.14	-48.6
G4237	Transect 5	21-Feb-97		-49.4
G4210	Borehole 1.10	10-Mar-97	-7.19	
G4223	Borehole 1.10	28-Nov-96	-7.01	-51.2
G4224	Borehole 1.11	27-Nov-96	-6.99	-51.7
G4225	Borehole 1.12	28-Nov-96	-7.12	-50.8

UPPER SWAKOP RIVER VALLEY				
G4212	Haigamkab	10-Mar-97	-6.02	
G4057	Haigamkab	05-Nov-96	-6.30	-44.6
G4219	Horebis North 3	03-Jan-97	-6.02	-46.1
G4220	Horebis North 4	03-Jan-97		-45.8
G4221	Swakop WW 21950	03-Jan-97	-6.32	-43.4
G4216	Soutberg	12-Jan-97	-0.88	-20.0
LOWER SWAKOP RIVER VALLEY				
G4063	Palmenhorst	08-Oct-96	-6.14	-39.8
G4209	Palmenhorst	10-Mar-97	-6.18	
G4059	Goanikontes well	05-Nov-96	-5.36	-41.8
G4058	Goanikontes	05-Nov-96	-1.79	-24.9
G4211	Goanikontes	12-Mar-97	-4.50	
G4178	Farm Blakeway	13-Feb-97	-6.58	-50.7
G4179	Farm Pampel	13-Feb-97	-5.13	-43.1
G4180	Farm Hoppe	10-Feb-97	-5.14	-43.9
G4181	Farm Hoppe well	10-Feb-97	-5.17	
G4182	Farm Erb	14-Feb-97	-5.52	
G4183	Horse farm	10-Feb-97	-5.57	
G4184	Plot 181	10-Feb-97	-6.16	-47.7
G4185	Farm Jooste	14-Feb-97	-5.90	-44.1
G4186	Plot 180	10-Feb-97	-4.92	
G4187	Farm de Kock	11-Feb-97	-5.99	-43.8
G4188	Farm Stiemert	10-Feb-97	-5.86	
G4189	Farm Nonidas	10-Feb-97	-5.30	
G4227	Farm van Heerden	25-Feb-97	-5.64	-41.7
G4213	Swakop Road Crossing	21-Jan-97	-1.80	-26.8
G4228	Rössing Foundation	24-Feb-97	-5.79	-44.3

Table 2: Nitrogen isotope analysis results

Sample number	Sample	Date	<sup>15</sup> N (‰AIR)	NO <sub>3</sub> -N (mg/l)
	KHAN RIVER			
G4235	Borehole I.9, draining U occurrence	21 Feb 1997	+18.8	31
	KHAN MINE GORGE			
G4239	Borehole J, near old mine, high δ <sup>18</sup> O	21 Feb 1997	+9.2	72
G4238	Khan Mine Well, below BH J	21 Feb 1997	+12.4	11.6
	LOWER KHAN RIVER			
G4225	Borehole I.12, near Swakop confluence	28 Nov 1996	+16.4	12.9
	UPPER SWAKOP RIVER			
G4216	Soutberg, high δ <sup>18</sup> O	12 Jan 1997	+12.6	36

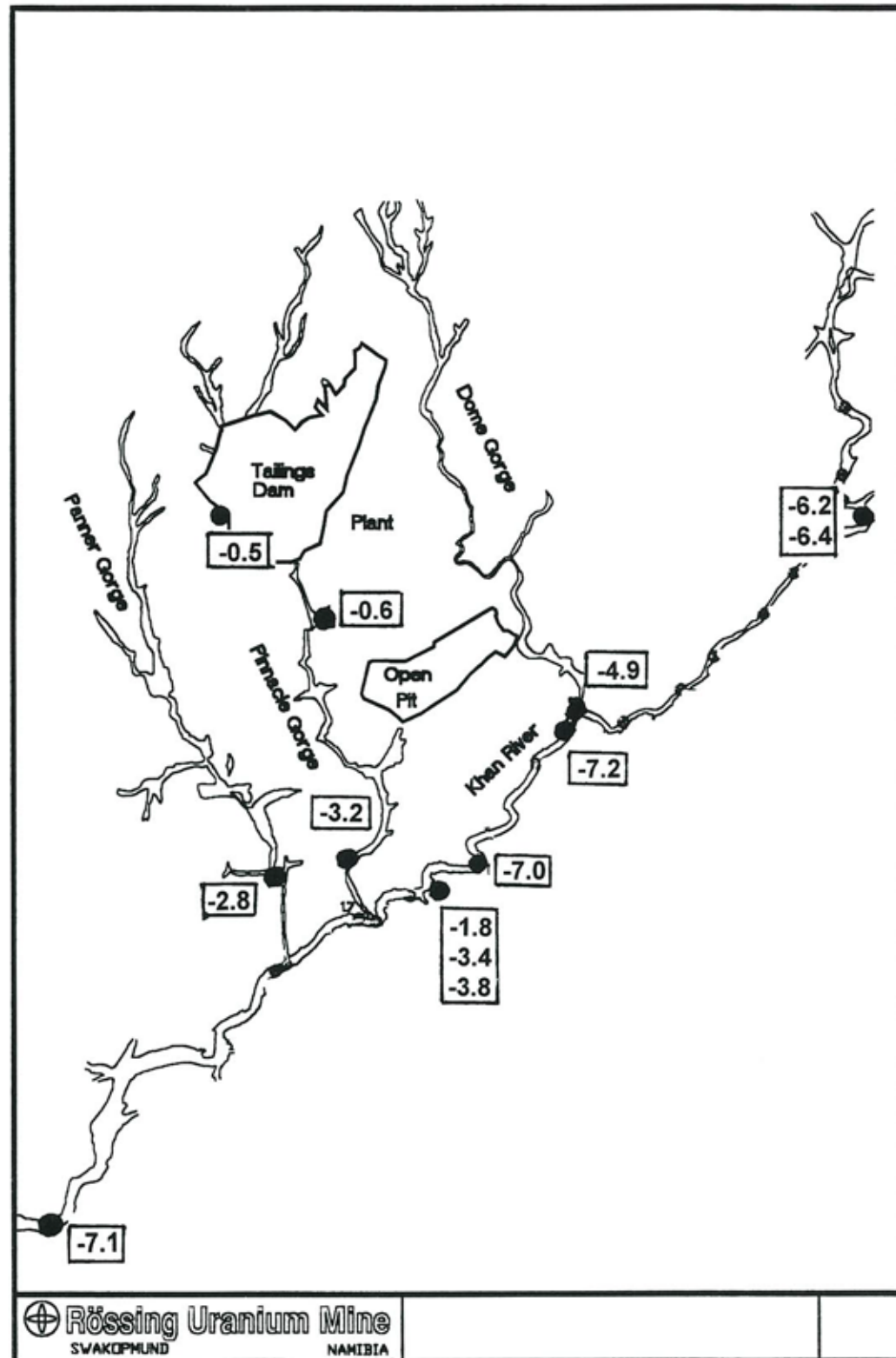


Figure 1: Map of the Rössing Mine area with <sup>18</sup>O values of water indicated.

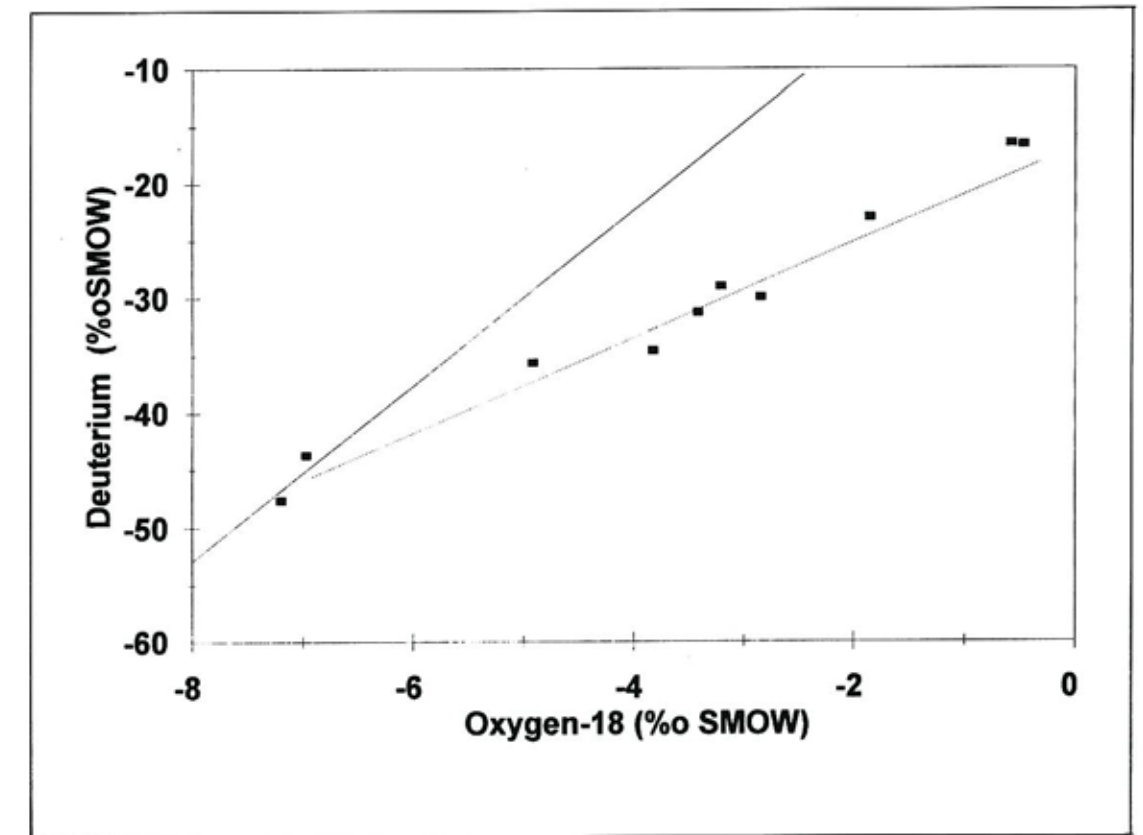
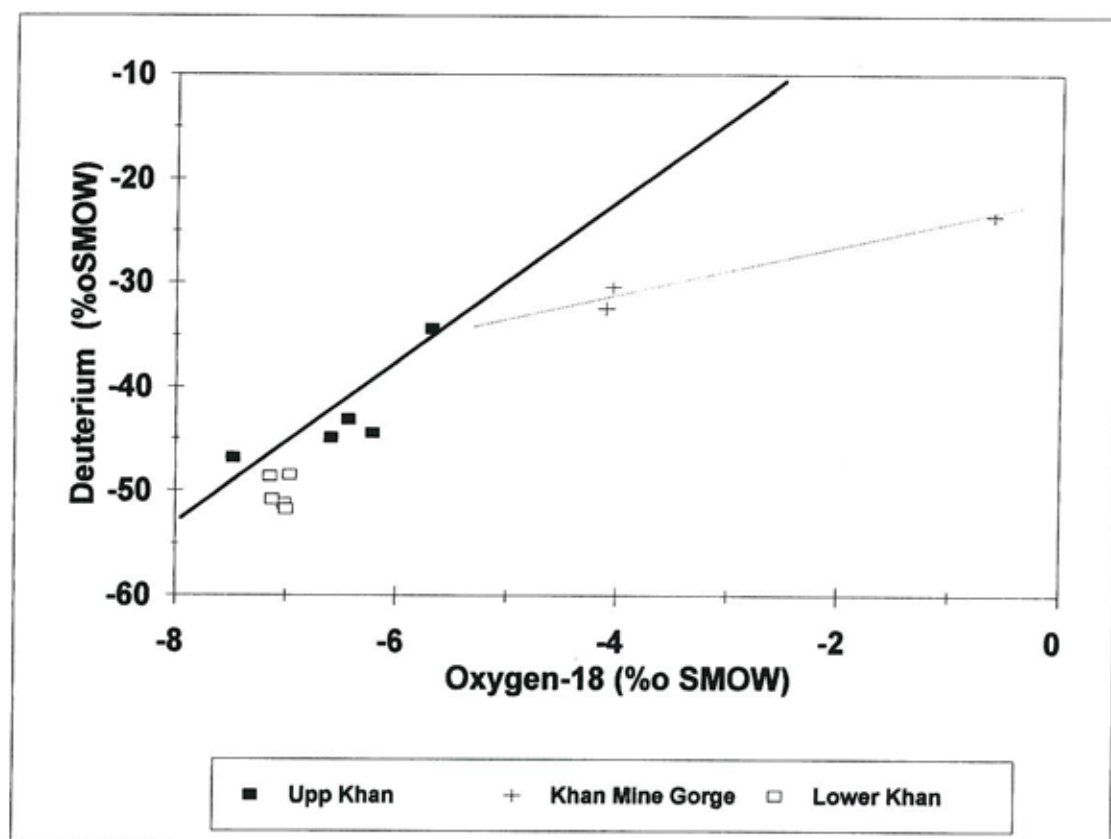
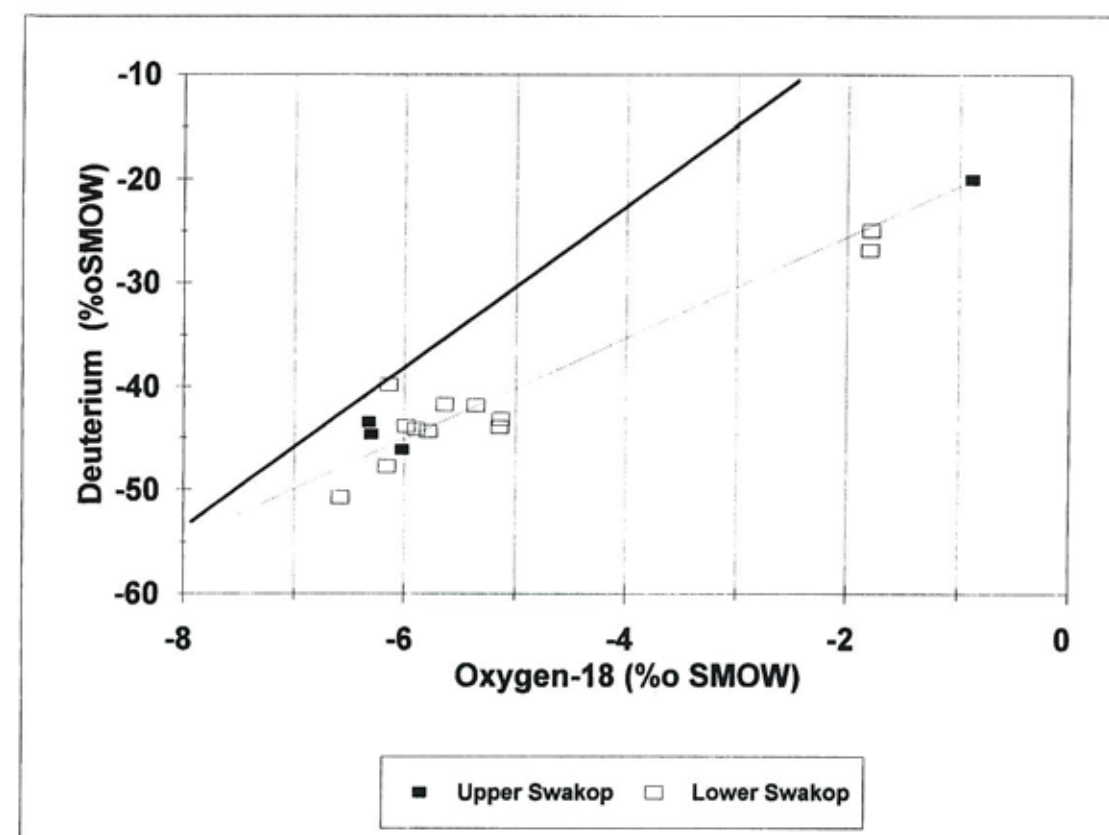


Figure 2: Plot of  $\delta D$  against  $\delta^{18}O$  for the mining area including the Khan river adjacent to it. The solid line is the Meteoric Water Line which represents most rain water. The broken line represents an Evaporation Line indicating the relation between the isotopes when water is enriched by evaporation.





**Figure 3:** Plot of  $\delta D$  against  $\delta^{18}O$  for the Khan river water samples. The solid line is the Meteoric Water Line which represents most rain water. The broken line represents a likely Evaporation Line connecting the sample points in the Khan Mine Gorge.



**Figure 4:** Plot of  $\delta D$  against  $\delta^{18}O$  for the Swakop river water samples. The solid line is the Meteoric Water Line which represents most rain water. The broken line represents a likely Evaporation Line connecting some open water samples with those from the farms downstream. It indicates the likely process by which the farm waters can undergo isotope enrichment.

