Stable Water Isotopes as Tracers at the Middle Mohlapitsi Catchment/ Wetland, South Africa

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Abstract—This paper presents the results of an investigation of isotope hydrology of the wetland in the Mohlapitsi and Olifants basins. Seventy seven water samples (from boreholes, auger holes, river and springs/drains) were taken during June 2011 through November 2013 for deuterium and oxygen-18 analyses. The springs and groundwater samples appear to form a distinct group, albeit with a wide spread, while the drain water samples (except drain located in MRB206 environment) generally cluster together. Furthermore, river water samples cluster together except water samples at Valis Village crossing and downstream river. The auger hole samples are quite variable with those associated with upstream transects grouping with the drains, while those associated with the downstream transects more similar to the spring. The indications are that the springs have a highly variable signature which may suggest that there are different types of springs to be found in the area; some that are directly associated with groundwater and some that are associated with the drainage of subsurface water circulating above the general level of the regional water table. The isotopic composition of water samples in the study area during low-flow (June 2011 and July 2012) and high-flow (November 2011 and December 2012) periods were similar.

Keyword-Wetland, Isotope Hydrology, Streamflow, Transect

I. INTRODUCTION

Deuterium (^{2}H) and Oxygen-18 (^{18}O) isotopes are used in order to characterize several different water dynamics within watersheds. Some of the applications include constraining residence time, or the time it takes for a molecule of water to move from one point to another and characterizing how water moves within the watershed [1]. Furthermore, these stable water isotopes trace outflows, for example, water lost to groundwater vs. streamflow of the water from the system. They also determine mixing and flow paths of water within a system [2].

Being powerful tools in hydrological studies, these water isotopes are naturally occurring within a catchment [3, 4]; and do not readily react chemically with rocks and minerals at temperatures encountered at or near Earth's surface. Moreover, they undergo fractionation during evaporation/condensation and through biological processes, with light isotopes preferentially evaporated or taken up [5, 6].

The relative abundance of oxygen-18 (0.204% of all oxygen atoms) and deuterium (0.015% of all hydrogen atoms) change slightly as a result of thermodynamic reactions that fractionate atoms of different masses [7]. The isotopic fractionation in water occurs through diffusion during physical phase changes such as evaporation, condensation, and melt; and temperature is the main cause of fractionation process [8]. During phase changes, diffusion rates differ due to the differences in bond strength between lighter and heavier isotopes of a given element. Heavy isotopic forms of water require greater energy to break hydrogen bonds than water containing lighter isotopes and consequently, will react more slowly [9–12].

Deuterium and Oxygen-18 isotope ratios in water samples can be analysed in order to determine not old water [13], or the water that falls directly from a storm event, or water that had fallen in a storm event in the past and may be stored in plants, soils, or groundwater. These ratios are represented by the notation per mil (represented with the symbol ‰) are compared with a standard, and are considered enriched (more of the heavier isotope) depleted with respect to the standard. Each standard corresponds to a particular isotope or isotope pair; this standard for water stable isotopes is Vienna Standard Mean Ocean Water (VSMOW). Ratios of heavy to light isotopes from a sample can be compared with these standards to determine if the sample is enriched or depleted relative to these standards. The degree of enrichment or depletion can indicate the source and age of the water [14]. The objective of this study is therefore, to contribute to the understanding of the

processes of water movement into and within the wetland based on an interpretation of environmental isotope [15].

II. STUDY AREA

Location and general description

This study was conducted at the Mohlapitsi Wetland, which lies in the former homeland area of Lebowa in the Capricorn District and in the middle part of the Limpopo basin (Figure 1). The wetland is a palustrine system covering an area of 120 ha [16]. The wetland is located in the B71C quaternary catchment (according to South African designation) and geographically on coordinates 24°6'0" South and 30°6'0" East. Agricultural activities have extensively modified the ecological status of the wetland system under study [16].
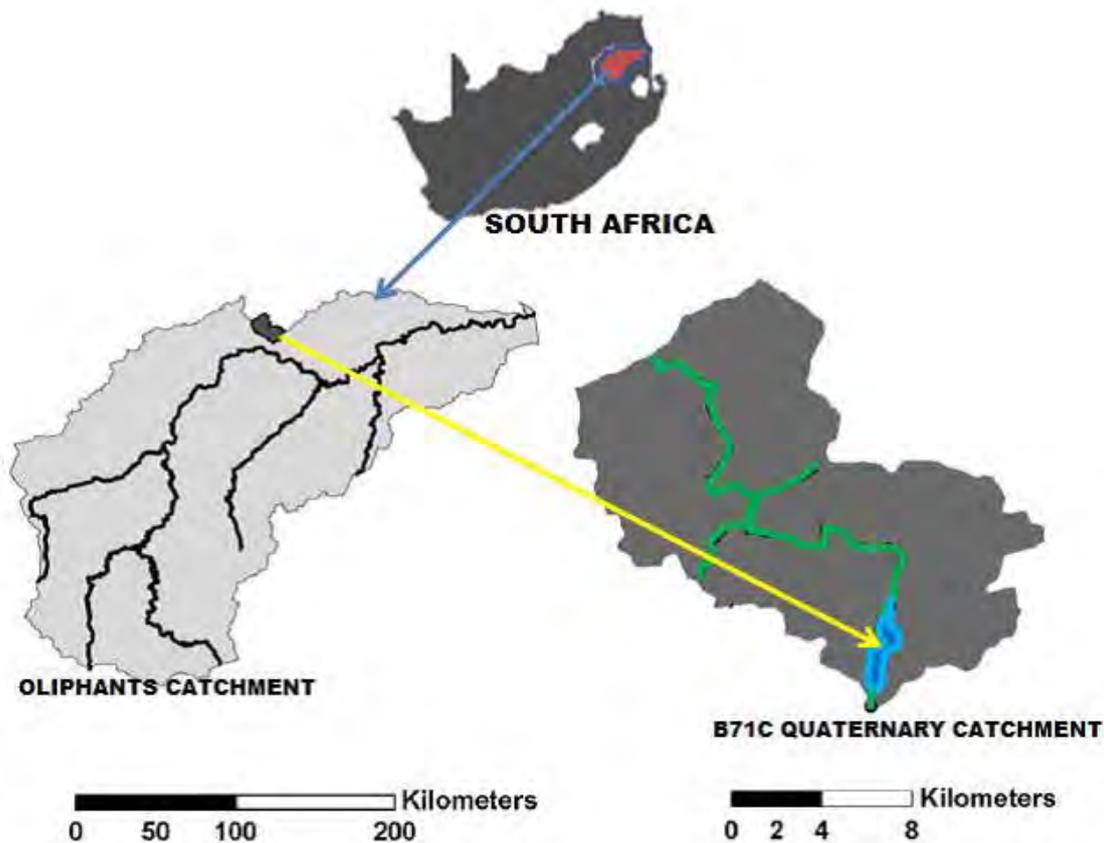
Figure 1 Map showing the location of the study area in B71C Quaternary Catchment within the Olifants Catchment [17]

The Mohlapitsi River is in Limpopo Province of South Africa and drains southwards from the Wolkberg Mountains into the Olifants River. The river flow shows reduction between gabion dam (approximately 3 km upstream of T1) and bridge. The upper part of the Mohlapitsi Catchment in Olifants Catchment is mountainous with peaks above 2050m and mainly covered by natural forest, whereas the lower reaches are alluvial valleys [17]. At the confluence with the Olifants River, the Mohlapitsi catchment is 490 km^2 and upstream of the wetland it is approximately 263 km^2. The valley is narrow and confined; with steep hill slopes on the edges of the valley bottom (Figure 2).

Figure 2 The Mohlapitsi Wetland in the valley bottom

III.   METHODOLOGY

A. Water sampling for environmental isotope

A total of 77 water samples (from drains, river, springs, boreholes and auger holes) were analyzed for ^{2}H and ^{18}O isotope analyses during June 2011, November 2011, July 2012, December 2012 and November 2013 (Table 1). Borehole samples were collected from Vallis and Mashushu villages during April 2007 for isotopic analysis (Figure 3) and both samples were taken from taps (not directly from the boreholes). All the samples were collected with polyethylene containers. The sample bottles were rinsed several times with water from the site as described by Gonfiantini [18].

Stable oxygen isotopic compositions were analysed by well-known CO_2–H_2O equilibration method [8, 18, 19, 20]. The equilibrated CO_2 gas was measured by a computer controlled GEO 20-20 isotope ratio mass spectrometer (Europa Scientific, Crewe, UK). After introducing 1 ml of water into 5 ml vials in the presence of Pt-on-alumina catalyst, the vials were put on a controlled heating block set at a temperature of 50°C. The vials were flushed with hydrogen for one minute and left for one hour to equilibrate hydrogen with the water sample after hydrogen gas was taken from a high pressure cylinder of 99.999% hydrogen and transferred into the 5 ml vials at a pressure of 2 bars as described by Herczeg et al. [13]; Kendall and Coplen [9]. The hydrogen, which is in equilibrium with water samples, was withdrawn from the vials using a gas-tight needle and introduced to the Isotope Ratio Mass Spectrometry for measurement as described by Kendall and Coplen [15]. Likewise, the hydrogen isotopic compositions were determined on a GEO 20-20 isotope ratio mass spectrometer after reduction of water to H_2 using zinc shots [18, 19].
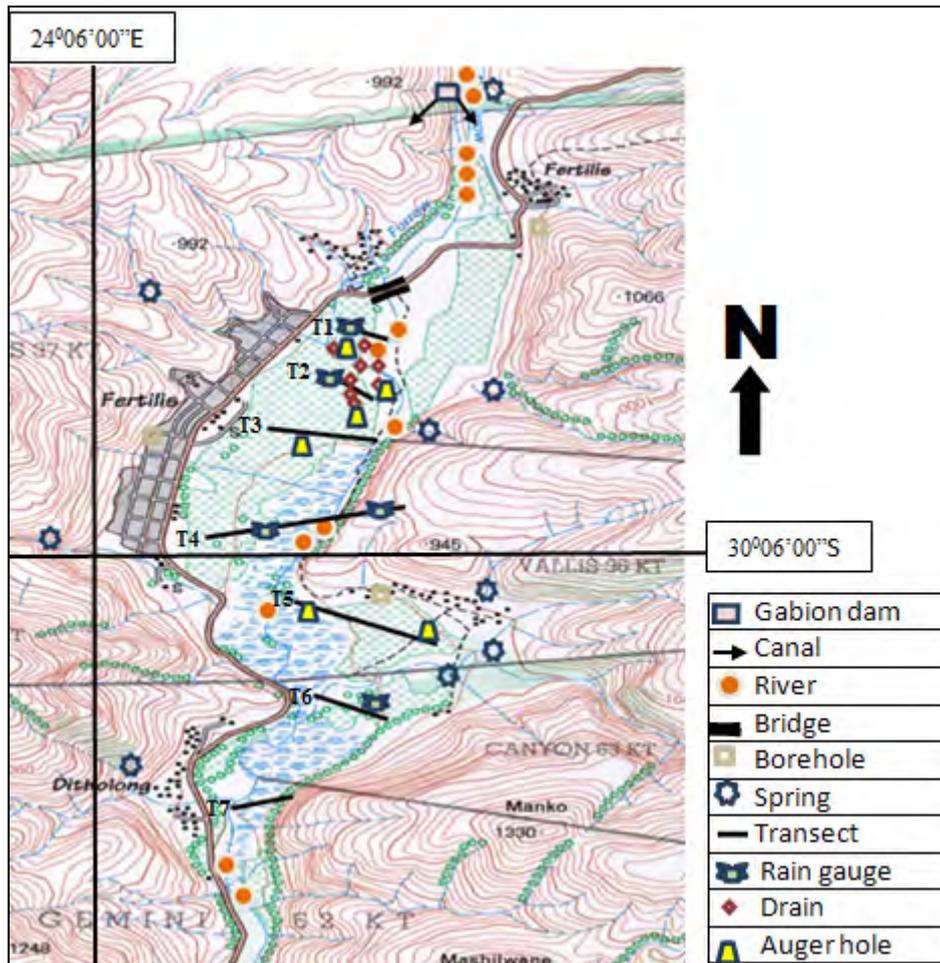
Figure 3: Locations of water resources and sampling points in the study wetland during 2007 through 2013

Analytical results were reported as $\delta^2H^0/_{00}$ and $\delta^{18}O^0/_{00}$, relative to VSMOW as described by Gonfiantini [6]. The δ values ($\delta^{18}O$, δ^2H) were calculated using the internationally accepted standard equation given as equation (1).

$$\delta(0/00) = \frac{Rsample - Rvsmow}{Rvsmow} X\ 1000 \qquad (1)$$

where, R is the isotope ratio $^2H/^1H$ or $^{18}O/^{16}O$.

Local meteoric water line (LMWL) was established and plotted together with global meteoric water line (GMWL) shown by Craig [7] as equation (2):

$$\delta D = 8\delta18\ O + 10 \qquad (2)$$

IV. RESULTS AND DISCUSSIONS

Five sets of environmental isotope samples (34 river, 16 spring, 14 drain, 7 auger holes and 6 boreholes) were collected and analysed during the entire study periods (Table 1 and Figure 4). The $\delta^{18}O$ and δD values of water samples are listed in Table1. The $\delta^{18}O$ and δD values of these water samples and the global meteoric water line (GMWL), with the equation $\delta D = 8\delta^{18}O + 10$ as described by Craig [7] and the local meteoric water line (LMWL) as $\delta D = 6.63\ \delta^{18}O + 5.44$ are shown in Figure 4.

Table 1 illustrates that drain at 200m south of T1 is enriched. Furthermore, Table 1 indicates that river upstream (δD = -2.48, $\delta^{18}O$ = -16.24) is enriched, while river at Fig trees environment (δD = -5.08, $\delta^{18}O$ = -21.70) depleted. In addition to this, drain at T206 and another drain at 50m south of T1with isotopic fingerprints of δD = -5 14, $\delta^{18}O$ = -26.60 and δD = -4. 56, $\delta^{18}O$ = -22.90 showed depletion and enrichment respectively. Auger holes at Transect two (T2) and T5 having an isotopic values of δD = -4 60, $\delta^{18}O$ = -23.0 and δD = -5 32, $\delta^{18}O$ = -28.70 showed enrichment and depletion respectively.

All June 2011 water samples lie above both LMWL and GMWL except Right Bank Spring 1(RB Sp1) with δD = -4.45, $\delta^{18}O$ = -26.14 plot at right of both lines; indicating there is evaporation and showed enrichment;

while Left Bank Spring 3 (LB Sp3), having $\delta D = -5.24$, $\delta^{18}O = -28.5$ is depleted (Table 1 and Figure 4). The rest of samples lie left of the lines; indicating there is no evaporation.

Table 1 δD and δ 18O isotopic values during the study period at the Middle Mohlapitsi Wetland

Sample Description	Jun.2011		Nov.2011		Jul.2012		Dec.2012		Nov.2013	
	$\delta^{18}O$ ‰ SMOW	δD ‰ SMOW	$\delta^{18}O$ ‰ SMOW	δD ‰ SMOW	$\delta^{18}O$ ‰ SMOW	δD ‰ SMOW	$\delta^{18}O$ ‰ SMOW	δD ‰ SMOW	$\delta^{18}O$ ‰ SMOW	δD ‰ SMOW
River upstream	-4.69	-24.72	-4.77	-34.5	-4.73	-24	-2.48	-16.24	-4.61	-22.2
River downstream	-4.88	-24.9	-4.81	-19.3						
River T2, downstream			-4.87	-23.89			-3.5	-18.71	-4.62	-21.1
River 3, T1			-4.78	-23.56						
River at Fig Trees							-3.43	-18.4	-5.08	-21.7
River after Jordaan Spring							-4.75	-24.4		
River100m above Jordaan							-2.69	-16.25	-4.49	-22.1
spring							-4.56	-22.5	-4.74	-22.5
River water under bridge 2							-3.37	-18.56	-4.61	-21.1
River upstream from										
Vallis crossing			-4.88	-21.98	-4.41	-23.6	-4.99	-26.6		
River upper crossing T1			-5.02	-22.65	-4.72	-23.9			-4.24	-18.7
River at Vallis crossing							-3.03	-16.81	-4.73	-21.3
Mohlapitsi R water T6 envir							-3.15	-18.16	-4.8	-22.7
Upstream LB Spring	-4.8	-25.44								
LB Spring 2	-5.26	-28.67							-5.88	-28.3
LB Spring 3	-5.24	-28.56							-4.63	-21.7
RB Spring 1 (Ditolong)	-4.45	-26.14								
RB Spring 2	-5.92	-34.23					-2.51	-14.16		
RB Spring 3	-5.43	-31.13					-4.71	-23.38		
Jordaan Spring					-4.71	-24.2	-3.85	-20.28		
Loumauwe Spring					-5.31	-28.4	-4.2	-24.54	-5.28	-23.4
T5 Spring					-5.49	-29.2				
RB drain 1			-4.7	-24	-4.57	-23.2			-4.65	-22
RB drain 2			-4.85	-25.4	-4.65	-24.5			-4.49	-20.1
Drain 200m south of T1					-4.61	-23.2				
Drain 400m S of T1					-4.72	-23.2			-4.74	-22.4
Drain 50 m S of T1					-4.56	-22.9				
Drain 400m S of T1					-4.56	-22.9				
Drain 200m S					-4.61	-23.4	-3.65	-18.4		

of T1

Drain at T206			-5.14	-26.6			
Auger hole at T501	-5.22	-27.6	-5.32	-28.7			
Auger hole at T101			-4.7	-23.8	-4.24	-20.59	
Auger hole near T104			-4.9	-25.3			
Auger hole at T302			-5.19	-29			
T2 Auger hole			-4.6	-23			
Vallis borehole			-5.67	-33	-3.64	-18.41	-5.56	-27.2
Mashushu borehole			-5.08	-27.7	-5.01	-25.68	-5.25	-24.3
River at 1st HW bridge							-4.74	-22.1
River at T7 environment							-4.78	-22.7
DWA weir site							-4.68	-22.2
River at Gabion dam							-4.86	-21.5

During November 2011, all except river downstream samples (δD = -4.77, $\delta^{18}O$ = -34.5) lie left of both meteoric lines; indicating no evaporation. In addition, during July 2012, Vallis borehole (δD = -5.67, $\delta^{18}O$ = -33.0) showed depletion in isotopic fingerprint and plots between the two lines (Table 1 and Figure 4). Transect five (T5) spring, drain 50m south of Transect one (T1) and MLB502 auger hole samples plot on LMWL. The rest of samples lie left of both lines.

Also, half of December 2012 samples plot left of both meteoric lines. Except river 100m above Jordaan Spring (δD = -4.56, $\delta 18O$ = -22.50) and drain 200m south of T1 (δD = -3.65, $\delta 18O$ = -18.40), other samples lie left of both meteoric lines. All November 2013 samples plot left of both meteoric lines and most river samples cluster together.
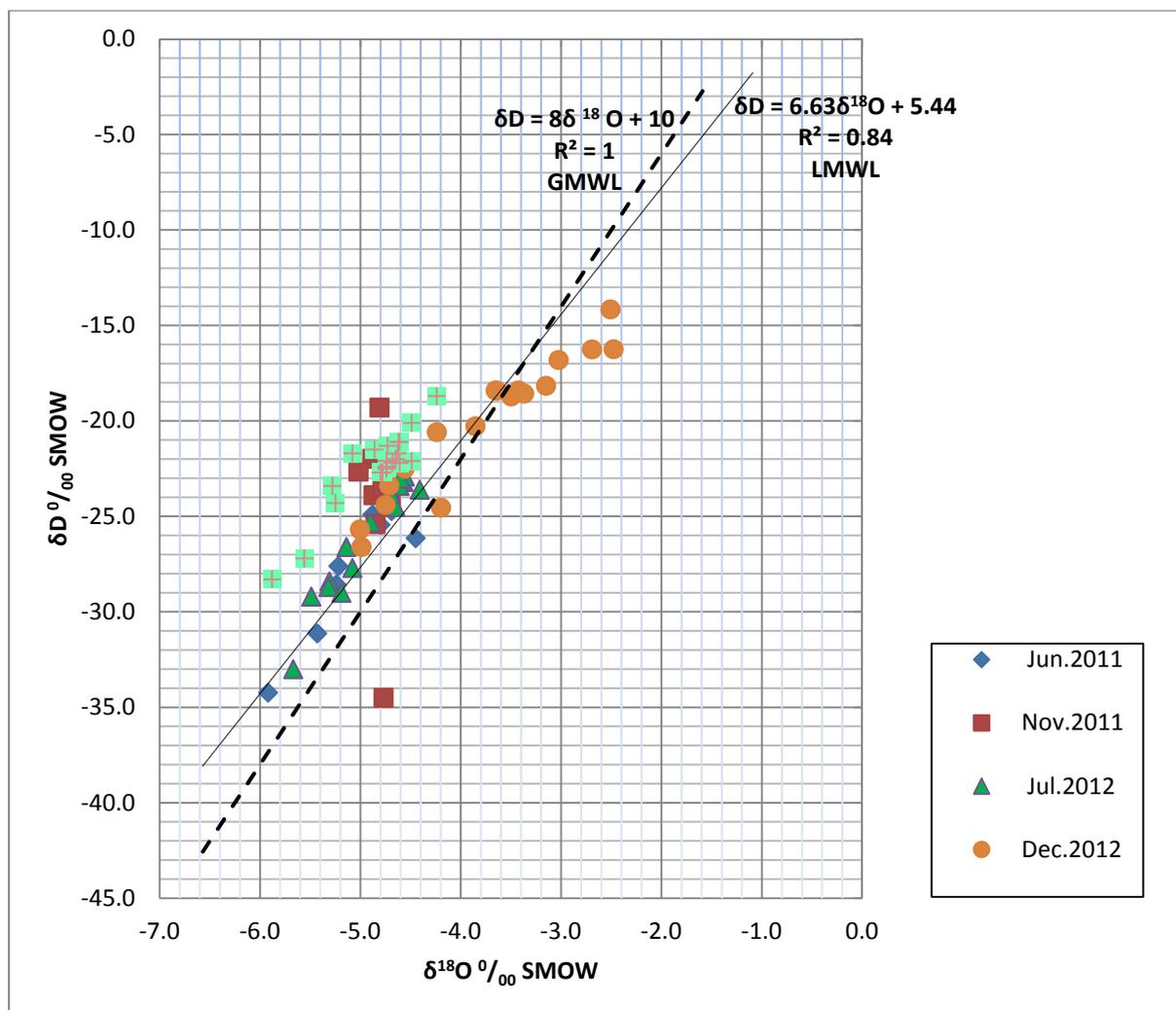
Figure 4 Deuterium and Oxygen-18 plot for water samples during, June 2010, November 2011, July 2012, December 2012 and November 2013 (Vienna-Standard Mean Ocean Water is used as the accepted zero point standard for expression of hydrogen and oxygen isotopes of water samples in delta units).

The isotopic composition of water samples in the study area during low-flow (June 2011 and July 2012) and high-flow (November 2011 and December 2012) periods were similar (Figure 4) and no seasonal variations were observed as shown on Table 2.

Table 2.   Statistical analyses of δD and ^{18}O during May 2007, December 2008 and April 2009.

Statistical Parameters	01 June 2011	01 November 2011	01 July 2012	01 December 2012	01 November 2013
Coefficient of variation	-0.09	-0.02	-0.07	-0.22	-0.08
Regression line(R^2)	0.84	0.08	0.93	0.91	0.84
Slope	6.56	-11.55	7.72	4.16	5.03
Y-intercept	5.46	-89.91	12.19	-4.45	1.89
Regression line	$\delta D = 6.56\delta^{18}O + 5.46$	$\delta D = -11.55\delta^{18}O - 89.91$	$\delta D = 7.72\delta^{18}O + 12.19$	$\delta D = 4.16\delta^{18}O - 4.45$	$\delta D = 5.03\delta^{18}O + 1.89$

This non-seasonal variation and the LMWL equation of June 2011 are similar to the results obtained by Coplen and Kendall [20]. The coefficient of variations (CV) for δD during June 2011, November 2011, July 2012, December 2012 and November 2013 are -0.09, -0.02, -0.07, -0.22 and -0.08 respectively, indicating that there is no significant seasonal variation (Table 2).

Figure 5 depicts the different isotopic signatures according to the source of water. The springs and groundwater samples appear to form a distinct group, while the drains and most river water generally cluster together; indicating they are from the same source. The auger hole samples are quite variable with those associated with upstream transects grouping with the drains, while those associated with the downstream transects more similar to the spring signatures (Figure 5). The indications are that the springs have a highly variable signature which may suggest that there are different types of springs to be found in the area, some that are directly associated with groundwater and some that are associated with the drainage of sub-surface water circulating above the general level of the regional water table [21].
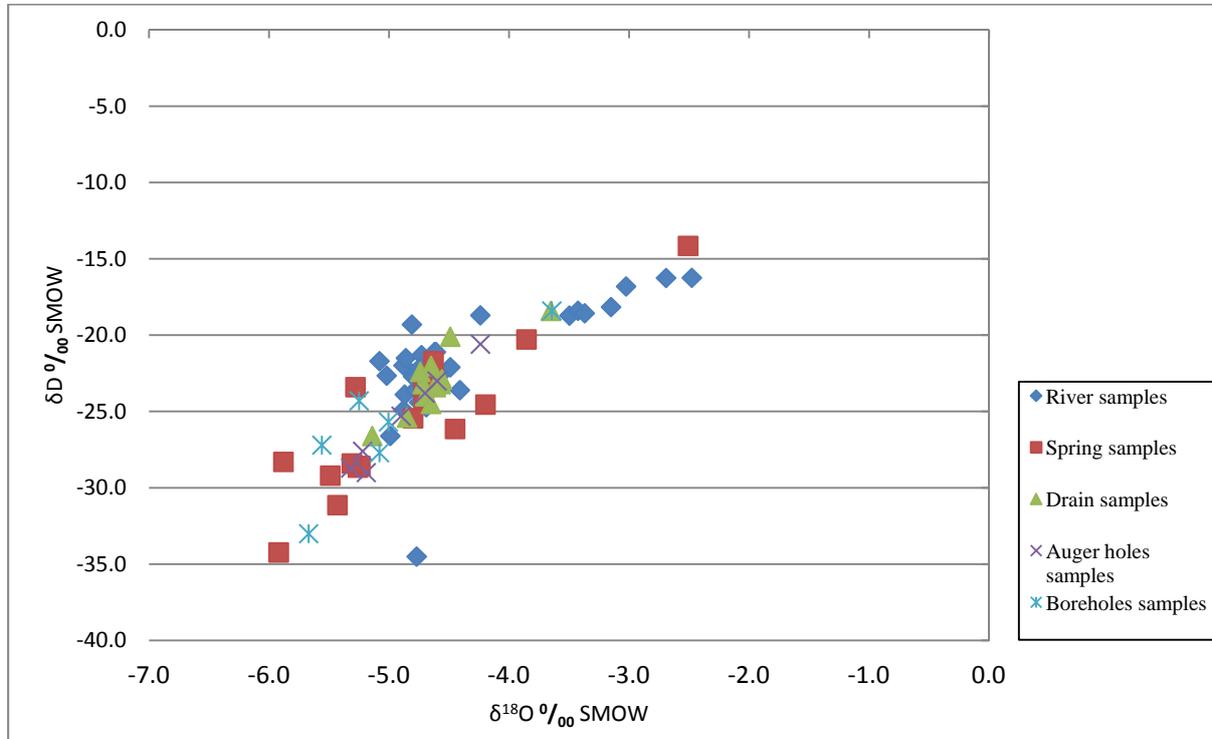
Figure 5. Deuterium and Oxygen-18 plot for water samples based on water source

V. CONCLUSIONS

To improve the understanding of the hydrology and the origin of water in the Mohlapitsi Wetland environmental isotope tracers were measured. The results of this investigation, assessment of the gaps in data and understanding and interpretations of the data with respect to the hydrological processes in the study wetland/catchment are summarised below.

- ✓ The clustering of stable isotope values of water samples from drains, river, and auger holes in the wetland and all of the river water samples, indicated that all water samples are derived from a similar source of water.
- ✓ The reduction in river flow between the gabion dam and the main road (at upstream bridge) during 2006 and the clustering of stable isotope values of drains, auger holes and river water samples, indicate that the upper part of the wetland hydrology is largely driven by inputs from the river water upstream. Field observations, discussions with locals, and the chemical tracer analyses, tend to support this conclusion.
- ✓ The average intercept values of the LMWLs of the 77 samples for June 2011, November 2011, July 2012, December 2012 and November 2013 are 5.46, -89.91, 12.19, -4.45, and 1.89‰ respectively. The regressions, $r^2 = 0.84$ for June 2011, $r^2 = 0.08$ for November 2011, $r^2 = 0.93$ for July, $r^2 = 0.91$ for December 2012 and $r^2 = 0.92$ for November 2013 indicate that the three datasets do not define coherent regional MWLs. June 2011 and July 2012 appeared to have approximately similar slopes and intercepts, suggesting that the waters draining the basins have a similar origin.
- ✓ Most samples except most December 2012 cluster and plot left of both meteoric water lines, indicating there is no evaporation.

The importance of environmental isotope tracers [22, 23] in tracing water dynamics in the Mohlapitsi Wetland is emphasized in this research. On the other hand, there are some limitations related to the costs and logistics of sampling and the cost of laboratory analysis. Secondly, a high level of expertise could be required for sampling and interpretation of the analysis.

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