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Isotope Hydrology in the Middle Mohlapitsi Catchment, 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. One hundred and twenty eight water samples were collected during May 2007 through November 2013 for deuterium and oxygen-18 analyses. The isotopic compositions of water samples at the study site catchment did not show any significant difference, indicating they are from the same source. This isotopic similarity between the upstream and the wetland aquifers confirmed the hydraulic interconnection between them. 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 study catchment. 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.

Keywords:- Wetland, Isotope hydrology, stream flow, 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. METHODOLOGY

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].

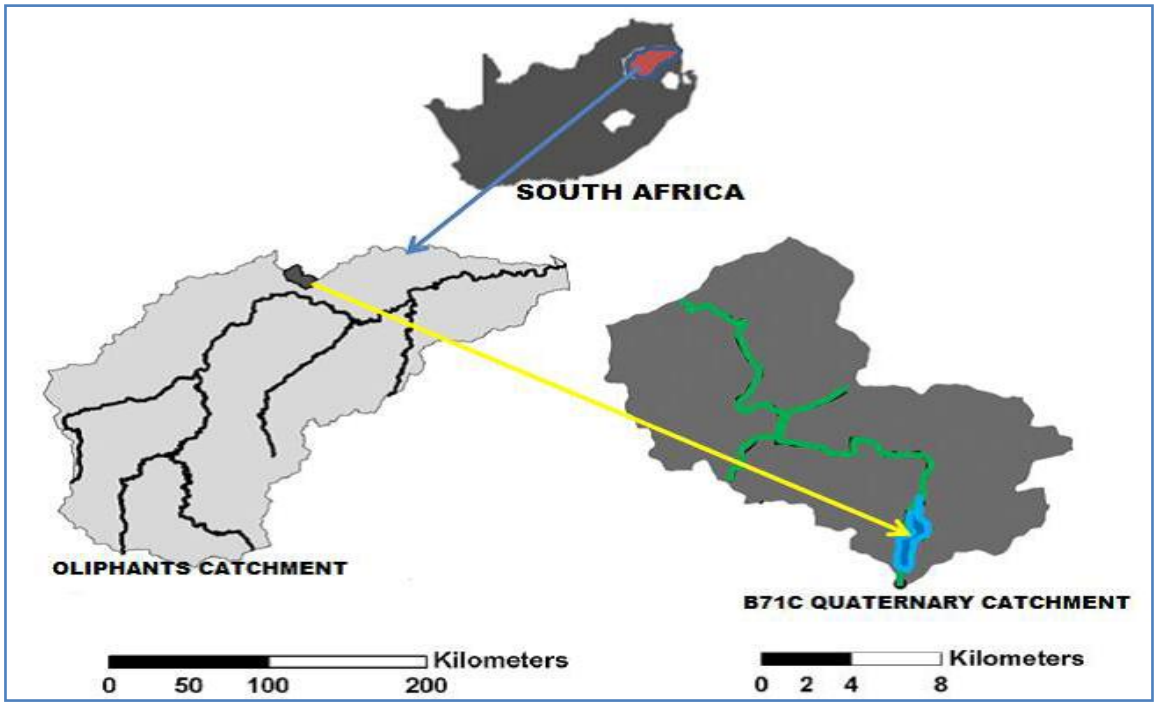

Figure 1 Map showing the location of the study area in B71C Quaternary Catchment within the Olifants Catchment [17]

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

2.1 Water Sampling

A total of 128 samples were collected randomly from piezometer wells, springs, river, drains and boreholes. The sampling sites are underlain by the Malmani Subgroup of the Chuniespoort Group. Groundwater samples from piezometer wells were collected manually, while borehole samples were directly taken from taps. All water samples were collected for isotopic analysis of stable isotopes (Oxygen -18, Deuterium). For ^{18}O and ^{2}H isotope sample were collected in 50ml airtight plastic bottles. The laboratory analyses of the collected samples were carried out at the iThemba Labs in Johannesburg, South Africa.

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

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

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

The Pretoria local meteoric water line (PLMWL) was established for the $\delta^{18}O$ and $\delta^{2}H$ of water samples collected during May 2007–November 2013 using the statistical analysis (Figure 3). The linear correlation is described by equation 2:

$$\delta D = 7.05\delta^{18}O + 7.6 \qquad (2)$$

Local meteoric water line (LMWL) was plotted together with global meteoric water line (GMWL) shown by Craig [7] as equation (3):

$$\delta D = 8\delta^{18}O + 10 \qquad (3)$$

Statistical data analysis was performed using STATA V13 statistical software. The analysis was performed in order to compare the isotopic finger prints between years and seasons.

III. RESULTS AND DISCUSSIONS

3.1 Stable Isotopes

The stable isotopic analysis of the water samples in the study area, the plot of δD and $\delta^{18}O$ values of the water samples and expected source are shown in Figure 3 with respect to global meteoric water line (GMWL) ($\delta D = 8\delta^{18}O+10$; Craig, 1981), Pretoria local meteoric water line ($\delta D = 7.05\delta^{18}O+7.6$. The Pretoria local water linePLMWL) was used as the closest local meteoric line available.

The stable isotopic composition of Oxygen-18 and Deuterium of these water samples were of depleted nature and the trend of depletion increased with the sampling year (Figures 3 and 4). Most December 2012 samples showed enrichment compared to other sampling years. However, they did not indicate evaporation effect and thus appears to be originating from any surface water bodies or from any anthropogenic activities such as agricultural return-flows, leakages from freshwater, wastewater pipe networks. The isotopic compositions ($\delta^{18}O$) of all samples at the study site and its surrounding catchments did not show any significant difference, indicating they are from the same source and recent infiltration water reaching the wetland aquifer. This isotopic similarity between the upstream aquifer and the wetland one confirmed the hydraulic interconnection between them. The effect of evaporation is quite clear in most of December 2012 samples, where they plot far below both GMWL and PLMWL because their isotopic compositions are slightly enriched with heavy isotopes indicating that during relatively heavy rainfall, rainwater is collected in the depressions and affected by evaporation which make it enriched in heavy stable isotopes and mixed with groundwater. This water then infiltrates and mixes with the water of the underlying wetland aquifer. Compared to other samples, the deuterium and Oxygen 18 values in all groundwater and borehole revealed depletion.

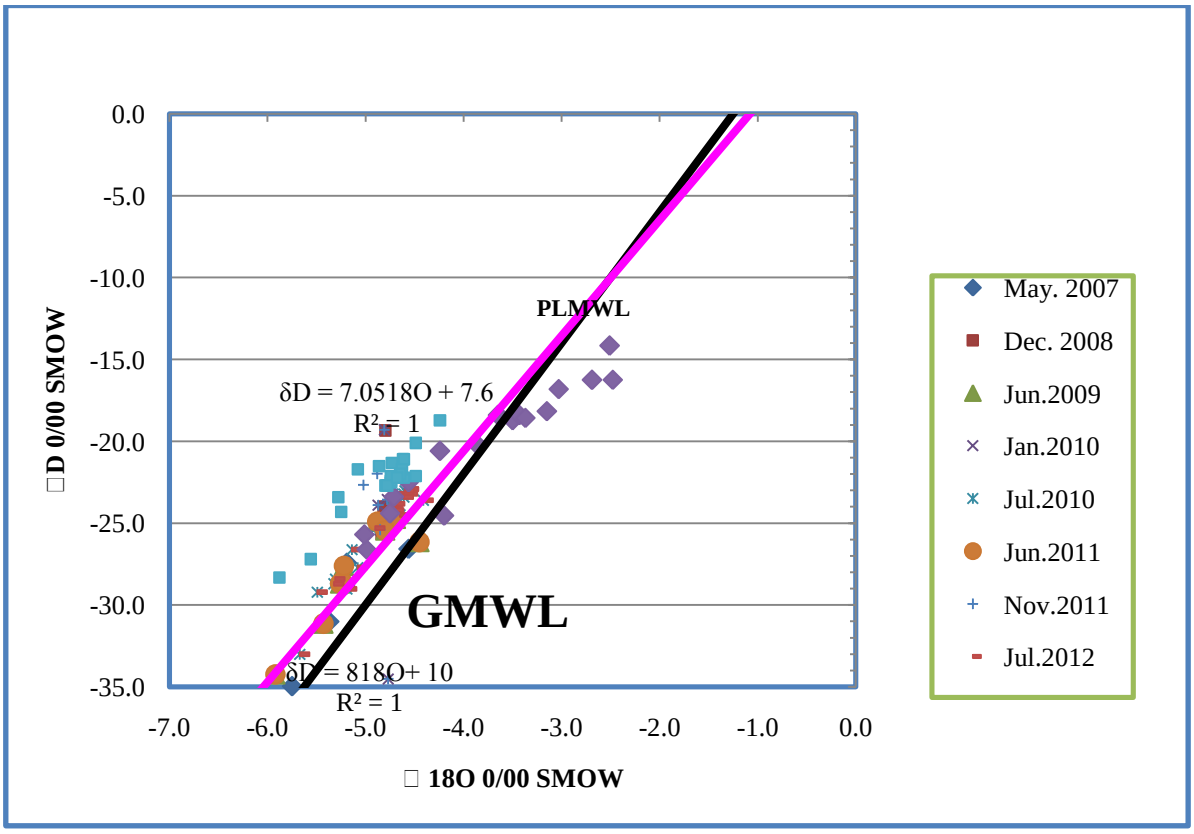

Figure 3 Cross-Plot of Deuterium versus Oxygen-18 for water samples during May 2007 - November 2013

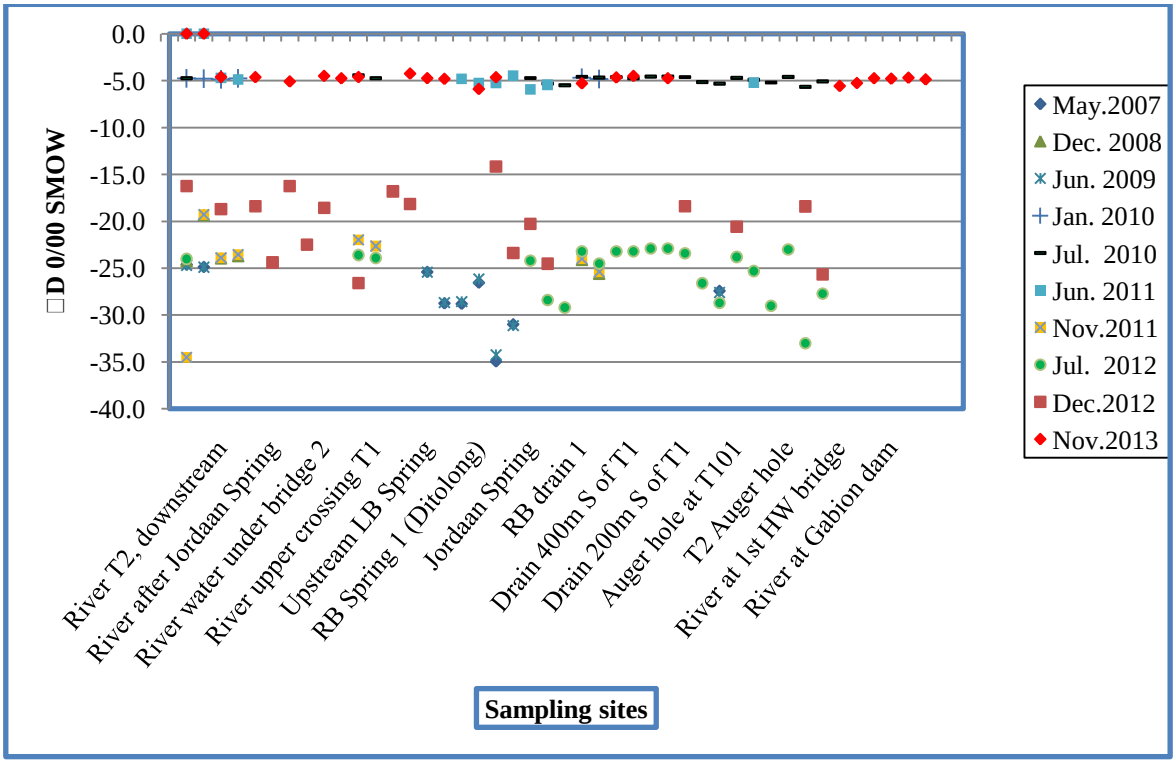

Figure 4 The isotopic composition of surface water and sub-surface water bodies in the study site

Figure 3depicts that river upstream (δD = -19.30, $\delta^{18}O$ = -2.48) is enriched, while river at fig trees environment (δD = -34.96, $\delta^{18}O$ = -5.92) depleted. Most water samples lie above both PLMWL and GMWL except Right Bank Spring 1(RB Sp1) with δD = -26.24, $\delta^{18}O$ = -4.45 plot at right of both lines; indicating there is evaporation and showed enrichment; while Left Bank Spring 3 (LB Sp3), having δD = -5.24, $\delta^{18}O$ = -28.5 is depleted (Figure 1). The rest of samples lie left of the lines; indicating there is no evaporation.

The isotopiccomposition of water samples did not show alarge seasonal variability. The $\delta^{18}O$ ranged between-4.56 and -5.75‰ for May samples,between -4.70 and -4.84‰ for December 2008, andbetween -4.45 and -5.92‰ for June 2009. In addition, the isotopic composition of $\delta^{18}O$ ranged -4.56 and -4.58‰ for 2010, -4.58 and -5.47‰ for 2011. Furthermore, the isotopic composition of $\delta^{18}O$ for 2012 and 2013 ranged from -4.24 and -5.67‰ and -4.24 and 5.88‰ respectively (Table 1).

The standard deviation of the data was 14.31 and there was no variation between seasons and years of sampling.

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 samples 100m above Jordaan Spring (δD = -4.56, $\delta^{18}O$ = -22.50) and drain 200m south of T1 (δD = -3.65, $\delta^{18}O$ = -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.

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 (Figs. 3 and 4) and no seasonal variations were observed as shown on Table 1.

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

Table 1 Statistical details of Deuterium and Oxygen-18 isotopes

Statistical parameters	May 2007		Dec 2008		Jun 2009		Jan 2010		Jul 2010		Jun 2011		N0v 2011		Jul 2012		Dec 2012		Nov 2013	
	^{18}O	D	^{18}O	D	^{8}O	D	^{18}O	D	^{18}O	D	^{18}O	D	^{18}O	D	^{18}O	D	^{18}O	D	^{18}O	D
Maximum	-4,56	-24.62	-4.72	-19.34	-4.45	-24.72	-4.70	-19.30	-4.41	-22.90	-4.45	-22.70	-4.70	-19.30	-4.41	-22.90	-2.48	-14.16	-4.24	-18.70
Minimum	-5.75	-34.56	-4.84	-25.60	-5.92	-34.23	-4.87	-34.50	-5.67	-33.00	-5.92	-4.84	-5.02	-34.50	-5.67	-33.00	-5.01	-26.60	-5.88	-28.30
Mean	-5.07	-28.05	-4.77	-23.50	-5.10	-27.93	-4.80	-25.11	-4.87	-25.41	-5.10		-4.84	-24.41	-4.87	-25.41	-3.76	-20.12	-4.83	-22.44

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 1).

Figure 4 depicts the different isotopic signatures according to the source of water. 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 (Fig 4). 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]

IV. 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 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.

✓ 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 constraints related to the finance and logistics of sampling and laboratory analysis. Secondly, large amount of finance could be required for training and interpretation of the analysis.

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