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Recent findings in Tritium Isotopes in Small Catchment: A Case of the Middle Mohlapitsi Wetland, SouthAfrica

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Abstract: Seasonal tritium variations in streamflow, groundwater (GW), spring flow, boreholes, piezometers and drains were analysed tocompare the hydrology of water resources in the study area. Fifty water samples were collected and analyzed in iThemba Labs for environmental tritium (^3H). Concentrations of tritium in the water resourceswere measured by scintillation counting after electrolytic enrichment. However, the results did not provide a temporal record of isotope variations in the various water sources; except the higher value for tritium (3.2TU) was measured during May 2008. The cause for such high concentration of tritium during May 2008 could be that during the study period, new rainfall water entered the spring storage and mixed with old water. The lowest tritium value measured for Valis bore hole (0.3 TU), indicating this water is the oldest.

Keyword: Borehole, Isotope, Groundwater, Piezometer, Streamflow, Tritium

I. INTRODUCTION

Tritium as a form of hydrogen is found naturally in both air and water. Tritium is most useful for distinguishing between pre-bomb and post-bomb recharge and is a naturally occurring radionuclide as well as one that is artificially produced [1]. It has one proton and two neutrons and emits low-energy beta particle [2]. Tritium is naturally produced in the atmosphere by cosmogenic processes and interacts with atmospheric nitrogen and oxygen. Atmospheric tritium is formed when cosmic rays bombard nitrogen to yield ^3H; and this occurs according to equation (1):

$$^{14}N + n \rightarrow {}^{12}C + {}^{3}H \quad (1)$$

where n is a neutron from cosmic radiation. Tritium atoms then combine with oxygen, forming water that subsequently falls as precipitation. Small amounts of natural tritium are also produced by alpha decay of lithium-7 in the earth [3].

About 3 to 5% of all neutrons in the upper atmosphere react with nitrogen to form ^3H [4]. The natural concentration of tritium in the atmosphere is uncertain, because few measurements were made prior to nuclear testing. However, the natural tritium concentration is estimated to be between 4 to 25 TU depending on location [5]. Tritium released from nuclear power plants is primarily produced by neutron activation of Boron and is released in liquid and gaseous effluents. Gaseous form of tritium effluents can be washed out by precipitation and show up in surface and groundwater samples [6]. In regular water 2 hydrogen atoms bond with oxygen to form a water molecule of H_2O; in Tritiated water however the tritium is used to replace one of the hydrogen atoms. When tritium is formed it often combines with oxygen in the form of HTO, where H is ^1H or ^2H; T is ^3H; and O is oxygen. This is recognized with a chemical symbol of HTO instead of H_2O. This is also called as tritium oxide. Tritium distribution in precipitation depends on latitude, proximity to the sea and distances from artificial sources or thermonuclear test

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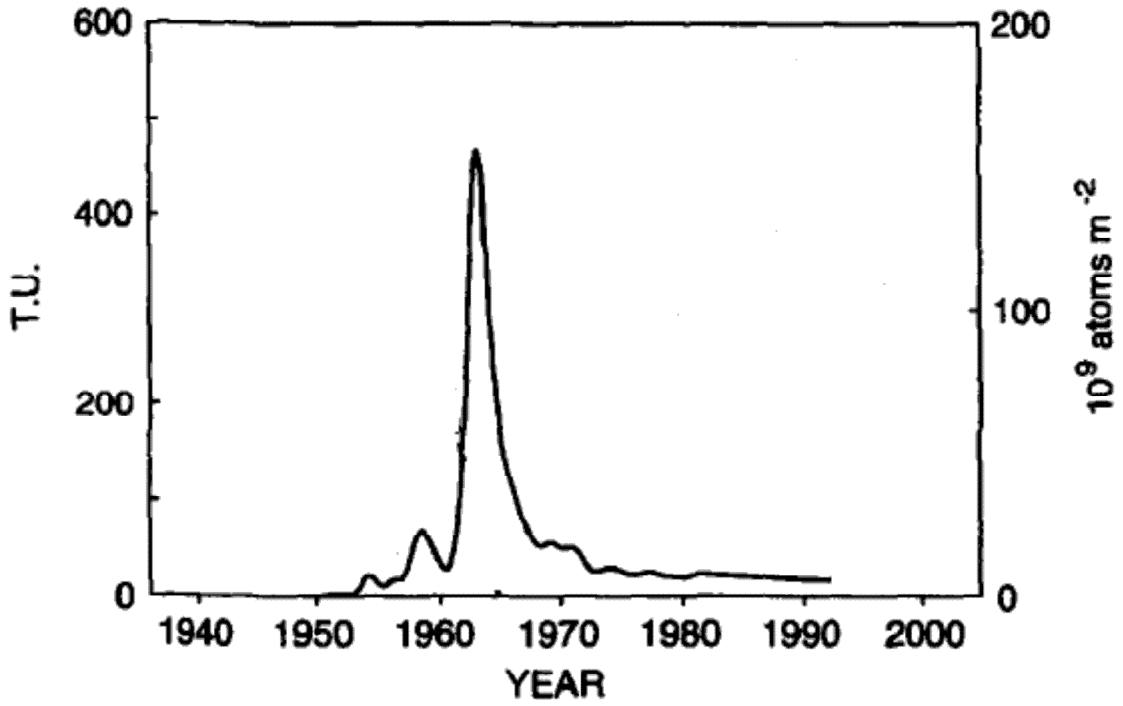

Figure 1: Tritium concentrations in rainfall. ^3H concentrationsare for Ottawa rainfall, and have been corrected for radioactive decay to 1995 [12]

zones. These factors and its radioactive decay mean that tritium can be used to determine how long water has been present in aquifers [7, 8].

Tritium (^3H) is one of historical tracers suitable for studies of young groundwaters. Concentrations of this isotope in the atmosphere increased during the late 1950s and early 1960s as a result of thermonuclear testing (Figure 1). This provided a slug-like input to groundwater systems, and could be used to identify groundwater which recharged during this time. 3H has been extensively used in studies of shallow groundwater systems [9, 10, 11].

Since ^3H undergoes radioactive decay with a relatively short half-life of 4537 days, the definition of the bomb peak is diminishing, and in some aquifers ^3H concentrations in samples recharged during the 1960s is not significantly above modem rainfall values [13]. This is particularly so in the Southern Hemisphere, where concentrations of ^3H in rainfall were an order of magnitude lower than in the Northern Hemisphere [14, 15].

Measurement and interpretation of the $^3H/^3He$ ratio in groundwater became an important technique that is available in recent years, which allow direct dating of single groundwater samples. $^3H/^3He$ are able to estimate groundwater ages with a precision of a few years or better, for groundwaters recharged since the 1950s. $^3H/^3He$ methods are now widely used in oceanography [16] and limnology [17, 18] to study the circulation of water masses. In this paper, we briefly describe the recent findings of tritium concentration in the study catchment.

II. STUDY AREA

Location and general description

This study was conducted at the middle Mohlapitsi Wetland in Capricorn District of South Africa, which lies in the lower part of the Oliphants basin (Figure 1). The wetland is a palustrine system covering an area of 183 ha [14]. Moreover, 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 [14].

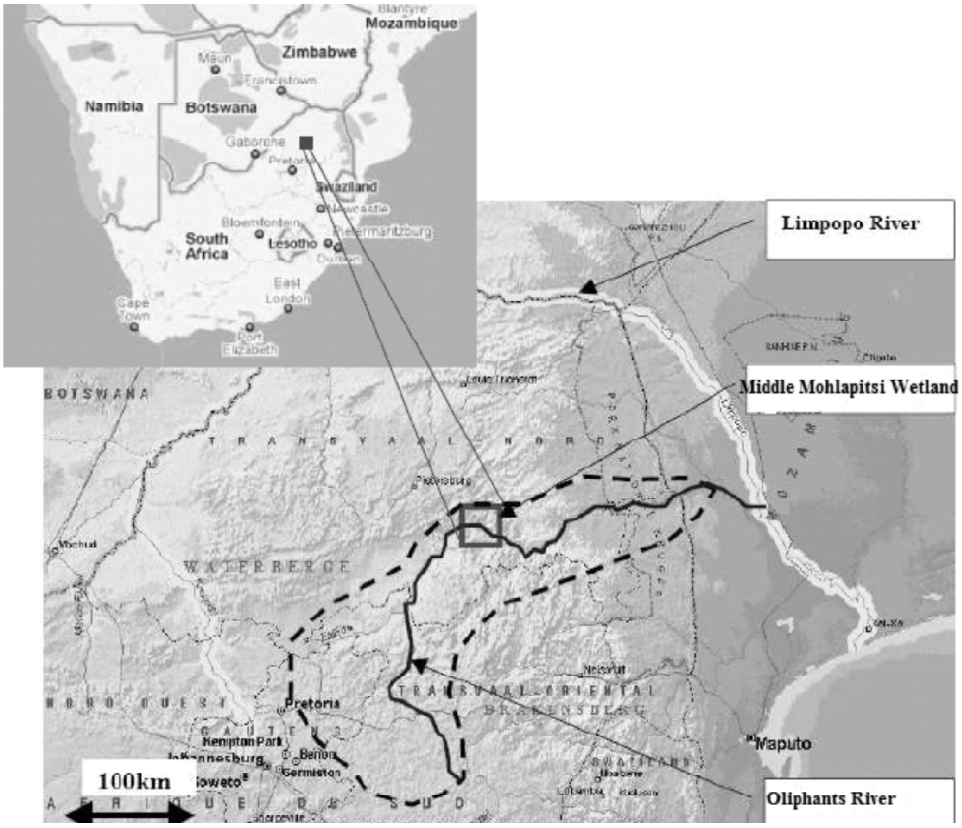

Figure 2: Location of the Middle Mohlapitsi wetland in the Limpopo Province and the Oliphants River basin [19]

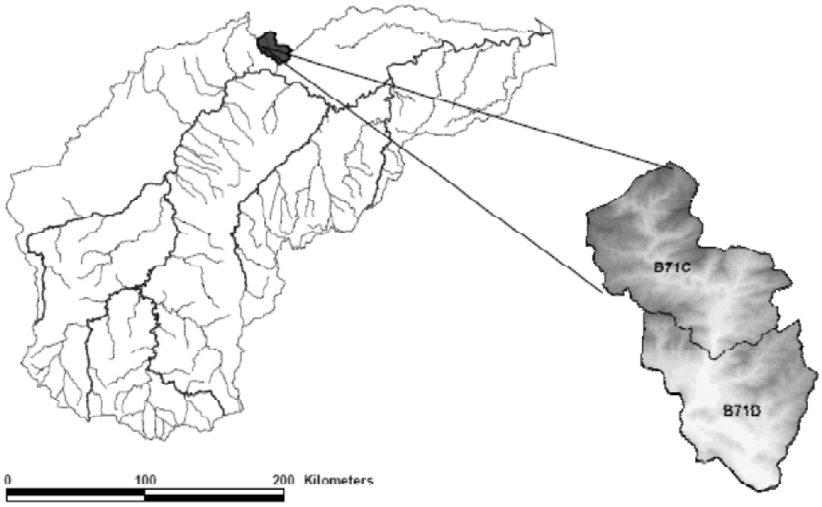

Figure 3: Delineation of the Oliphants River basin, the Middle Mohlapitsi catchment (B71C, B71D) and the Middle Mohlapitsi wetland (B71C) [19]

The Mohlapitsi River is in Limpopo Province of South Africa and drains southwards from the Wolkberg Mountains into the Oliphants 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 Oliphants 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 4).

Figure 4: The Mohlapitsi Wetland in the valley bottom[19]

III. METHODOLOGY

A. Water sampling for tritium isotope analysis

A total of 50 water samples (from drain, river, springs, boreholes and piezometers) were collected for tritium analyses during May 2010, December 2011, April 2012, and October 2013 (Figure 5). Borehole samples were collected from Vallis and Mashushu villages during all sampling times except May 2010 for isotopic analysis 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 Rozanski *et al.* [20].

As ^{3}H enters groundwater systems and begins to radioactively decay, the noble gas ^{3}He is produced. In the unsaturated zone, dissolved ^{3}He generated from ^{3}H decay can be lost to the atmosphere. Below the water table, dissolved ^{3}He concentrations will increase as groundwater becomes older. Although groundwaters contain ^{3}He from several sources other than ‘H decay, determination of both ^{3}H and tritiogenic ^{3}He have be used as a residence time [21]. Hence, the residence time of GW in the study site was calculated using equation 2.

$$t = \lambda^{-1} \ln\left(\frac{3He}{3H} + 1\right) \tag{2}$$

where t is the estimated groundwater age, λ is the ^{3}H decay constant, and ^{3}H and ^{3}He were measured in tritium units. Tritium decays by electron emission with 12.43 years by β particle, and its λ is between 5.5 and 5.69 kev. For ^{3}H, one tritium unit (TU) represents one atom of tritium in 10^{8} atoms of hydrogen. Concentrations of tritium in the groundwater were measured by scintillation counting after electrolytic enrichment as described by Clarke and Fritz[22]. Analytical uncertainties usually result in errors in age estimates of less than 10% [23]. Sensitivity of ^{3}H/^{3}He age to recharge temperature was taken less than 0.5 years at ^{0}C-1. Sensitivity to excess air was approximately -5.0 years per cm3 kg-1 of excess air for very young water, decreasing to -0.25 years per cm^{3} kg^{-1} for water approximately 25 years old. Although, in theory, excess air and radiogenic ^{3}He can be estimated and corrected for, in practice this may not always be so straightforward. Air entrapment or gas stripping during sampling was a possible source of error [23]. Furthermore, diffusive loss of ^{3}He to the atmosphere has been shown to lead to underestimates of ages of surface water bodies, and will similarly lead to underestimates of groundwater ages [24]. Diffusive loss of ^{3}He to the atmosphere is greatest when helium concentrations near the water table are largest, such as when a large ‘H spike is injected in the aquifer and begins to decay.

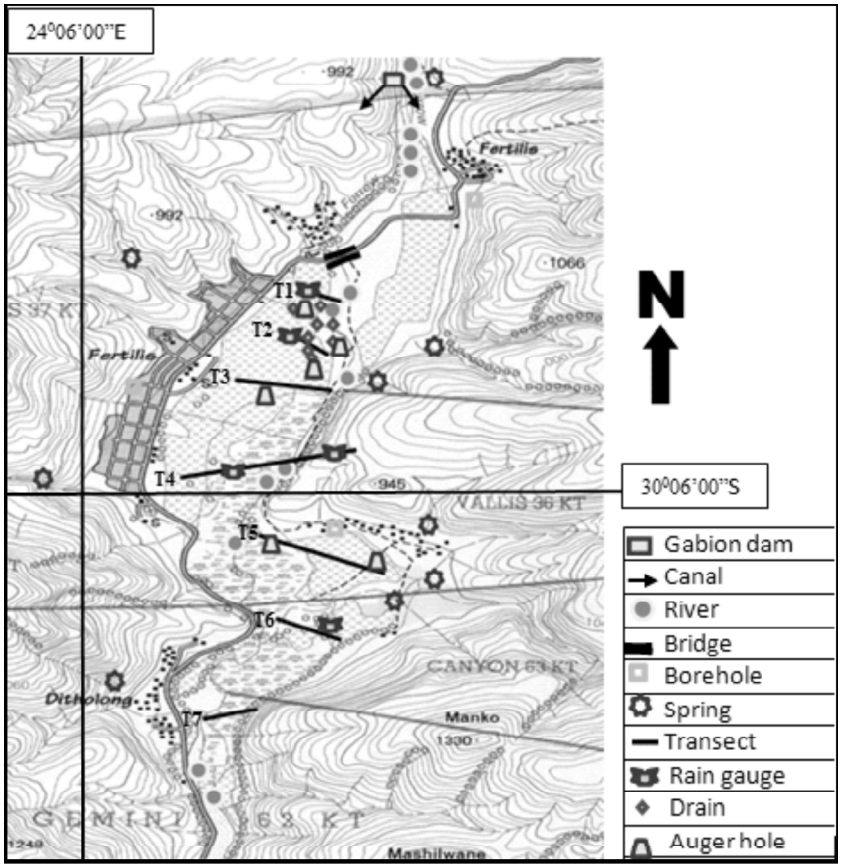

Figure 5: Locations of water resources and sampling points in the study wetland during 2007 through 2013 (own analysis)

IV. RESULTS AND DISCUSSIONS

Table 1 and Figure 2 present the tritium-specific activities (TU) for all water samples during sampling periods of May 2010, December 2011, April 2012 and October 2013. There was no noticeable trend within tritium values across the various springs that were sampled, which was consistent with the variability in the isotopic signatures of the spring water. Also, during April 2010, the three left bank springs (Jordaan Spring, Loumauwe Spring and spring at T5 environment) did not show significant variation. The higher tritium values (TU=1.4) and the smaller (TU=0.6) periodic oscillation observed for Piezometer T510, during April 2012 and December 2011 respectively, could be due to the small amount of precipitation during April 2012. Furthermore, during April 2012, all five piezometer samples did not show variation. The tritium values for the river water samples were much more consistent, but did not show any strong seasonal variations, while it might have been expected that the dry season river samples would show up as older water originating from sources with longer residence times.

The higher values for tritium were observed at Left Bank Spring 1 (TU=3.2, during May 2010), located at the top extreme end of a study area as compared to Vallis Borehole (TU=0.2, during May 2012). This result is in agreeable with the result obtained by Thatcher [25] that the atmospheric concentration of tritium in western Washington was estimated to range from 3 to 5 TU. The cause for high concentration of tritium at the study area during May 2012 could be that during the study period, new rainfall water entered the spring storage and mixed with old water. This further strengthens the argument that the spring waters come from different sources with different residence times and ages.

The Vallis borehole sample appears to be the oldest water (0.2TU); indicating its age is about40 years. This would be expected as the concentration of tritium in groundwater decreases by radioactive decay [26]. The results of Vallis Borehole during December 2009 and April 2010 were consistent (Table 1 and Figure 2). The next oldest

Table 1
Tritium values during May 2010, December 2011, April 2012 and October 2013

Sample description	*May2010* TU	*Dec.2011* TU	*Apr.2012* TU	*Oct.2013* TU
Right Bank (RB) Spring 1	3.2			
Left Bank (LB) Spring 2	0.8			
LB Spring 3	0.7			
RB Spring 4	1.4			
RB Spring 5	1.0			
RB Spring 6	1.7			
River Upstream	1.9			
River downstream	1.2			
Groundwater at piezometer T510	0.8			
River below downstream new bridge		1.9		
Rive at downstream new bridge		1.6		
River upstream culvert, north of Fertilis village		2.1		
River at Transect 1(T1) environment		1.4		
Right Bank Spring 1		1.7		
Right Bank Spring 2		1.3		
Right Bank Drain at T1 environment		2.3		
Right Bank Drain at T2 environment		1.6		
Vallis Borehole		0.2		
Mashshu Borehole		0.7		
Groundwater at piezometer T510		0.6		
River downstream of Jordaan Spring			1.4	
River upstream of Jordaan Spring			2.4	
River at Vallis village crossing			1.7	
River upstream			1.7	
Piezometer T510			1.4	
Piezometer T101			1.6	
Piezometer T201			1.6	
Piezometer T104			1.7	
Piezometer T302			1.2	
Jordaan Spring			1.3	
Loumauwe Spring			0.6	
Left Bank Spring at T5 environment			0.7	
Mashushu Borehole			0.9	
Vallis Village Borehole			0.3	
River below downstream new bridge				1.4
Right Bank Spring 1				1.9
Piezometer T201				1.2
RB Spring 4				1.1
Rive at downstream new bridge				1.4
River at Vallis village crossing				1.7
Piezometer MRB302				1.2
River upstream				1.3
River downstream				0.8
Mashushu bore hole				0.6
Right bank spring, LBS 3				1.2
Loumauwe Spring				0.9
Jordaan Spring				1.3
Piezometer MRB 101				0.9
Drain T1				1.3
Valis borehole				0.7

water after Vallis borehole is Loumauwe Spring (TU=0.6), located at left bank environment (Table 1 and Figure 2); indicating its age less than 45 years [27, 28]. All other water samples plotted between 0.8TU and 4TU; indicating a mix of sub-modern and modern water.

Also, all samples that fall below 0.8TU indicate sub-modern water (prior to 1950s). The drain sample is of the same order of magnitude as the river water suggesting that the drainage water has a short residence time in the wetland. The majority of the piezometer water samples are also similar to the river water and have relatively high tritium values. However, the sample taken at T5 had a very low tritium value during May 2010, while the sample from the same site during December 2011 was more consistent with the other piezometer sites. This may suggest that some spring water is contributing to the wetland subsurface water content during the dry season.

Only comparative ages of water samples are referred to and no absolute aging of water based on tritium has been attempted. While these comparative values have provided some information about the age and possible movements of water in the wetland environment, a more intensive and better planned programme of tritium analysis would have provided a more complete assessment. It may be concluded that this study has therefore demonstrated some potential for the use of tritium water analyses in wetland studies, but that the sampling scheme used within this study does not provide conclusive answers about different ages (and residence times) of different water sources.

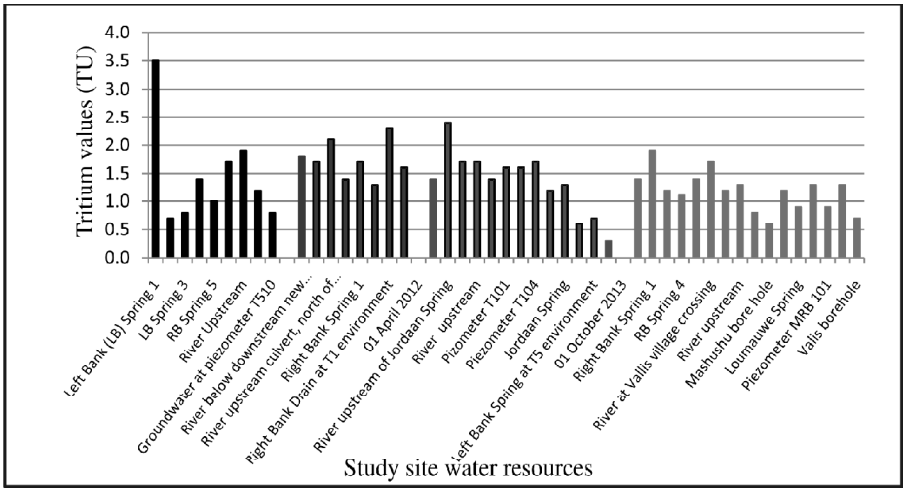

Figure 6: Tritium Values during May 2010, December 2011, April 2012 and October 2013

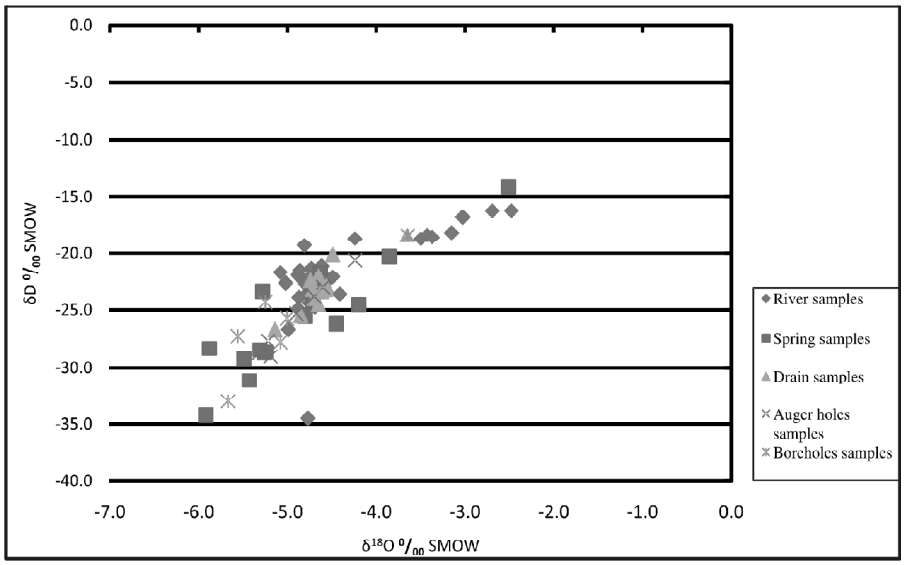

Figure 7: Deuterium and Oxygen-18 plot for water samples based on water source

Figure 7 shows the relationship between measured tritium in a sample and the $\delta^{18}O$ signature. As $\delta^{18}O$ values increase, the probability of finding tritium in that sample also increases. No tritium is observed in any sample that has a $\delta^{18}O$ value less than -6 and the majority of samples with measureable amounts of tritium have $\delta^{18}O$ signatures between -6 and -4‹.

V. CONCLUSIONS

To improve the understanding of the hydrology and the origin of water in the Mohlapitsi Wetland environmental isotope tracers were measured. Tritium, the radioactive isotope (^3H) of the element hydrogen, is an excellent tracer of ground water because it is incorporated into water molecules of rainfall that recharges ground water, and its movement within the ground-water system is not restricted by chemical or physical processes.

Concentration of tritium in water samples shows seasonal variations. The maximum concentrations occur in late April 2012 or end of summer; the next maximum concentrations occur in December 2011 or middle of summer (Table 1 and Figure 3). All samples that lie below 0.8TU indicate the existence of sub-modern water (prior to 1950s); while those that fall between 0.8 and 4TU indicate a mix of both modern and sub-modern waters. The cause for elevated concentration of tritium during May 2010 measured at left bank spring located about 3 km north of T1could be that during the study period, new rainfall water entered the spring storage and mixed with old water. Hence, this further strengthens the argument that the spring waters come from different sources with different residence times and ages.

Furthermore, the presence of tritium in groundwater samples at concentrations greater than 1 TU indicates that the ground water was recharged after the start of atmospheric testing of thermonuclear weapons. Atmospheric tritium from weapons testing continues to decay, and tritium concentrations in nowadays rainfall are still distinguishable from tritium concentrations in ground water recharged prior to the period of bomb testing.

Ground water containing tritium concentrations between the detection limit and 1 TU may be considered to have been recharged prior to the bomb testing period or is predominantly older water that may have mixed with a smaller fraction of modern ground water recharged after 1953 [22].

Groundwater samples with concentrations less than 0.4 TU are considered to contain little bomb tritium, indicating that ground water in these samples was recharged prior to 1953. Tritium concentrations between 0.4 and 1.0 TU were considered to fall in a range where a clear distinction between modern and pre-modern ground water could not be assigned based on tritium data alone.In general, the presence of tritium in groundwater sample means that the groundwater was recharged after post bomb-tritium era (1963) regardless of how HTO water was measured.

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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