

## The Hydrogeochemistry of the Mayes Water Fall, North Central Nigeria.

Aga, T<sup>1\*</sup>, Isah, B<sup>1.</sup>, Zang, C<sup>2.</sup>, and Piwuna, R.M<sup>1.</sup>

*1Department of Geology, University of Jos, Jos, Nigeria*

*2Department of Science Laboratory Technology, University of Jos, Jos, Nigeria*

*\*Corresponding Author: Aga, T*

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**Abstract:** *The Mayes waterfall is situated in the south western part of Sha-Kaleri Younger Granite Complex in Nigeria and covers an area that is approximately twenty-four (24) square kilometers. The rock types found in the study area include the migmatite-gneiss and biotite granite. The gabbros occur within the migmatite-gneiss of the Nigerian Basement Complex as boulders of different sizes and along river channels as dykes. The water samples that are genetically related were shown by Stiff diagram, which displayed the same shape while those that displayed different shapes have different sources. The water chemistry of Mayes waterfall and its tributaries which showed Ca + Mg type water as suggested in the piper diagram is controlled by the environment through which the water passed and mostly affected by the chemical weathering of some rock types. The topaz found within the river channels could be responsible for the high concentration of fluoride in some of the samples analysed.*

**Keywords-** *Hydrochemistry, Mayes waterfall, Tributaries, Piper, Stiff.*

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### I. INTRODUCTION

The study area lies between latitudes 09°08'30''N and 09°04'00''N and longitudes 008°42'30''E and 008°45'30'' E in Wamba Local Government Area, Nassarawa State, Nigeria (Fig. 1). The Mayes water fall, which derived its source from the rivers in Sha in Plateau State is situated in Massenge and lies within the adjoining high lands and hilly massifs of the Sha-Kaleri Younger Granite Complex, North Central Nigeria. The fall is located in the north eastern end of the study area and flows approximately in the N- S direction. The topography of the study area is generally moderate to high and the fall flows over a steep region that is about 800m above sea level reflected in the digital elevation model (Fig.2).

Geologically, the genesis of the Mayes waterfall like some others is most commonly formed when a river is young when the channel is seldom narrow and deep. When the river courses over resistant bedrock, erosion happens slowly, while downstream the erosion occurs more rapidly. As the watercourse increases its velocity at the edge of the waterfall, it plucks material from the river bed. Whirlpools created in the turbulence as well as sand and stones carried by the water course increase the erosion capacity [1]. Activities of erosion at the base of the fall are very evident owing to the exposure of the basement rocks comprising of migmatite gneiss and gabbroic dykes. The drainage pattern is morphologically controlled at the upper section of the fall, very typical of crystalline geologic environment which develops on uniformly erodible rocks and characterized by the branching of tributary streams in a model resembling tree branches, hence exhibits a dendritic pattern of drainage. At the middle and lower section of the fall, it is structurally controlled, as an almost linear trend with some network of fractures and joints meeting at varying angles, hence, a trellis drainage pattern [1]. The Mayes waterfall is subject to heavy seasonal fluctuations in flow as a result of seasonal rains of the north central, Nigeria. Between the month of June and October, flow increases dramatically and the water looks muddy as a result of some dissolved chemical elements in water. However, during the dry season, the velocity of water flow reduces and appears settled and clean.

Water chemistry analysis is often ground work of studies of water quality, pollution, hydrology, geothermal waters; and it can also be used to aid in prospecting for ore deposits. Physico-chemical parameters play an important role in the quality of any type of water body. The normal ranges of physico-chemical characteristics indicate the good water quality. The quality and quantity of surface water bodies like lakes and tanks depend upon on the climate, catchments, geography of the area and inputs and outputs both natural and manmade [2]. The variation in hydrochemistry of water can be used as an indicator to understand water-rock interactions and geochemical processes during flow in the aquifers [3].

The objective of this study is therefore to classify the water samples analyzed into classes based on the cations and anions present in the water, and to determine the interaction of the waters with their environment whether or not, they are genetically related.

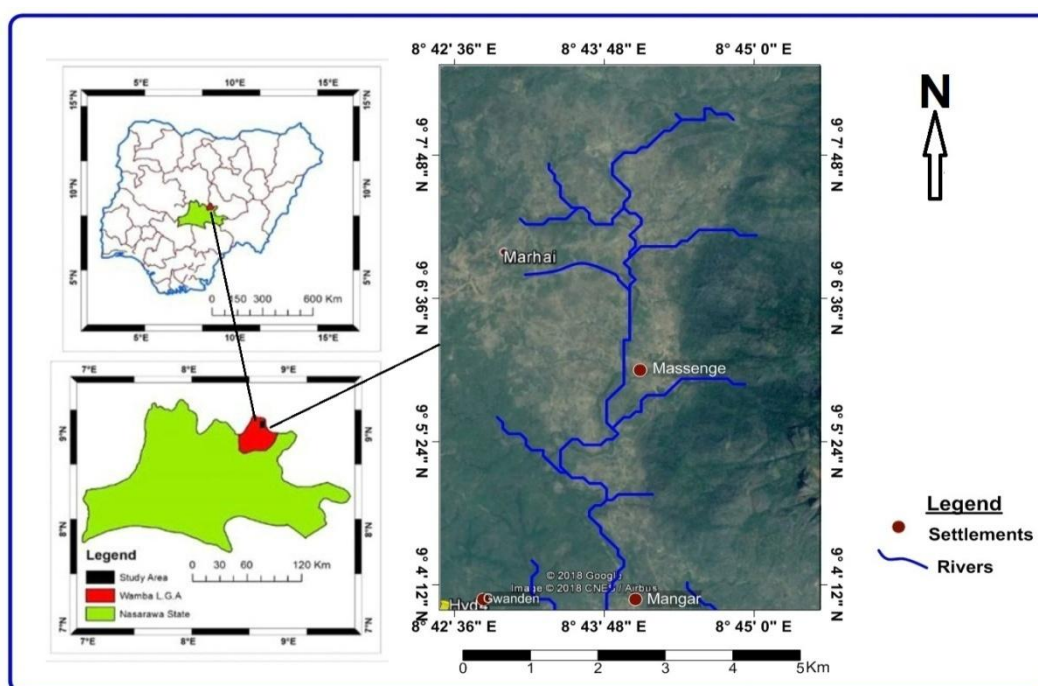


Fig. 1: Location Map of the Study Area

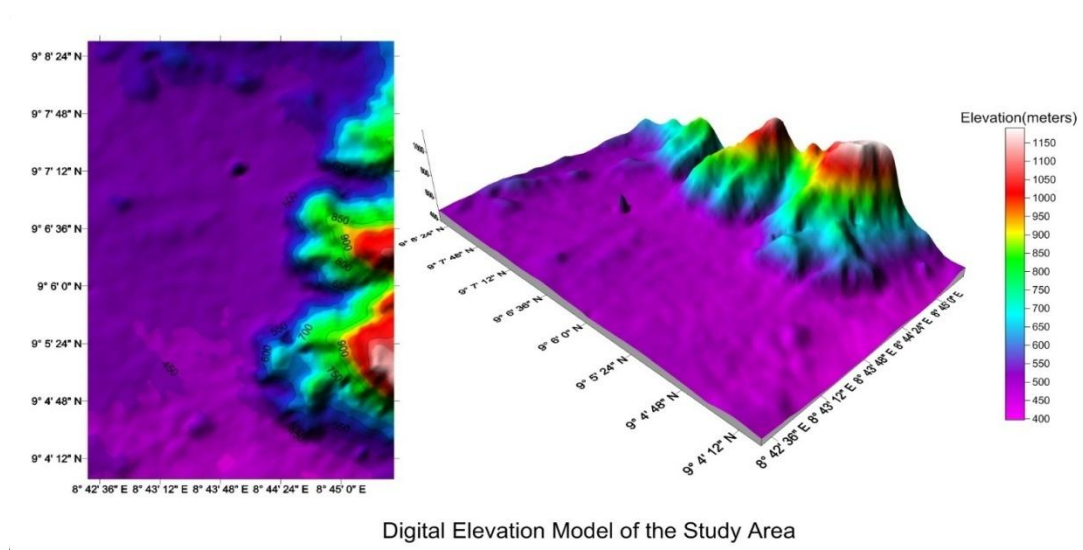


Fig. 2: Topographical expression of the study Area

## II. Methodology

A total of sixteen surface water samples were collected at different points in the study area. However, Six (6) of these samples were collected from the waterfall at different intervals (Fig.3). To avoid contamination, sample containers used were washed with the water samples, filled and closed air-tight. Proper labeling including the samples numbering and location were done. The geographical location of each sample was determined with a hand held Global Positioning System (GPS). The samples were acidified with two drops of tetraoxosulphate VI acid, in order to conserve the samples and also to prevent unwanted reactions. The samples were analysed for major and secondary constituents. The Titrimetry method using the Digital HachTitrator Model 1690 only for  $\text{HCO}_3$  and the Spectrometry method using Hach Digital Spectrometer Model 2400 for the analysis of the Cations and Anions were employed in the analysis of the water samples.

Piper, Stiff and Ion balance diagrams were plotted using the analytical data obtained from the water chemistry analysis to determine water type and water quality through the use of RockWare aq.QA software. The digital elevation model and drainage maps were generated using Golden Surfer 13 software.

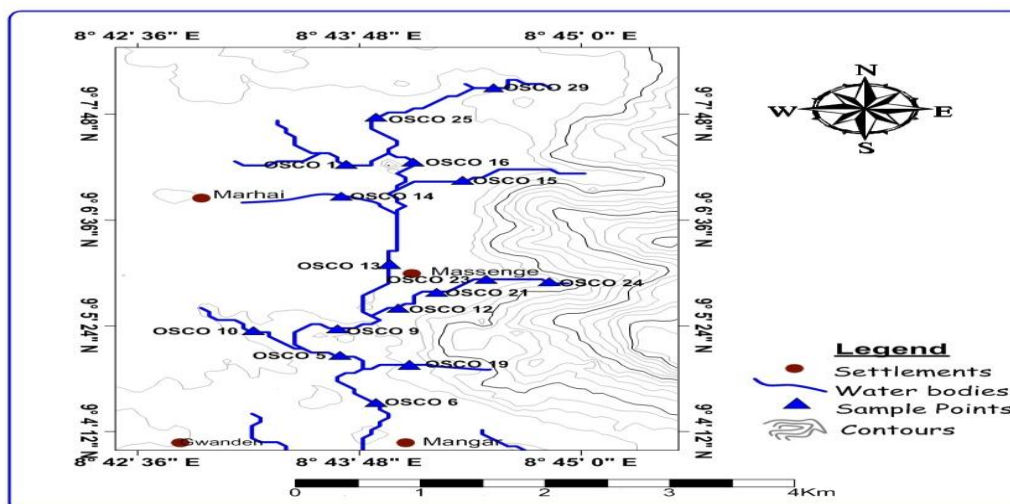


Fig.3: Drainage/Sample Location Map of the Study Area

### III. RESULTS AND DISCUSSIONS

The results of the analysis are presented in the tables below;

Table 1: Water Analysis (mg/l) for the Major Constituents

S/N	SAMPLES	SO <sub>4</sub>	Mg	Ca	Na	Cl
1	OSCO9	32.20	39.17	48.92	0.167	90.11
2	OSCO10	30.11	48.78	52.66	0.301	84.27
3	OSCO24	43.66	49.83	37.11	0.102	97.27
4	OSCO29	39.08	57.72	76.15	0.386	73.62
5	OSCO15	36.66	47.88	72.83	1.002	64.28
6	OSCO13	30.07	49.27	61.04	0.701	54.62
7	OSCO23	46.08	53.01	41.96	0.28	66.87
8	OSCO6	27.89	36.07	57.11	0.271	68.21
9	OSCO25	29.103	29.88	68.27	0.012	77.01
10	OSCO1	27.62	43.01	60.01	0.091	48.62
11	OSCO21	44.27	50.02	39.74	0.53	68.97
12	OSCO16	41.62	37.07	43.87	0.068	61.08
13	OSCO14	37.08	28.87	51.62	0.73	49.28
14	OSCO5	28.87	23.67	46.66	0.408	49.28
15	OSCO12	46.93	35.61	53.92	0.73	75.62
16	OSCO19	48.21	34.82	61.11	0.28	66.01

Table 2: Water Analysis (mg/l) for the Secondary Constituents

SAMPLES	HCO <sub>3</sub>	K	Fe	NO <sub>3</sub>	NO <sub>2</sub>	F
OSCO9	289	9.66	0.397	107.11	0.00	0.641
OSCO10	302	7.43	0.401	111.29	0.00	0.55
OSCO24	211	8.87	8.03	140.11	0.00	0.78
OSCO29	266	5.43	0.573	127.62	0.01	0.62
OSCO15	397	7.06	0.427	98.27	0.00	0.48
OSCO13	208	6.67	1.88	101.77	0.00	0.51
OSCO23	239	8.11	7.43	137.19	0.002	1.72
OSCO6	337	10.01	0.296	77.83	0.00	0.41
OSCO25	278	9.10	0.119	98.11	0.00	0.520
OSCO1	252	7.07	0.708	71.79	0.00	0.78
OSCO21	243	4.62	4.07	122.00	0.00	1.12
OSCO16	366	5.80	5.12	87.22	0.004	1.36
OSCO14	300	3.90	2.103	81.67	0.00	1.18
OSCO5	291	6.80	0.399	64.28	0.00	0.316
OSCO12	258	8.00	9.63	108.00	0.00	1.96
OSCO19	281	7.9	4.22	78.22	0.003	1.37

**Table 3: Water Analysis (mg/l) for the Minor Constituents**

SAMPLES	PO <sub>4</sub>	Cd	As	Se	Cu	Ni	Pb	Zn
OSCO9	21.96	0.00	0.062	0.00	0.221	0.00	0.00	1.00
OSCO10	32.77	0.00	0.018	0.00	0.311	0.00	0.00	1.02
OSCO24	38.01	0.001	0.007	0.001	0.482	0.001	0.013	2.03
OSCO29	23.11	0.00	0.023	0.01	0.167	0.00	0.00	1.63
OSCO15	22.07	0.00	0.006	0.00	0.108	0.00	0.00	0.913
OSCO13	29.011	0.00	0.002	0.00	0.101	0.00	0.001	1.88
OSCO23	36.73	0.00	0.011	0.002	0.403	0.00	0.016	2.017
OSCO6	10.728	0.00	0.003	0.00	0.201	0.00	0.00	0.91
OSCO25	31.06	0.00	0.012	0.00	0.110	0.00	0.00	0.634
OSCO1	23.711	0.00	0.006	0.001	0.34	0.00	0.001	0.793
OSCO21	30.27	0.00	0.001	0.00	0.507	0.00	0.005	2.28
OSCO16	33.62	0.00	0.007	0.001	0.114	0.00	0.008	0.714
OSCO14	29.68	0.00	0.018	0.00	0.481	0.00	0.00	1.03
OSCO5	31.18	0.00	0.003	0.00	0.109	0.00	0.00	0.62
OSCO12	36.21	0.00	0.005	0.012	0.445	0.002	0.027	2.003
OSCO19	21.20	0.00	0.002	0.017	0.371	0.00	0.007	1.087

Analysis of sample OSCO29 obtained from a tributary of Mayes waterfall as the water sample with the highest concentration of Ca<sup>2+</sup> and Mg<sup>2+</sup> with concentration 76.67mg/l and 57.72mg/l respectively (Table 1). The high concentration of Calcium can be attributed to gradual deposition and dissolution of carbonate minerals while the weathering of magnesium rich mineral like olivine contained in the gabbros of the study area contributes towards the enrichment of the magnesium. The tributaries of Mayes waterfall OSCO15 and OSCO6 have Na<sup>+</sup> and K<sup>+</sup> concentrations of 1.002mg/l and 10.01mg/l respectively (Table 1).

The primary source of Na<sup>+</sup> is from the weathering of the plagioclase feldspars of the igneous and metamorphic rocks of the study area while the potassium is a product of weathered orthoclase, microcline and biotite of the igneous and metamorphic rocks of the study area. OSCO19 (tributary of Mayes waterfall) has the highest SO<sub>4</sub><sup>2-</sup> concentration of 48.21mg/l and is a by-product of the oxidation of sulphides from igneous rocks and volcanic source. OSCO24 has the highest concentration of Cl<sup>-</sup> (97.27mg/l) while OSCO012 has the highest concentration of F<sup>-</sup> (Table 2).

Chloride in Mayes waterfall can be enriched through liquid inclusions in rocks and minerals while the source of chloride in surface water is transported in the atmosphere and carried to the earth by rain. Fluoride can be enriched through the weathering of topaz mineral found along the river channel which is highly rich in fluorine [Al<sub>2</sub>(SiO<sub>4</sub>)(F,OH)]. OSCO23 (Mayes waterfall) has the highest concentration of NO<sub>3</sub><sup>-</sup> with concentration 137.19mg/l (Table 2).

Although, igneous rocks contain small amount of soluble nitrate, its presence in water either emanates from organic sources or from industrial and agricultural chemicals. OSCO15 (tributary of Mayes waterfall) has the highest concentration of HCO<sub>3</sub><sup>-</sup> at 397.00mg/l. The major source of bicarbonate in water is the sewage system and the dissolution of carbonates. OSCO12 (Mayes waterfall) has the highest concentration of Fe<sup>2+</sup>, with concentration 9.63mg/l. The weathering of pyroxene, amphiboles, magnetite, pyrite, biotite and garnets releases large quantities of Fe<sup>2+</sup> which usually converts to relatively insoluble and stable oxides. A small amount of Fe<sup>2+</sup> is transported by surface and subsurface water. The enrichment of iron in the streams could be from the gabbros of the study area which contain pyroxene and biotite.

Some minor and secondary elements are of potential importance in the interpretation of the geological history of water as well as serve as ore mineral detectors when found in anomalously high concentrations. For example, the natural concentration of arsenic, copper, zinc, lead and nickel can be used to aid prospecting in these ore deposits. Arsenic and lead can be gotten from mine water and industrial wastes. Since some of these rivers including Mayes waterfall took their source from Plateau State, the possible enrichment of arsenic and lead could be anticipated from the tin mine waters.

### Physical Parameters

Total Dissolved Solid (TDS): Is the residue left when a certain amount of water is vaporized. Concentrations expressed in mg/l are essentially equivalent to ppm except in saline water where the total dissolved solids (TDS) is equivalent to 7000mg/l. The chemical composition of water is bound to be affected by the environment from which it originated as well as human and natural processes such as evaporation, precipitation, weathering, erosion and runoff leaching are major factors. The aim of carrying out this research is to determine the level of interaction the water in the study area has with the environment. The TDS in water sample can be represented by the sum of the ionic concentration of the major constituents which are usually Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Cl<sup>-</sup>, HCO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>. Samples OSCO 13 and OSCO 15 have the lowest and highest dissolved solids 409.31mg/L and 625.14 mg/L respectively (Table 4).

Conductivity: Varied between 565  $\mu\text{mho/cm}$  – 824  $\mu\text{mho/cm}$ , the lowest value 565.58  $\mu\text{mho/cm}$  was at OSCO 5 and highest 824.45  $\mu\text{mho/cm}$  at OSCO 10 and OSCO 29 with an average value of 715.1954  $\mu\text{mho/cm}$ . The conductivities compared with total dissolved solid of water samples are about 68.5% higher with values of 409.31 – 625.14 (mg/L) (average 490.14875 mg/l) and 565.58 – 824.45  $\mu\text{mho/cm}$  (average 0.521  $\mu\text{s/cm}$ ) for TDS and conductivity respectively (Table 4). This may be as a result of increase in concentration due to ion exchange between the rocks and water.

### Water Type

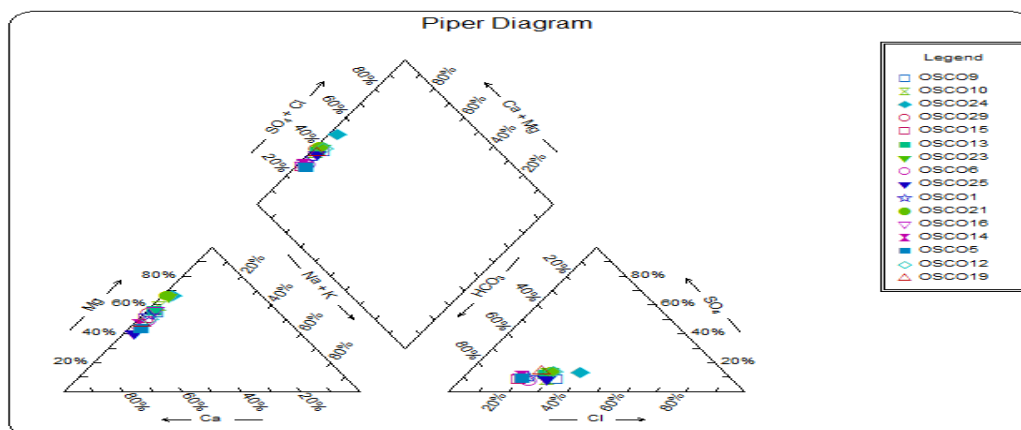
The water type – e.g., Ca-HCO<sub>3</sub>, Mg- HCO<sub>3</sub> or Na-SO<sub>4</sub> – is determined by finding the predominant inorganic cation and anion, figured on the basis of electrical equivalents. In determining water type, Aq•QA software accounts whenever possible for the carbonate speciation in solution, using the sum in electrical equivalents of the CO<sub>3</sub> and HCO<sub>3</sub> concentrations to represent carbonate. If carbonate is the dominant anion by this criterion, Aq•QA states the water type in terms of whichever of the species is present in larger equivalent concentration (e.g., Ca-HCO<sub>3</sub>, Mg- HCO<sub>3</sub> or Na-CO<sub>3</sub>) as reflected in (Table 4).

**Table 4: Physical Parameters and Generated water Types for the Samples**

SAMPLES	Dissolved solids (mg/L) Measured	Density (g/cm <sup>3</sup> ) Calculated	Conductivity ( $\mu\text{mho/cm}$ ) Calculated	Water Type
OSCO9	507.88	0.99742	732.61	Mg-HCO <sub>3</sub>
OSCO10	524.25	0.99743	824.45	Mg-HCO <sub>3</sub>
OSCO24	446.62	0.99737	757.14	Mg-HCO <sub>3</sub>
OSCO29	517.06	0.99742	824.45	Mg-HCO <sub>3</sub>
OSCO15	625.14	0.9975	817.69	Mg-HCO <sub>3</sub>
OSCO13	409.31	0.99734	676.09	Mg-HCO <sub>3</sub>
OSCO23	454.1	0.99737	743.32	Mg-HCO <sub>3</sub>
OSCO6	535.22	0.99744	702.61	Mg-HCO <sub>3</sub>
OSCO25	490.12	0.9974	701.98	Ca-HCO <sub>3</sub>
OSCO1	437.24	0.99736	639.56	Mg-HCO <sub>3</sub>
OSCO21	450.01	0.99737	711.41	Mg-HCO <sub>3</sub>
OSCO16	554.08	0.99745	702.66	Mg-HCO <sub>3</sub>
OSCO14	470.27	0.99739	623.51	Ca-HCO <sub>3</sub>
OSCO5	445.52	0.99737	565.58	Ca-HCO <sub>3</sub>
OSCO12	477.55	0.99739	720.2	Mg-HCO <sub>3</sub>
OSCO19	498.01	0.99741	699.86	Ca-HCO <sub>3</sub>

### Piper Diagram

Piper diagram is a tri-linear representation of the ions found in water (cations and anions). It shows graphically, the nature of a given water sample and also dictates the relationship to other samples. For example, by classifying similar samples in the piper diagram, we can identify geologic units with chemically similar water and define the evolution in water chemistry along the flow path. The concentrations are expressed as mg/l in piper diagram.



**Fig. 4: Piper Diagram for the Water Samples.**

From the piper diagram plotted, all the water samples are  $\text{Ca}^{2+} + \text{Mg}^{2+}$  type water.  $\text{Ca}^{2+}$  is highest at the northern end of the fall with concentration of 60mg/l, decreases in the middle part with concentration 37.11mg/l and increased at southern part with concentration of 58.92mg/l.  $\text{Mg}^{2+}$  on the other hand, increases from the northern part and highest at the middle part with concentrations 43.01mg/l to 53.01mg/l, and decreased towards the southern part (Fig. 4). However, details regarding the geochemical interpretation of water samples can be found in [4] and [5].

### Stiff Diagrams

Stiff diagrams are a way of representing analyses from an individual water sample [6]. A Stiff diagram is basically a graph that has concentration (in meq/L) on the horizontal axis and the major cations and anions on the vertical axis. The central vertical line represents zero concentration, and the cation concentrations are to the left while the anion concentrations are to the right. The concentrations are plotted, and the points are joined with a solid line to create a small polygon. The utility of these diagrams are that they give the viewer and instantaneous picture of the water chemistry and give room for comparison between waters from different sources [7].

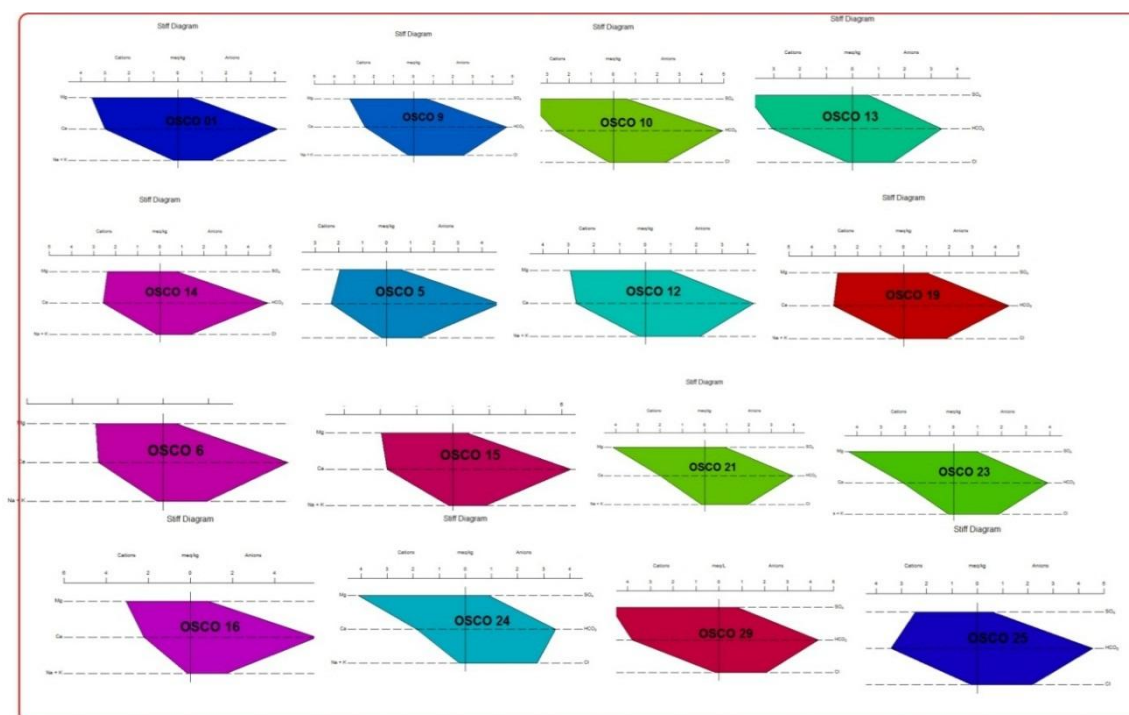


Fig. 5: Stiff Diagrams of the Mayes Water Samples

From the above plotted stiff diagram, those water samples that showed the same shape are genetically related implying they have the same source. Hence it can be deduced that samples OSCO1, OSCO9, OSCO12, OSCO16 and OSCO15 are genetically related. OSCO5, OSCO25, OSCO14 and OSCO19 also have the same source. OSCO6 and OSCO15 are genetically related. OSCO21, OSCO23 and OSCO24 have same source. While, OSCO29, OSCO13 and OSCO10 displayed different shapes hence, have different sources (Fig. 5).

### Ion Balance/Collins Diagram

Ion balance diagram [8] is a stacked bar graph with left stack representing Cations, the right parallel stack Anions. It displays concentrations (not ratios) for individual samples but as it is a cumulative chart, the values are not readily apparent. The total height of the bar approximately reflects TDS. Collins/Ion balance diagram is used to check error in water analysis and hence, help to determine the correctness of water analysis.

$\% \text{ balance error} = \frac{\sum \text{cations} - \sum \text{anions}}{\sum \text{cations} + \sum \text{anions}} \times 100$  - conc. in meq/l. Error should be less than 10% for surface and ground water, if it is greater, the analysis is said to not have passed the validation check. From the diagram, if the bars of anions and cations are equal, it means that the cations and anions are balanced. From the ion balance diagrams below, both bars of the following water samples OSCO1, OSCO 13 and OSCO

29 are almost equal in height. This implies that errors made during the analysis of these water samples are almost negligible.

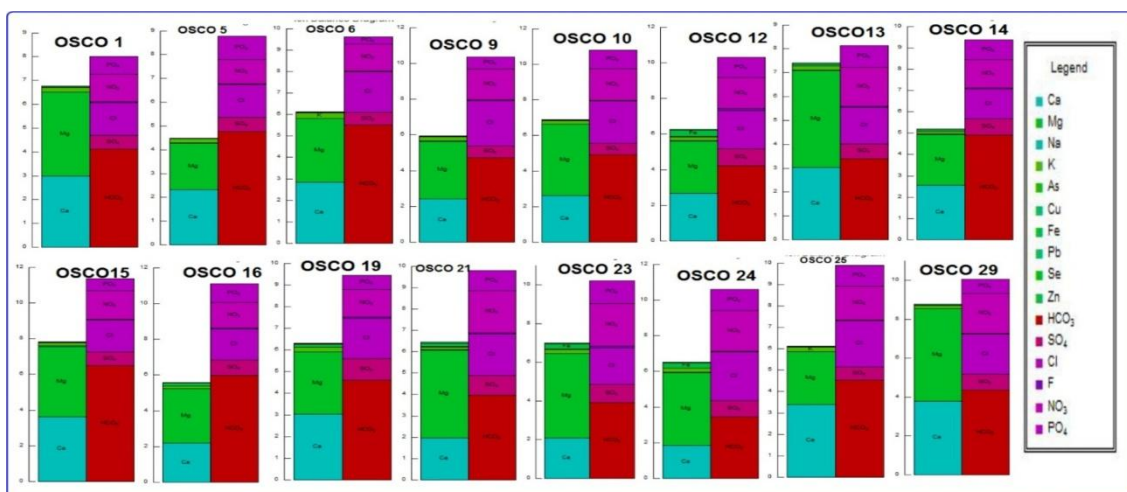


Fig. 6: Ion Balance diagram for Mayes Water Samples.

OSCO6, OSCO9, OSCO10, OSCO12, OSCO14, OSCO15, OSCO16, OSCO19, OSCO21, OSCO25, OSCO23, OSCO24 and OSCO5 have unequal stacks with OSCO13, OSCO1 and OSCO29 displaying high cations stacks while the rest displayed high anions stacks (Fig.6). This suggests that the cations and anions are not balanced in the above listed water samples.

#### IV. CONCLUSION

The fluid analysis and the piper diagram plotted on the sixteen water samples showed predominantly Mg-HCO<sub>3</sub> type and a few Ca-HCO<sub>3</sub> type waters, while the Stiff diagrams showed the water samples that displayed the same shape and thus, suggests that they are genetically related (have the same source) while those that displayed different shapes have different sources.

The water chemistry of Mayes waterfall and its tributaries which showed a few Mg/Ca-HCO<sub>3</sub> type water which is controlled by the environment through which the water passed and mostly affected by the chemical weathering (spheroidal weathering) of rocks (biotite granite and migmatite gneiss). The changes in the TDS and conductivity values also suggested rock-water interaction as a factor that contributes to the types of water revealed by the study.

Water chemistry analysis is used extensively to determine the possible uses water may have or to study the interaction it has with its environment. The gemstone (topaz), found within the river channels could be responsible for the high concentration of fluoride in some of the samples analysed. The ion balance diagrams are unequal in height and as such reflects a general imbalance in the Anions and Cations in the samples though the error in some few samples are negligible.

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