Assessment of Seasonal Variation in Surface Water Quality of the Mooi and Vaal Rivers Network, South Africa

Alusani Manyatshe, Elvis Fosso-Kankeu, Divan van der Berg, Nico Lemmer, Frans Waanders, Tutu Hlanganani

Abstract**—**Seasonal assessment of surface water is an important aspect as it can provide a better understanding about the pollution in water, resulted from the anthropogenic sources. In this study, the surface water samples were collected in two campaigns (wet and dry seasons), which correspond to the wet and dry seasons, respectively. 44 surface water samples collected the vicinity of Potchefstroom, South Africa and the physico-chemical characteristics determined by specific analyses. The following parameters were measured *in situ*: pH, dissolved oxygen (DO), oxido reduction potential (ORP) and electrical conductivity (EC). Whereas, the total alkalinity, major anions (sulphate, nitrate, cyanide, and chloride) and trace metals (Ca, Mg, As, Cd, Fe, Pb and U) were analysed in the laboratory. The main objective of this study was to identify the seasonal impact on the pollution of surface water. The results showed that elevated concentration of parameters were mainly predominantly in wet season, which may be due to the washout of contaminants from polluting sources into surface water during summer heavy rainfall. Elevated concentration of trace metals were observed to be above the recommended limit of water guideline, making the water unfit for human consumption.

Index Terms**—** Physical-chemical parameters, wet and dry seasons, major anions, trace metals.

I. INTRODUCTION

The pollution of toxic metals originated from anthropogenic sources such as mining activities, industrial wastewater, agricultural runoff, water treatment plant and commercial sewage are of great environmental concern locally and worldwide [1]. Effluence from these sources, especially mining activities are responsible for the elevated concentration of heavy metals in surface water .i.e. Rivers [2, 3]. Heavy metals enter into the river water from mining areas through various ways such as mine discharge, run-off, chemical weathering of rocks and soils, wet and dry fallout of atmospheric particulate matter [4, 5]. Flow in rivers is a function of many factors including precipitation, surface runoff, interflow, groundwater, and pumped inflow and outflow. Seasonal variations of these factors have a strong effect on flow rates and hence the concentration of pollutants in the river water [6]. Due to spatial and temporal variations in water chemistry, a surveys and monitoring program is necessary as it can provide a better knowledge about the river hydrochemistry and pollution [7], and this can also ensure effective and efficient water management. Metal contaminants are crucial due to their potential toxicity, bio-accumalative, long persistence in the environment and organism, especially human beings [8, 9]. When heavy metals enter into the aquatic environment, they are transported as dissolved species in water or as integral part of suspended sediments [2]. Some of the heavy metals like Cu, Fe, Mn, Ni and Zn are essential as micronutrients for life processes in plants and microorganisms, however; metals like Cd, Cr and Pb can be toxic even at very low concentration in water [10]. For example, the toxicity of Cd can cause kidney damage and pains bones in man [11], Pb causes renal failure and liver damage, and Cr cause nephritis, anuria and extensive lesions in the kidney [12]. In the North West Province, South Africa, gold mining activities situated adjacent to the catchment areas of Wonderfonteinspruit are responsible for the degradation of surface water quality. Large amount of tailings dumps have been produced for more than a century by these gold mines. These dumps contain elevated concentrations of uranium and other toxic heavy metals which contaminate the receiving water [13]. Several studies have been conducted in the surface water of study area due to the pollution from these respective gold mines [14, 15, 16, 17]. In this study, surface water samples were collected along the Mooi and Vaal Rivers network to assess the temporal variation between the wet and dry season and evaluate the status of the river water quality with respect to drinking and agricultural irrigation purposes. The main objective was to identify the seasonal impact on the pollution of surface water.

II. MATERIALS AND METHOD

2.1 Sampling

The Mooi River originated at the Bovenste Oog in the Mathopested area (near Ventersdorp) and its main tributary is the Wonderfonteinspruit [18]. The catchment of Wonderfonteinspruit receive pollution from the gold mining activities situated adjacent to the area, this pollution contain elevated concentrations of uranium and other heavy metals [19]. Mooi River is the tributary of the Boskop Dam,

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Potchefstroom Dam and the Vaal River downstream of the city of Potchefstroom [20]. People living in Potchefstroom and the neighbouring countries depend on the surface water for drinking (mostly after treatment) and irrigation purposes. The sampling sites where chosen due to the risk of pollution from gold mines and other alternative sources i.e. run off from agricultural land.

Forty-four surface water samples were collected along the Mooi and Vaal Rivers network in the vicinity of Potchefstroom in two campaigns (wet and dry seasons); which correspond to the wet and dry season respectively. The water samples were collected and kept in a clean 500 mL plastic bottle according to accepted method [21]. Before use, the bottles were washed with the distilled water and then rinsed with the water of sampling site. At the dams, water samples were collected in different depths varied from 1 to 4 m using a depth-sampler. The water bottles were labelled according to the corresponding sampling site and date of the collection. Coordinates of each sampling site were measured using a GPRS device. The following physico-chemical parameters were measured *in situ* using a pH combined electrode with integrated temperature probe: Temperature (°C), pH, Electrical conductivity EC (mS/cm), Dissolved oxygen (mg/L), and Redox potential Eh (mV). The probes were calibrated before use in the field. The samples were then immediately transported to the laboratory in cooler boxes containing ice packs and stored at 4°C prior to analysis.

2.2 Data analysis

The alkalinity (as HCO_3^- and CO_3^-) was measured through titration method with 0.1 M H_2SO_4 acid, whereas the concentration of chloride was titrated with silver nitrate and potassium dichromate solution. The concentrations of sulphate (SO_4^{2-}), nitrate (NO_3^-) and cyanide (CN^-) were measured using a COD and Multiparameter Bench Photometer HI 83099 (Hanna Instruments Inc., USA). The total content of trace elements was analyzed using an inductively coupled plasma optical emission spectrometer (ICP-OES) (Agilent Technologies, USA).

2.3 Data treatment

The statistical analysis of the data was conducted using the Microsoft Excel 2010. One-way ANOVA was performed to determine the significant difference between the surface water samples collected during wet and dry seasons, respectively. A level of $p < 0.05$ was used in all the comparisons. The mean, standard deviation, minimum and maximum of metal and anion concentrations were calculated and considered to determine the variance between the two seasons.

TABLE I
MAXIMUM PERMITTED CONCENTRATION IN DRINKING WATER AND P. VALUES OF STATISTICAL ANALYSIS

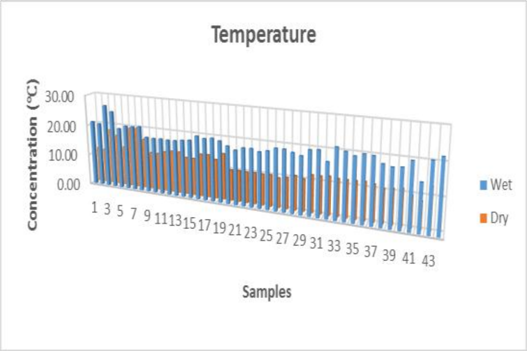
Parameters	**Unit**	**Drinking water (2005)**	**P.Values**
		Max	
pH	-	9.50	> 0.05
EC	mS/cm	3.70	> 0.05
Eh	mV	-	> 0.05
DO	mg/L	-	< 0.05
Alkalinity	$CaCO_3$	-	< 0.01
SO_4^{2-}	mg/L	600.00	> 0.05
NO_3^-	mg/L	20.00	< 0.05
Cl^-	mg/L	600.00	> 0.05
CN^-	mg/L	0.07	> 0.05
Ca	mg/L	300.00	< 0.01
Mg	mg/L	100.00	< 0.01
As	mg/L	0.05	> 0.05
Fe	mg/L	2.00	< 0.05
U	mg/L	-	> 0.05
Pb	mg/L	0.05	< 0.01

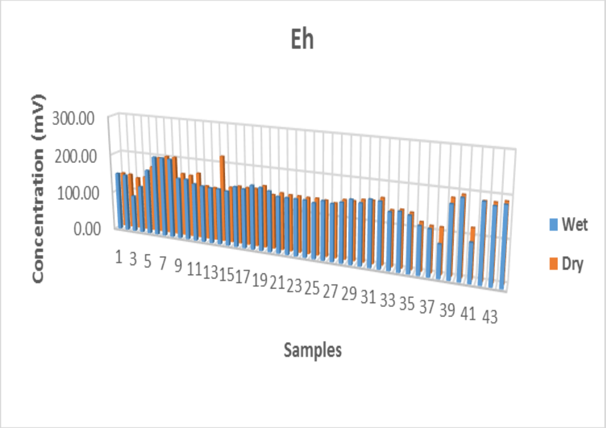
III. RESULTS AND DISCUSSION

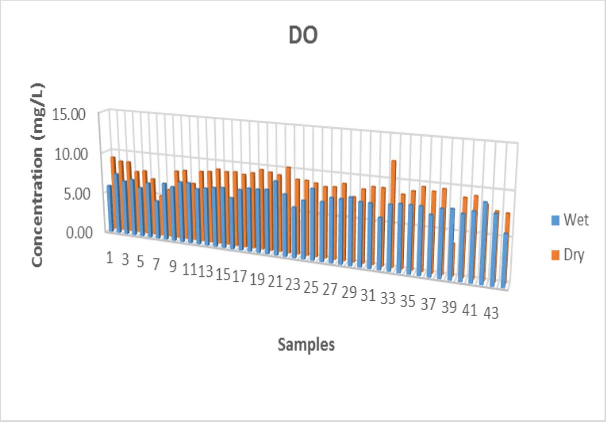
3.1. Physical parameters

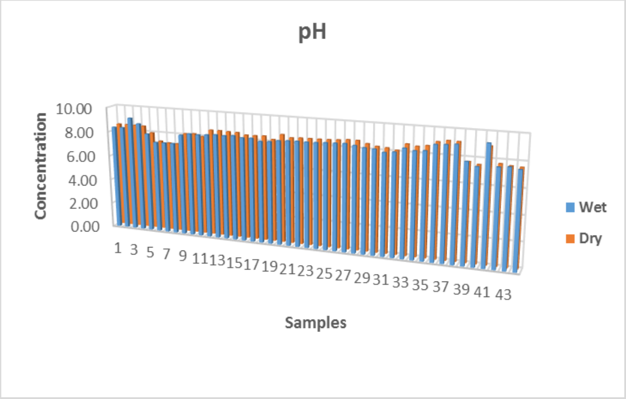
The concentration of pH varied from 7.39 to 9.34 and 7.24 to 9.14 in wet and dry season, respectively (Fig. 1). Mean concentrations was 8.29 in wet season and 8.32 in dry season. It is apparent from Figure 1 that all the values measured in both seasons were alkaline and this can be attributed to the dolomite rocks which have covered large part of the study area or the use cyanide during the extraction of gold. Hence it was observed that the concentrations of cyanide were high in both campaigns.

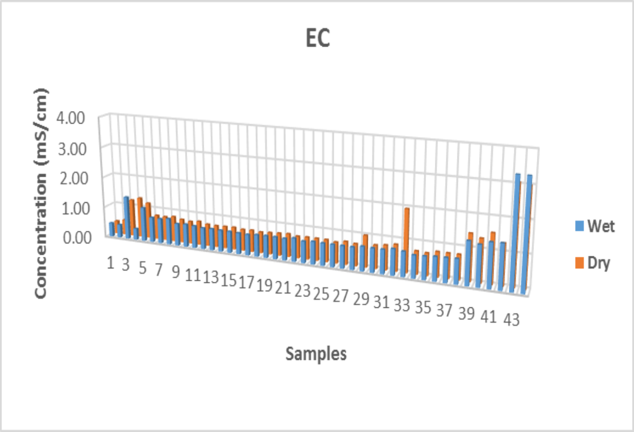
The statistical analysis shows that there was no significant different ($P > 0.05$) between the wet and dry seasons. All the pH values collected at different seasons shows to be within the permissible limit of SANS (South African National Standard) drinking water guideline. The values of conductivity shows almost similar trend in both seasons, with the mean of 0.92 and 0.97 mS/cm observed in wet and dry season, respectively (Fig. 1). The highest value (3.36 mS/cm) of conductivity was measured in wet season at sampling points 43 and 44. This elevated value of conductivity can be due to the presence of ions, since these points are situated within the water retain dam. However, the variation was not significantly different ($P > 0.05$) between the two seasons and all the values measured in both seasons were observed to be within the SANS drinking water guideline. The values of dissolved oxygen varied between 4.70 and 9.00, 3.70 and 12.10 mg/L in wet and dry season, respectively (Fig. 1). High values recorded in dry season can be correlated to the low values of temperature in winter. The mean values were 7.27 and 8.51 in wet and dry season, respectively. The variation shows significant different ($P < 0.05$) between the two seasons.











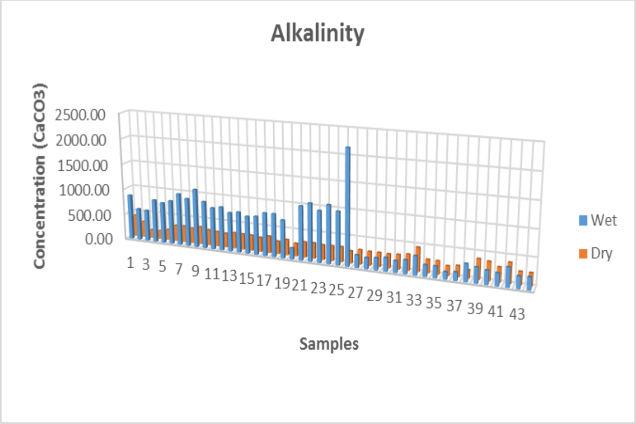


Fig 1. Seasonal variation in the concentration of field parameters and alkalinity

High values of temperature measured in summer could be responsible for the low values of DO, as reported by Gao and Song [22], water with low values of temperature is capable of holding more oxygen. The values of Eh ranged from 94.00 to 204.57 and 112.00 to 219.00 mV in wet and dry season, respectively (Fig. 1). The mean values were 151.23 and 153.52 mV in wet and dry season, respectively. Low values of Eh measured in both seasons can be attributed to the pH values which was alkaline. The variation shows no significant different ($P > 0.05$) between the two seasons. The values of total alkalinity ranged from 140.00 to 1136.00 mg/L in wet season and 160.00 to 460.00 mg/L in dry season (Fig 1). Mean values of 582.28 and 281.21 mg/L were observed in wet and dry season, respectively. The variation was highly significantly different ($P < 0.01$) between the two seasons. There is no specific standard for total alkalinity set by the SANS drinking water guideline. High concentration of alkalinity measured in wet season can be attributed to the dolomite rock which has covered large part of the study area; especially upstream [18]. Hence, elevated values of calcium and magnesium were mostly observed in water samples collected upstream of study area.

3.2. *Major anions*

The concentration of major anions measured in two seasons is presented in Fig 2, 3 and 4. In general, all the anions excluding the nitrate showed no significant variations between the two seasons. However, there was a variation of concentrations within the sampling points in different seasons. For example, the concentration of sulphate varied from 0.00 to 1360.00 and 0.00 to 1500.00 mg/L in wet and dry season, respectively. The mean concentration was 211.51 mg/L in wet season and 213.14 mg/L in dry season. Low values recorded in wet season could be attributed to the dilution effect from heavy rainfalls in summer season. The concentrations of cyanide ranged between 0.00 and 78.00 mg/L in wet season and 0.00 to 73.00 mg/L in dry season. The mean concentrations were 5.37 and 4.56 mg/L in wet and dry season, respectively. There was no significant variation ($P > 0.05$) between the wet and dry season. The concentration of chloride varied from 10.00 to 183.33 mg/L and 3.33 to 183.33 mg/L in wet and dry season, respectively. Mean values were 58.91 and 63.57 mg/L in wet and dry season, respectively. High values of chloride were observed in sampling points close to the anthropogenic sources, especially next to tailing dumps. However, it was observed that the concentrations were within the recommended values of drinking water guideline (Table 1). The concentrations of nitrate ranged from 0.00 to 28.00 mg/L in wet season and 0.00 to 11.20 mg/L in dry season. Highest concentration measured in wet season can be attributed to the use of nitrogenous fertilisers in agricultural areas. For example, the concentration of nitrate were 28.00 mg/L at sampling point 35 during wet season and it decreases to 0.40 mg/L in dry season. The mean values of nitrate were 4.43 mg/L in wet season and 1.58 mg/L in dry season. The variation were significantly different ($P < 0.05$) between the two seasons, this was expected since the run off from agricultural land is the main source of nitrate in water.

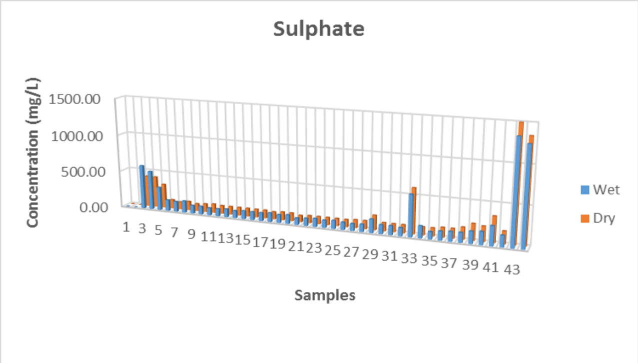


Fig. 2 Seasonal Variation in concentration of sulphate

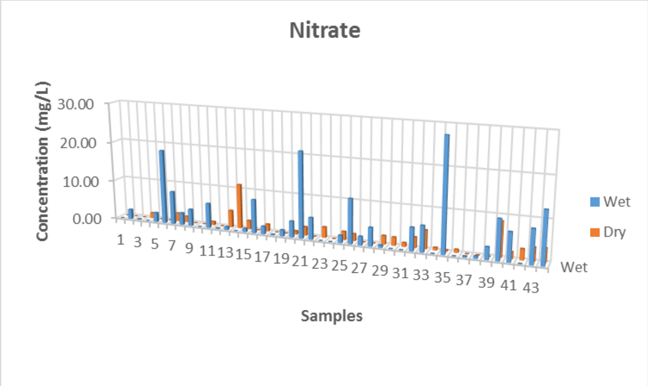


Fig.3 Seasonal Variation in concentration of Nitrate

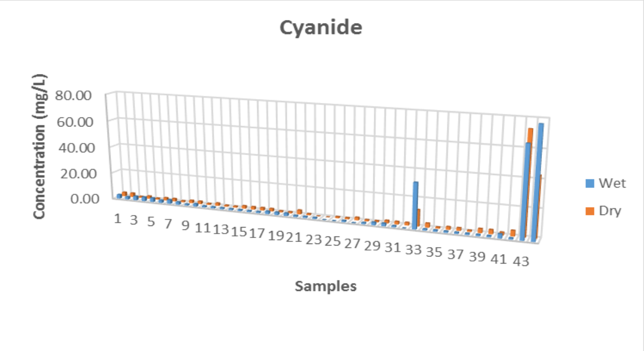
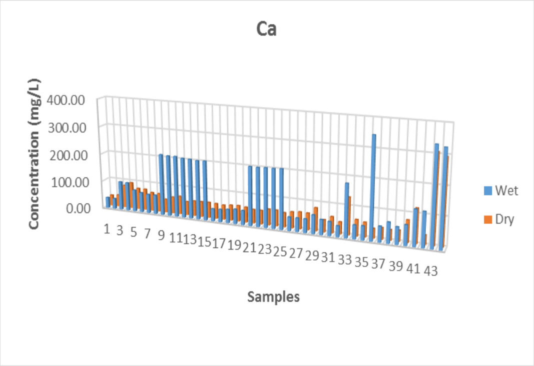
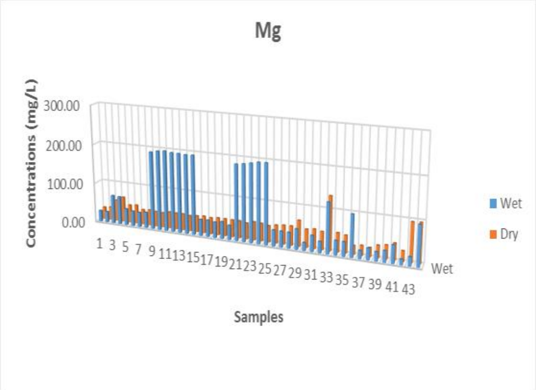


Fig. 4 Seasonal Variation in Concentration of Cyanine

3.3. *Heavy metals*

The results of measured heavy metals in surface water are shown in Fig. 5. The concentration of Ca varied from 37.61 to 352.00 mg/L and 34.27 to 308.82 mg/L in wet and dry season, respectively; with mean of 125.57 mg/l in wet season and 54.83 mg/L in dry season. There was a major significant variation of Ca concentration ($P < 0.01$) between the wet and dry season. It is apparent from figure 5 that the values of Ca measured in wet season highly exceeded the recommended limit of SANS drinking water guideline, however; the concentration decreased in water samples collected in dry season. The mean concentrations of Mg were 85.50 mg/L in wet season and 45.99 mg/L in dry season. There was a significant variation in the concentration of Mg ($P < 0.01$) between the wet and dry season.





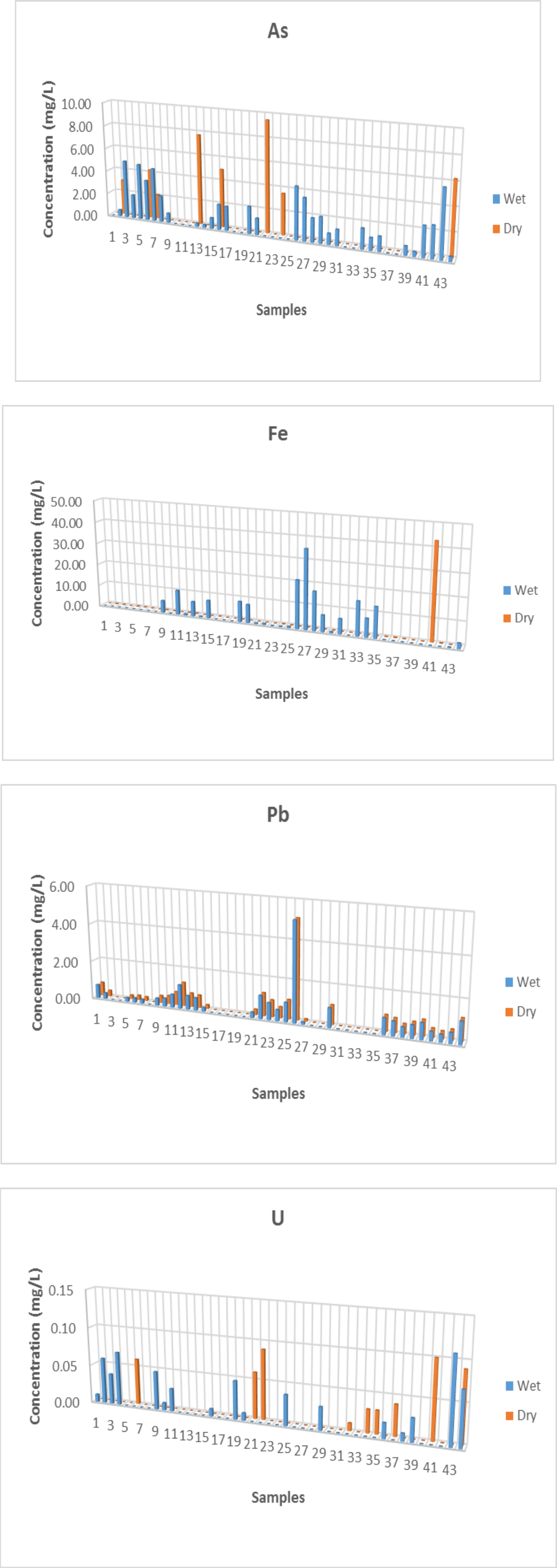


Fig. 5 Seasonal Variation in concentration of heavy metals

Elevated concentration of Ca and Mg can be attributed to the dolomite rocks which have covered large part of the study area [18]. The obtained mean concentration of arsenic (As) was 1.48 and 0.94 mg/L in wet and dry season, respectively. The mean concentrations of arsenic were observed to be above the recommended value of drinking water guideline (Table 1). The results of one-way ANOVA show that there was a significant difference between the concentrations of arsenic measured in wet and dry season, which reflects changes in water geochemistry. The concentration of Fe ranged from 0.00 to 36.00 mg/L and 0.00 to 42.87 mg/L in wet and dry season, respectively. The mean concentrations of Fe were 4.22 mg/L in wet season and 1.04 mg/L in dry season. There was a significant variation ($P < 0.05$) of Fe concentration between the wet and dry season. However, it can be seen from the figure that the concentrations of Fe were above the recommended limit in both seasons. The concentration of U varied from 0.00 to 0.10 mg/L in wet season and 0.00 to 0.09 mg/L in dry season. The mean concentrations of U were 0.01 mg/L in wet season and 0.01 mg/L in dry season. There was no specific standard for uranium set by SANS guideline for drinking water. However, according to WHO [23], the maximum concentration of uranium in drinking water is 0.03 mg/L. It was observed that some of the sampling points have exceeded the required limit, especially those situated or close to mining activities. The analysis shows that there was no significant variation between the concentration of U measured in wet and dry season. The mean concentrations of Pb were 0.51 mg/L and 0.10 mg/L in wet and dry season, respectively. The concentration of Pb showed highly significant variation ($P < 0.01$) between the water samples measured in wet and dry season. Non-significant variation of U observed between the wet and dry seasons indicated that the polluting sources contributed pollution in both campaigns.

IV. CONCLUSION

The statistical analysis shows that there was a significant difference between the level of certain parameters measured in surface water samples from the wet and dry season, respectively. A decreasing trend was observed from wet to dry season. Elevated concentration measured in wet season can be attributed to the large flow of effluents from anthropogenic sources, especially gold mining activities. However, the parameters which did exhibit significant change are also those less susceptible to variation in terms of their spatial distribution or some of the parameters were slightly conservative. The significant difference observed in surface water shows that there was a change in water geochemistry.

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