SPECTACULAR JOURNALS
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Research Journal of Environmental Science and Toxicology Vol. 3(1) pp. 001-017, July, 2024
Available online http://spectacularjournals.org/rjest

Original Research Article

Determination of Heavy Metal Concentrations in Osun River using Physicochemical Parameters and Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) Technique

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Abstract

The concentrations of some heavy metals in Osun river at three different locations in Osun State, Nigeria were determined using physicochemical parameters and inductively coupled plasma optical emission spectroscopy techniques (ICP-OES). Three points (a, b, c) were located along the river and samples were collected in triplicates, before the rainy season (1), during the rainy season (2), and after the rainy season (3). The results revealed that the physicochemical parameters were within permissible limits except BOD and conductivity which were higher in some locations and seasons. Varying levels of essential nutrients such as Na, Mg, Ca and K were detected with the highest concentrations found to be Na followed by Ca and Mg. Toxic elements such as Cd, Fe, Cr, Mn, Ni, Al, and Pb were above the permissible limits across all points and seasons with Cd being the highest. This shows that the river is polluted and the potential sources of the metals may be due to sewage discharge, human waste discharge, landfill run off and precipitation-induced leaching. Citizens and tourists should be educated on the dangers of drinking the river water due to the associated health risks of the present heavy metals such as cardiovascular diseases, carcinogenic effects, and neurological disorders and further studies should be carried out on the river from time to time to monitor the pollution.

Key words: Osun river, Physicochemical, Inductively coupled plasma optical emission spectroscopy techniques (ICP-OES).

INTRODUCTION

Life depends on water, and surface water from rivers and lakes is the most affordable source of water for daily needs like drinking, washing, and doing laundry as well as for recreational, farming, and religious purposes. The amount of waste that rivers get makes it extremely difficult to meet the water quality requirements for various uses (Olajire and Imepekperia, 2001; Elleta, 2012). Eletta (2012) states that uncontrolled management of wastes from industries, dumpsites, and agricultural activities, as well as human waste from some individuals, wash into the river. The waste materials present in rivers are harmful to aquatic life and humans alike, as they contain heavy metals, polycyclic aromatic hydrocarbons (PAHs), volatile organic compounds (VOCs), and many other contaminants. Due to their extensive residential length in the environment, heavy metals are not biodegradable. Because of their accumulative nature and toxicity, heavy metals have emerged as a serious environmental problem (Islam *et al*., 2015, Martin *etal*., 2015). Over a few decades, Nigeria has faced environmental issues posed by waste discharges and anthropogenic activity on riverine ecosystems. Rural areas and the lack of proper infrastructure are contributing factors in this. River water levels of heavy metals can easily rise due to anthropogenic activities (Sanchez *et al*., 2007). Many rivers contain leachates of heavy metal-containing fertilizers and agrochemicals from farm settlements. Heavy metals may experience frequent changes during their passage through the riverine system as a result of adsorption, precipitation, and dissolution processes (Abdel Ghani *et al*., 2007). Fish tissues can accumulate heavy metals, which are the most significant types of aquatic contaminants (Islam *et al*., 2015; Martin *et al*., 2015). The gradual and permanent build-up of metals in aquatic fauna's organs and host environment is a threat to their survival.

Heavy metal exposure has been connected to kidney damage, several malignancies, developmental retardation, and even death. Therefore, measuring the amounts of heavy metals in the riverine ecology is an important scientific topic. In the human context, rivers face a variety of hazards all the time (Alloway and Ayres, 1997). With a length of 267 kilometers, the Osun River is among Nigeria's longest rivers. The river in Osogbo, the capital city of Osun State, has grown to be a popular tourist destination worldwide. The Osun River's catchment region is impacted by both natural processes including soil erosion, rock weathering, leaching, and human activities like improper waste discharge, runoff from municipal and/or household sewage, agricultural practices, and abattoir wastes.

It is not impossible that part of biological and chemical wastes from institutions, chemical laboratories and industries would end up in Osun River due to its proximity to major Institutions like Osun State University, Fountain University and some private hospitals. Several villagers, farmers and individuals make use of OsunRiver as one of the main sources of water for domestic,agricultural and irrigation purposes. Among these are dwellers of Coker Village, Swanlux farmers, local fishermen, and others.

It is necessary to determine the level of heavy metal concentrations for the aforementioned relevant activities because of the river's importance as a national monument and an international cultural heritage site, as well as its use for recreational and religious purposes using ICP-OES instead of Atomic Absorption Spectrophotometer (AAS).

MATERIALS AND METHODS

Study Area and Location

This study was carried out in Osun river, located at Osogbo, Osun state. Three sample sites were located for the collection of the water samples and designated point A, B and C. Point A was located at the Osun-Osogbo sacred grove main shrine as shown in Figure1. It is the main point where traditional worship activities take place with coordinates 7°45'21.9"N 4°33'04.6"E.

Point B was located about 1.5 kilometers downstream of point A within the grove and Muslim grammar school is located along the way. Several building constructions occur around point B with few residential homes. Ritual bathes and defecation also occur at this point and it is close to the highway leading to Fountain University. Point B has a coordinate of 7°45'02.0"N 4°32'58.9°E and is shown in Figure 1.

Point C is located downstream of Point B around Aregbesola area along Gbongan road, Osogbo. Point C has a bridge above it and is located in the middle of the city where several activities takes place. Solid wastes, faeces is discharged in and around the river and a welding shop is situated very close to the river at the downside of the bridge. It has a coordinate of 7°46'06.4"N 4°32'22.9°E and is shown in Figure 1.

Sampling and analyses

Water samples were collected between May, 2023 and Febuary, 2024 at 5m away from the shrine. Water samples from the three different points at the Osun river were collected thrice, before the rainy season (designated 1), during the rainy season (designated 2), and after the rainy season (designated 3). The water samples were put into pre-cleaned sterile bottles washed with 10% hydrochloric acid, rinsed with distilled water and tightly sealed until the time of collection. At the point of collection, the bottles were first rinsed with the water samples thoroughly and then filled. Temperature and pH of the water samples were recorded at the point of collection. The samples were then analyzed for the physicochemical parameters and heavy metal concentration using ICP-OES technique.

Statistical Analysis

Statistical analysis was carried out using Microsoft excel to determine the mean and standard deviation. Multivariate anova (MANOVA) test was carried out to determine thedifferences usingStatistical Package for Social Sciences (SPSS).

RESULTS AND DISCUSSION

Physicochemical Parameters of Osun River

Physicochemical parameters of Osun river based on the seasons of collection at the three points are shown in Table 1, 2 and 3 with their mean and standard deviation.

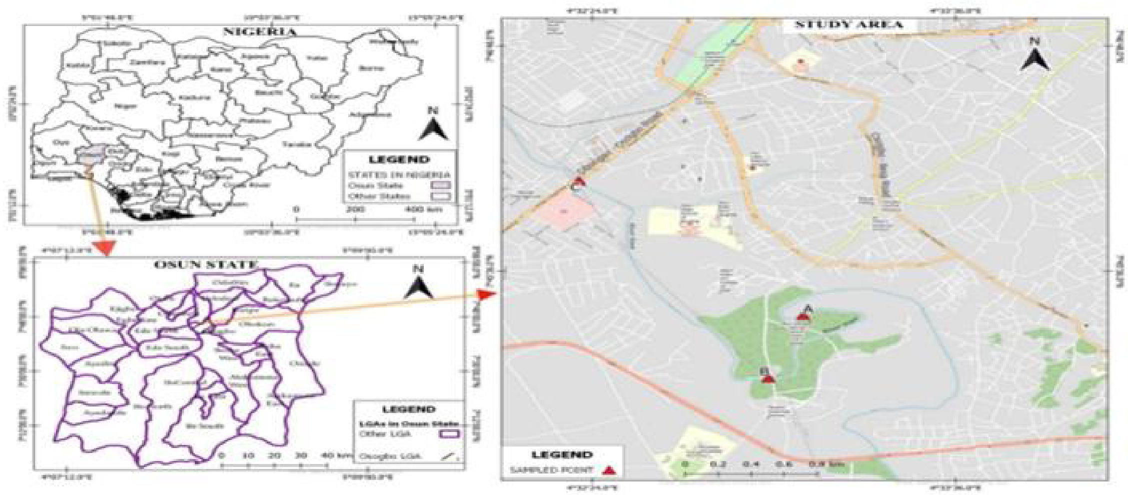

Figure 1. Map Showing Study Area and three Points of Sample Collection

Table 1. Physicochemical parameters across seasons in location A

	A2	A1	A3	WHO (2017/2010)
DO (mg/L)	$7.96^{a} \pm 0.08$	$12.85^{b} \pm 0.03$	$14.37^{c} \pm 0.02$	≥ 5
Hardness(mg/L)	$114.48^{a} \pm 0.07$	$115.72^{b} \pm 0.18$	$117.45^{c} \pm 0.16$	500
Alkalinity (mg/L)	$60.24^{a} \pm 0.06$	$64.49^{b} \pm 0.03$	$75.64^{c} \pm 0.03$	200
Turbidity(NTU)	$2.79^{a} \pm 0.004$	$2.86^{b} \pm 0.02$	$2.91^{c} \pm 0.01$	5
BOD (mg/l)	$5.74^{a} \pm 0.09$	$6.27^{b} \pm 0.04$	$6.53^{c} \pm 0.001$	5
TDS (PPM)	$83.27^{a} \pm 0.29$	$249^{b} \pm 0.82$	$83.27^{c} \pm 0.21$	1000
pH	$3.000^{a} \pm 0.270$	$4.000^{b} \pm 0.071$	$7.000^{c} \pm 0.071$	6.5-8.5
Temperature^{0}C	$24^{a} \pm 0$	$21.5^{a} \pm 0$	$26^{a} \pm 0$	25-30
Conductivity (µs/cm)	$205.90^{a} \pm 0.08$	$527.67^{b} \pm 0.47$	$166.75^{c} \pm 0.09$	600
NaCl	$0.40^{a} \pm 0$	$1.00^{b} \pm 0$	$0.30^{c} \pm 0$	250

The mean with different superscript shows a significant difference for each physicochemical across the three seasons in location A

Table 2. Physicochemical parameters across seasons in location B

	B2	B1	B3	WHO (2017/2010)
DO (mg/L)	$9.52^{a} \pm 0.004$	$11.41^{b} \pm 0.01$	$12.84^{c} \pm 0.01$	≥ 5
Hardness(mg/L)	$105.01^{a} \pm 0.01$	$96.38^{b} \pm 0.1$	$89.66^{c} \pm 0.03$	500
Alkalinity (mg/L)	$58.62^{a} \pm 0.01$	$73.68^{b} \pm 0.04$	$95.37^{c} \pm 0.044$	200
Turbidity(NTU)	$3.19^{a} \pm 0.01$	$2.85^{b} \pm 0.02$	$2.81^{b} \pm 0.01$	5
BOD (mg/l)	$4.64^{a} \pm 0.06$	$5.60^{b} \pm 0.03$	$5.74^{b} \pm 0.09$	5
TDS (PPM)	$72.09^{a} \pm 0.01$	$388.33^{b} \pm 0.47$	$82.51^{c} \pm 0.5$	1000
pH	$6.200^{a} \pm 0.071$	$6.900^{b} \pm 0.071$	$6.900^{b} \pm 0.071$	6.5-8.5
Temperature^{0}C	$27.67^{a} \pm 0$	$27.13^{a} \pm 0$	$28.33^{a} \pm 0$	25-30
Conductivity (µs/cm)	$145.20^{a} \pm 0.16$	$175.00^{b} \pm 0$	$166.76^{c} \pm 0.42$	600
NaCl	$0.267^{a} \pm 0$	$0.73^{b} \pm 0.05$	$0.30^{a} \pm 0$	250

The mean with different superscript shows a significant difference for each physicochemical across the three seasons in location B.

Table 3. Physicochemical parameters across seasons in location C

	C2	C1	C3	WHO (2017/2010)
DO (mg/L)	6.31^{a}±0.004	12.65^{b} ±0.03	14.36^{c}±0.02	≥ 5
Hardness(mg/L)	90.15^{a}±0.01	86.10^{b} ±0.09	84.62^{c}±0.004	500
Alkalinity (mg/L)	44.55^{a}±0.14	47.98^{b} ±0.01	60.83^{c}±0.01	200
Turbidity(NTU)	2.69^{a}±0.01	2.53^{b} ±0.005	2.43^{c}±0.01	5
BOD (mg/l)	4.02^{a}±0.01	3.86^{b} ±0.005	6.76^{c}±0.03	5
TDS (PPM)	390.67^{a}±0.47	88.00^{b} ±0.08	87.55^{b} ±0.09	1000
Ph	6.200^{a}±0.071	6.900^{b} ±0.071	6.900^{b} ±0.071	6.5-8.5
Temperature^{0}C	23.5^{a}±0	21.2^{a}±0	24^{a}±0	25-30
Conductivity (µs/cm)	829.33^{a}±0.47	176.24^{b} ±0.33	174.56^{c}±0.03	600
NaCl	1.57^{a}±0.05	0.30^{b} ±0	0.30^{b}±0	250

The mean with different superscript shows a significant difference for each physicochemical across the three seasons in location C.

Temperature

Water temperature plays an important role in influencing the quality of rivers, it affects the rate of chemical reaction and biological activities that occur in it and can be used as a first parameter in predicting the effect of anthropogenic activities on the aquatic ecosystem (Annalakshmi and Amsath, 2012). It was observed that the water samples had temperature range within the permissible limits in all the points and time of collection with the highest value of temperature of 26±0^{0}C in A3 while 21.5±0^{0}C, 24±0^{0}C, 21.4±0^{0}C, 25±0^{0}C, 23±0^{0}C, 21.2±0^{0}C, 23.5±0^{0}C, 24±0^{0}C for A1, A2, B1, B2, B3, C1, C2, C3 respectively. There is no significant difference between temperature across all seasons in each locations and this implies that the observed differences in other measured parameters may not have been significantly influenced by temperature.

pH

The pH is the scale of intensity of acidity and alkalinity of water and measures the concentration of hydrogen ions. Alow pH would cause more dissolution of metals in the river and aquatic organisms are affected by pH due to the dependence of their metabolic activities on it. The variations of the values obtained for pH of the water samples were below neutral indicating acidity in A1, A2, C1 and C2 with values of 3.1±1.270,4.1±0.071, 3.1±0.071 and 3.2±0.071 respectively. 6.9±0.071, 7.0±0.071, 6.2±0.071, 6.9±0.071 and 6.9±0.071 were observed for A3, B1,B2,B3 and C3 respectively. A3, B1, B2, B3, C1, C2 and C3 are within the range of what was measured in Osun river (Anifowose and Oyebode, 2019). Table 1 shows that there is a significant difference between pH across

Dissolved Oxygen (DO)

DO is very crucial for the survival of aquatic organisms and it is a fundamental factor for evaluating the quality of water (Annalakshmi and Amsath, 2012). Table 1, 2 and 3 shows that the samples exhibited significant variations in DO between seasons. This pattern most likely represents how biological activity and seasons affect the saturation levels of oxygen in water bodies although increased precipitation during the rainy season can lead to changes in water circulation patterns and enhance the breakdown of organic matter in aquatic environments which might cause oxygen deprivation. High DO levels(5.0–6.0 mg/L) are needed to maintain a healthy aquatic ecosystem (Anifowose and Oyebode, 2019) and DO observed in this study had higher DO levels and also above the minimum permissible limit with the lowest to be6.31±0.004 in C2 therefore the river is able to sustain aquatic life. Table 1, 2 and 3 shows that there is a significant difference between the dissolved oxygen across the three seasons at point A, B and C respectively.

Biochemical Oxygen Demand (BOD)

Biochemical oxygen demand, a measure of organic pollution, rises from the dry season prior to the rainy season. Enhanced organic matter decomposition and nutrient cycling in water bodies during times of decreased precipitation are reflected in the increase in biochemical oxygen demand.

Presence of BOD observed in all the samples were higher than the WHO limit with exception of C1, C2 and B2 having 3.86±0.005mg/l, 4.02±0.01mg/l and 4.64±0.06mg/l respectively. 6.27±0.04mg/l, 5.74± 0.09mg/l, 6.53±0.001mg/l, 5.6±0.03mg/l, 5.75±0.09mg/l and 6.76±0.03mg/l were observed in A1, A2, A3, B1, B3 and C3 respectively. Table 1 and 3 shows a significant difference between BOD across seasons in point A and C respectively and Table 2shows no significant difference in BOD between season 1 and 3 but difference in season 2 at point B.

Alkalinity

Alkalinity in natural water is as a result of free hydroxyl ion and hydrolysis of salts formed by weak acid and strong base. High alkalinity which is above 500mg/l is usually associated with high pH, hardness and total dissolved solids in water and it is claimed that hardness is not considered a health concerns at levels found in drinking water (Titilawo *et al*., 2019). The variations observed in alkalinity across the seasons in all locations were lower than the limit with the highest in B3 with 95.37±0.044 and lowest in C2 with 44.55±0.14. Table 1, 2 and 3 shows that there is a significant difference between alkalinity across all the seasons at point A, B and C respectively.

Total Hardness

Greater mean values were recorded for total hardness as well as for alkalinityafter the rainy season as opposed to before rainy and rainy seasons. These metrics, which have an impact on ecosystem health and water quality, are frequently modified by geological variables, increased mineral leaching from soils and decreased dilution may be the causes of higher readings after the rainy seasons which have an impact on ecosystem health and water quality, are frequently modified by geological variables, increased mineral leaching from soils and decreased dilution may be the causes of higher readings after the rainy seasons. The variations of total hardness observed in this study across seasons in all locations were lower than the limit with the highest value in A2 with 117.45±0.07 and lowest in C3 with 84.62±0.004.Table 1, 2 and 3 shows that there is a significant difference between total hardness across all the seasons at point A, B and C respectively.

Turbidity

Turbidity is an indication of suspended materials in river water of which high levels of it indicate the possible presence of clay, silts, microorganisms and other suspended solids in water. The turbidity observed across all seasons did not exceed the permissiblelimitand is within the range discovered by Titilawo *et al*., (2019) with the highest in B2 with 3.19±0.01 and lowest in C3 with 2.43±0.01. Table 2 and 4 show a significant difference across the seasons at point A and C respectively and Table 3 shows no significant difference between season 1 and 3 and significant difference between season 2 in point B.

Total Dissolved Solids (TDS)

TDS is an indication of pollution which indicates materials transported in suspended form and values with high TDS are potentially unhealthy (Titilawo *et al*., 2019). The TDS observed were below limits withthe highest value observed in C2 with 390.67±0.47 and lowest in B2 with 72.09±0.01. Table 1 and 2 show a significant difference across the seasons at point A and B respectively and Table 3 shows no significant difference between season 1 and 3 and significant difference between season 2 in point C.

Sodium Chloride Content (NaCl)

Chloride in fresh water is released through human urine and faeces, and the disposal of sewage and industrial wastes (Julie and Vasantha, 2010). Seasons and points exhibit significant variations in the NaCl concentration, with point C showing the highest mean value during the rainy season. Elevated NaCl levels in aquatic bodies during the rainy season highlight the impact of precipitation and runoff.

The highest value was observed in C2 with 1.57±0.05 and lowest in B2 with 0.27±0.05. Table 1 shows a significant difference across the three seasons in point A, Table 2 shows no significant difference between season 2 and 3 but significant difference in season 1 at point B. Table 3 shows no significant difference between season 2 and 3 but difference in season 1 at point C.

Conductivity

Conductivity estimates the amount of total dissolved salts, ions or solids dissolved in water which is controlled by various factors such as the geology of the area that determines the chemistry of the soil and ultimately the water (Titilawo *et al*., 2019). Conductivity measured for all the points in the three seasons were below the permissive limit with exception to C2 which has the highest value with 829.33±0.47 and lowest in B2 with 145.2±0.16 and Table 1, 2 and 3 shows that there is a significant difference between conductivity across all the seasons at point A, B and C respectively.Past findings indicated that sewage disposal tends to increase the conductivity levels of the receiving water body due to high concentrations of salts and ions in the sewage (Suthar *et al*., 2010) and urban surface run-off also contribute to conductivity and the relationship between conductivity,

Table 4. Descriptive Analysis of the Elements and Heavy Metals across all Seasons and Points showing Mean and Standard Deviation

Metals	All Seasons (mg/L)	WHO (2007) (mg/L)	USEPA (2010) (mg/L)
Sodium (Na)	18.48±23.34		20mg/L
Magnesium (Mg)	4.82±0.35	75	
Potassium (K)	4.05±0.53	50	
Calcium (Ca)	17.09±1.52	75	
Barium (Ba)	0.12±0.07		2.0
Vanadium (V)	0±0		
Chromium (Cr)	0.32±0.1	0.1	0.1
Manganese (Mn)	0.14±0.05		0.05
Iron (Fe)	4.82±1.41	0.1	0.3
Cobalt (Co)	0±0		
Nickel (Ni)	0.17±0.06		0.1
Copper (Cu)	0.46±0.69	1.0	1.3
Zinc (Zn)	0.16±0.08	5.0	5.0
Arsenic (As)	0.01±0.02	0.05	0.01-0.05
Aluminium (Al)	0.62±0.22		0.05-0.2
Lead (Pb)	0.08±0.03		0.05
Silver (Ag)	0.01±0.01		0.10
Thorium (Th)	0±0		
Uranium (U)	0±0		
Cadmium (Cd)	23.66±39.36	0.03	0.005
Thallium (Tl)	0±0		0.002
Beryllium (Be)	0±0		0.004
Selenium (Se)	0.01±0.02	0.01	0.05

TDS and NaCl content could be seen in the three sample points as shown in Table 1, 2 and 3. As conductivity is highest in A1, B1 and C2 with mean values of 527.67,175.00 and 829.33 respectively, TDS/NaCl content is also highest in A1, B1 and C2 with values of 249.00/1, 388.33/0.73 and 390.67/1.57 respectively.

Essential Elements and Heavy Metals

The ICP-OES technique detected 23 elements in Osun river of which four are essential elements present in river (Na, Mg, K, Ca) and twelve elements are categorized as heavy metals (Cr, Fe, Co, Ni, Cu, Zn, As, Pb, Ag, Cd, Tl, U). The descriptive analysis of all elements compared with permissible limits is shown in Table 4.

Sodium (Na)

Figure 2 shows that sodium tends to be higher in C3 and was on the average in all other seasons. Table 4.shows that Na was below standard limit across all the seasons and points.

Magnesium (Mg)

Figure 3 shows that Magnesium (Mg) was determined in all seasons and points but it shows highest percentage at point C3 and it is below the permissible limit across all seasons and points.

Potassium (K)

Figure 4 shows that K was determined in all percentage in B1 and it is within the permissible limit across all the seasons and points as shown in Table 4. Seasons and points with highest p

Calcium (Ca)

Figure 5 shows calcium was determined in all seasons and points with highest percentage in C3 and Table 4 shows that it is below permissible limit across all seasons and points.

Barium (Ba)

Figure 6 shows Ba was determined in all seasons and points with C3 having the highest percentage. Ba is below the permissible limit across all seasons and points as shown in Table 4.

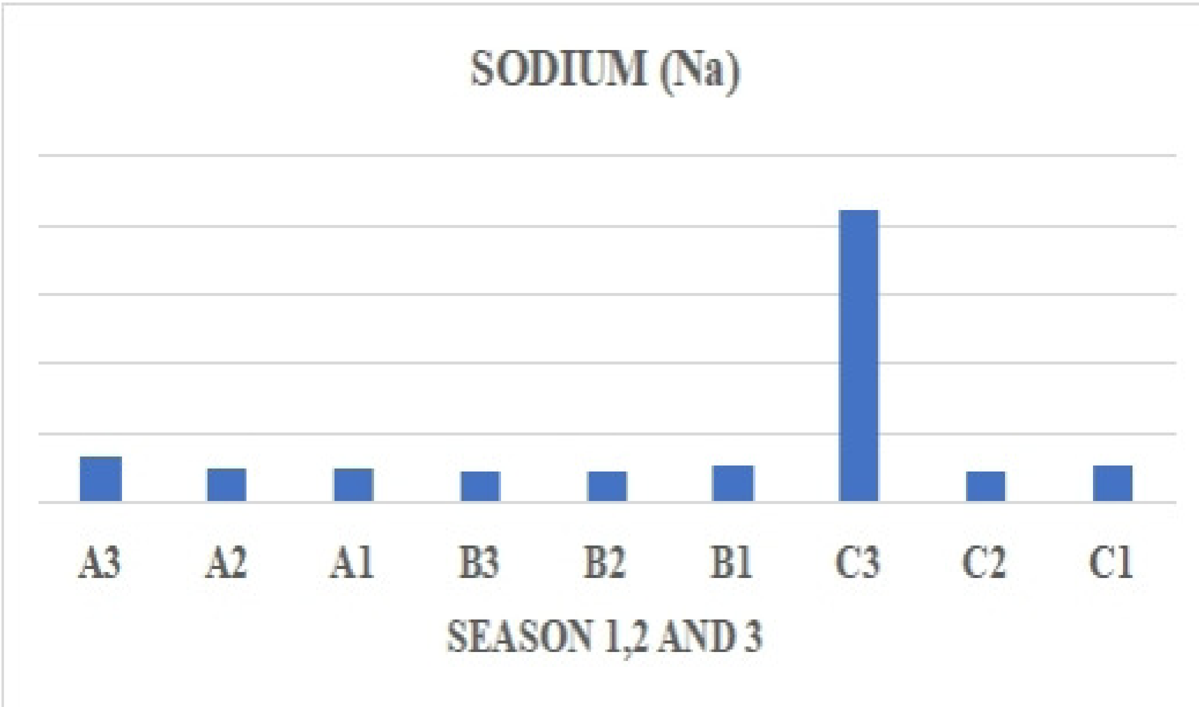

Figure 2. Bar Chart for Sodium (Na)

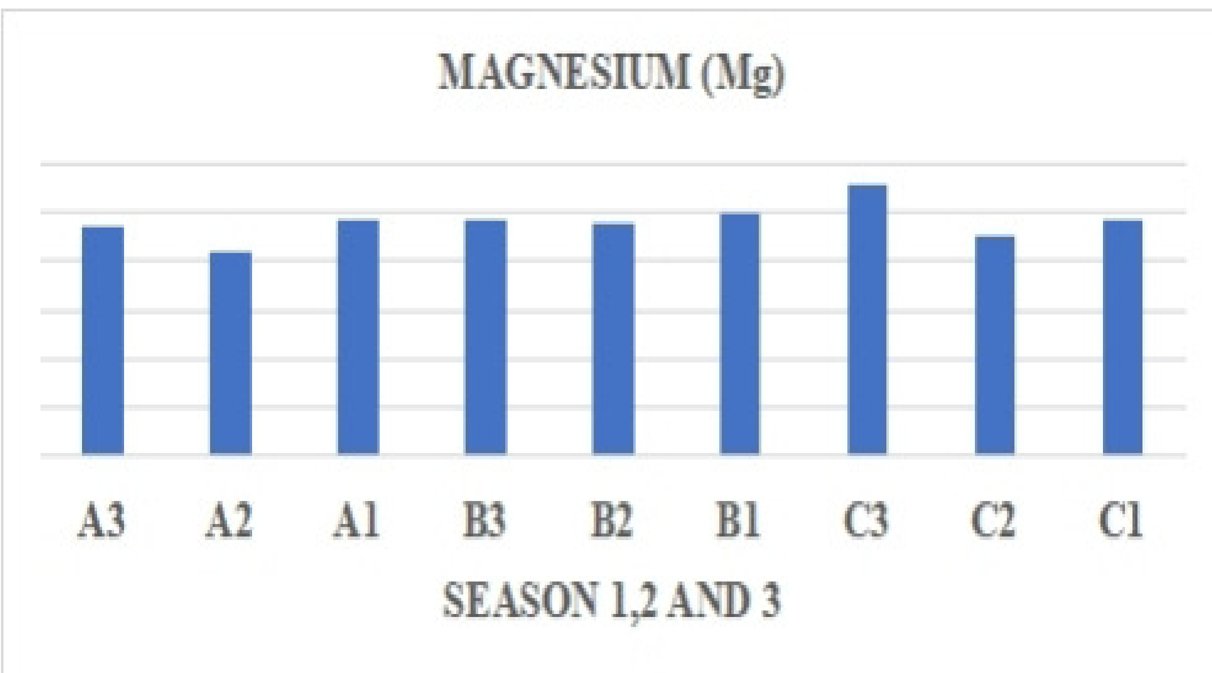

Figure 3. Bar Chart for Magnesium (Mg)

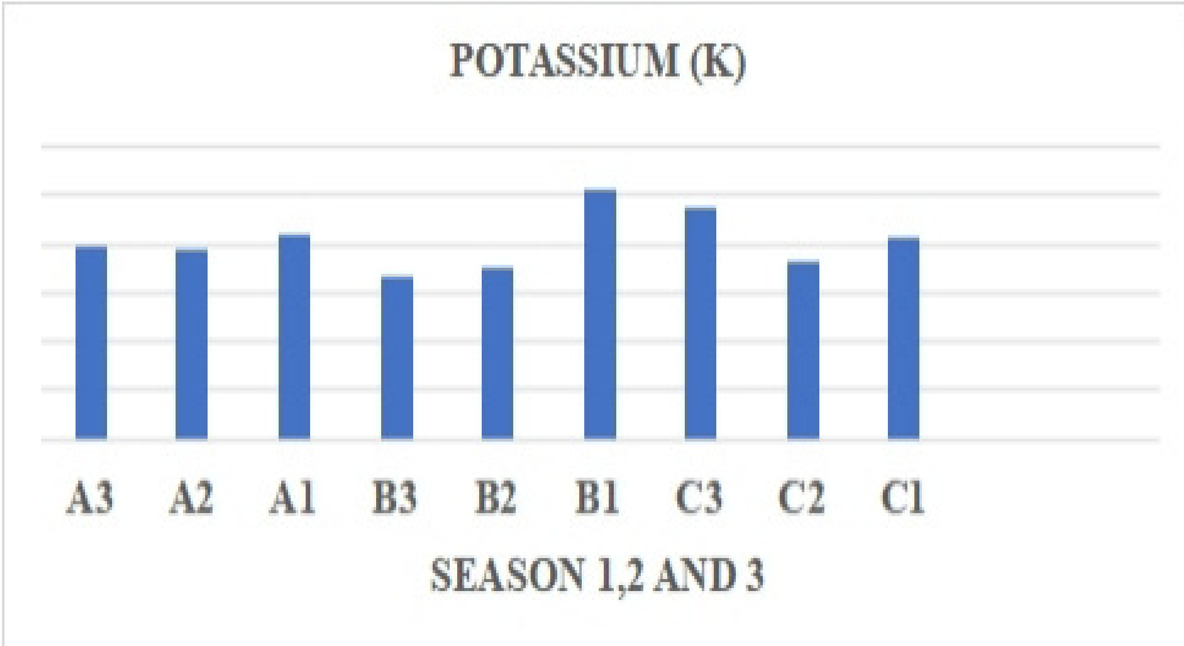

Figure 4. Bar Chart for Potassium (K)

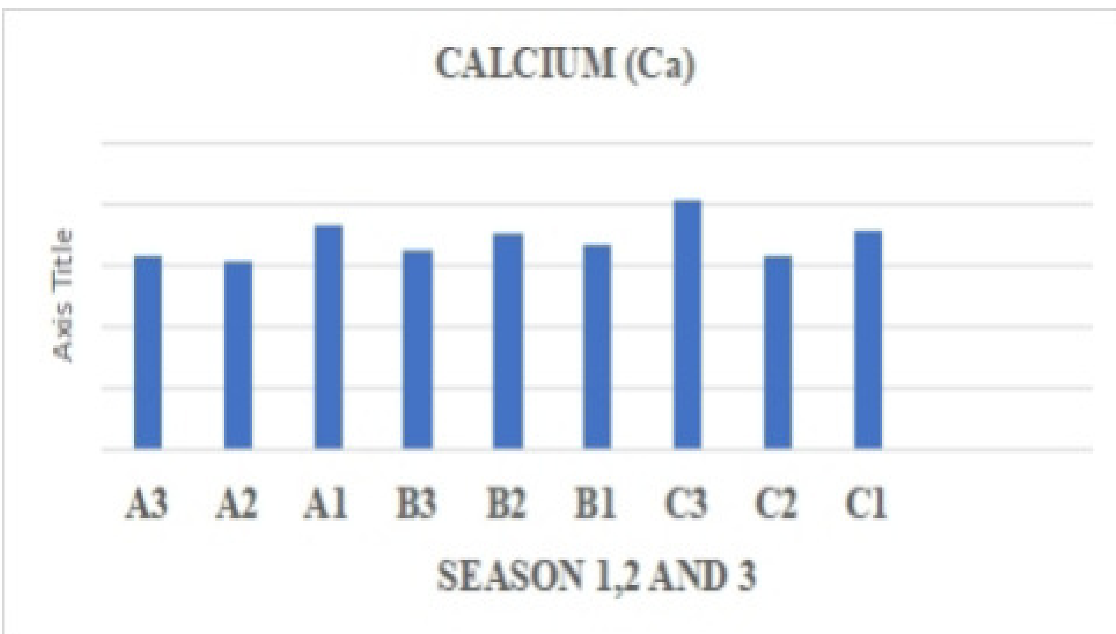

Figure 5. Bar Chart for Calcium (Ca)

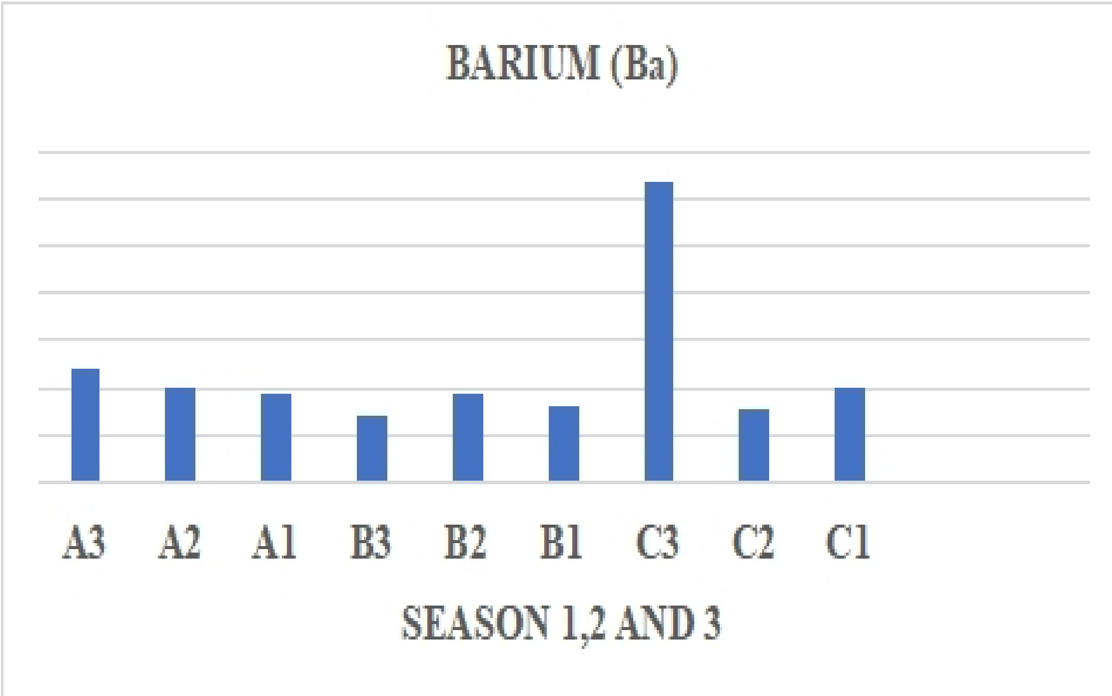

Figure 6. Bar Chart for Barium (Ba)

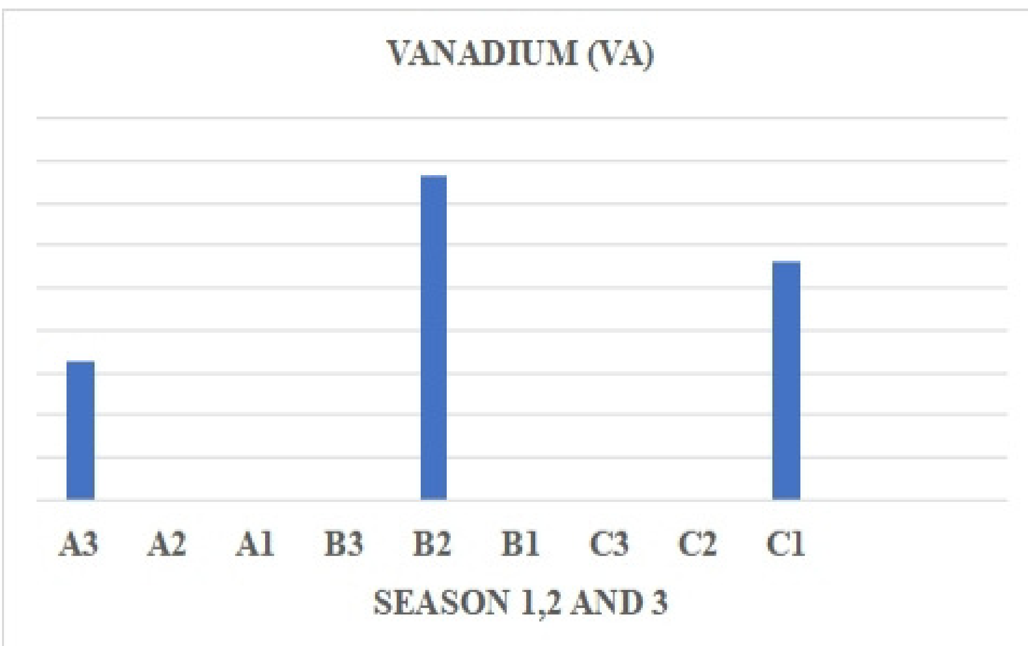

Figure 7. Bar Chart for Vanadium (Va)

Vanadium (Va)

Table 4 shows that Va is of no significant presence across all the seasons and points but little concentrations was determined in A3, B2 and C1 with highest percentage in B2 as shown in Figure 7.

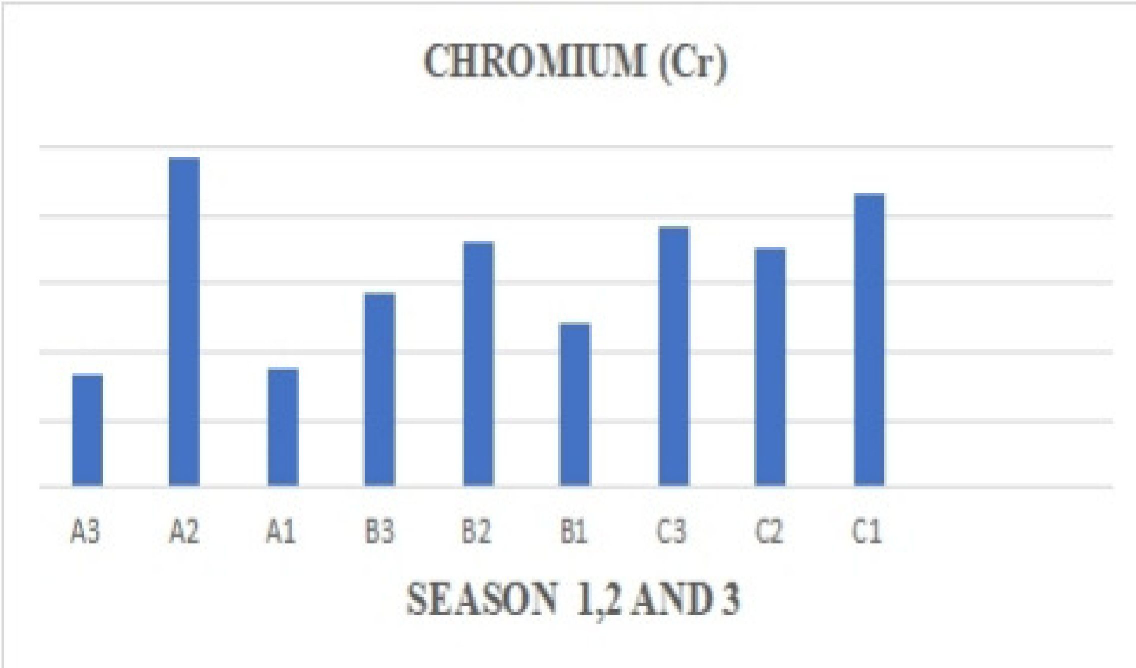

Figure 8. Bar Chart for Chromium (Cr)

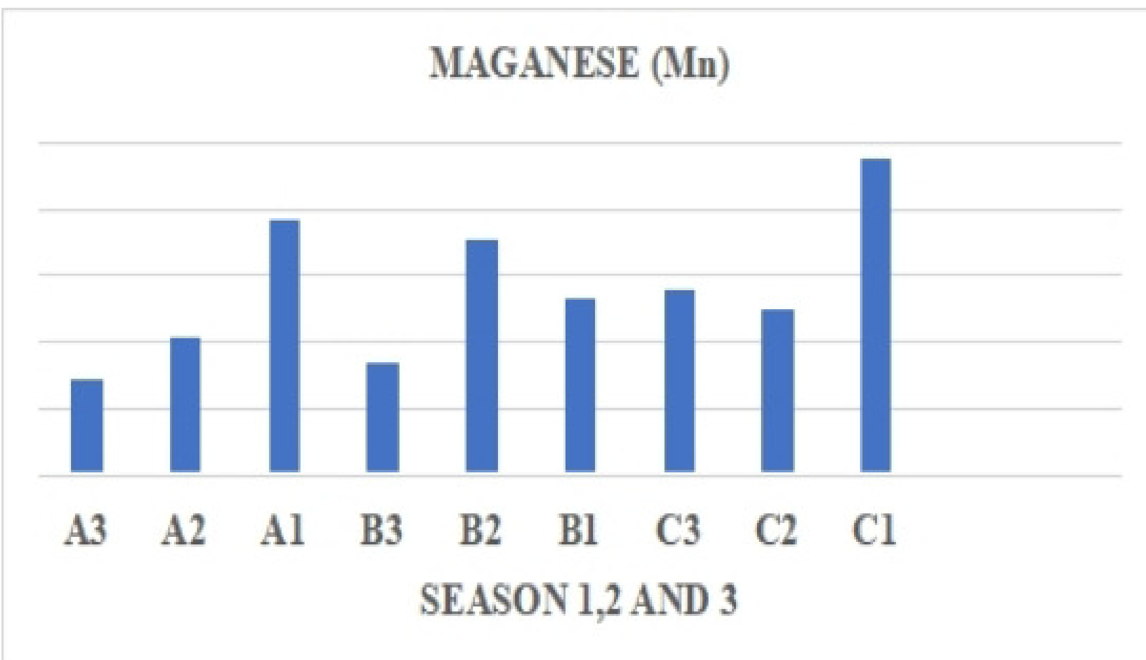

Figure 9. Bar Chart for Manganese (Mn)

Chromium (Cr)

Figure 8 above show Cr was determined in all seasons but it shows highest percentage at point A2 after which it was high in C1. Table 4 shows that Cr was above standard permissible limit across the three seasons and points with a value of 0.32±0.1.

Manganese (Mn)

Figure 9 shows that Mn was determined in all seasons but it shows highest percentage at C1 after which it was higher in A1. Table 4 shows that Mn was above the permissible limit across all the points and seasons with a value of 0.14±0.05.

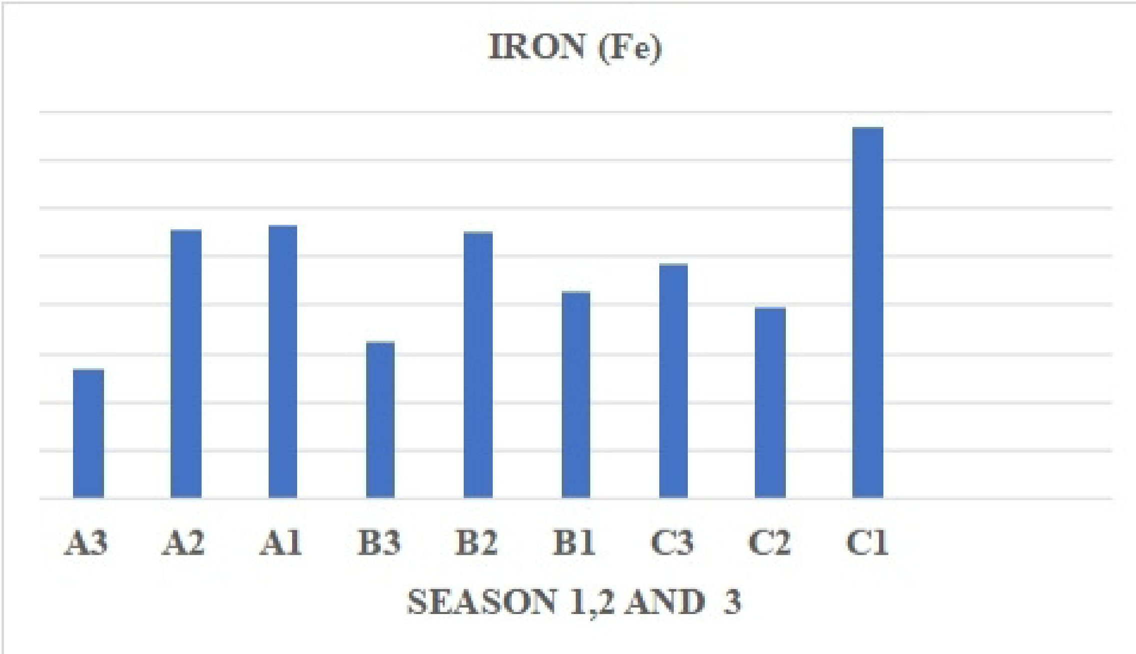

Figure 10. Bar Chart for Iron (Fe)

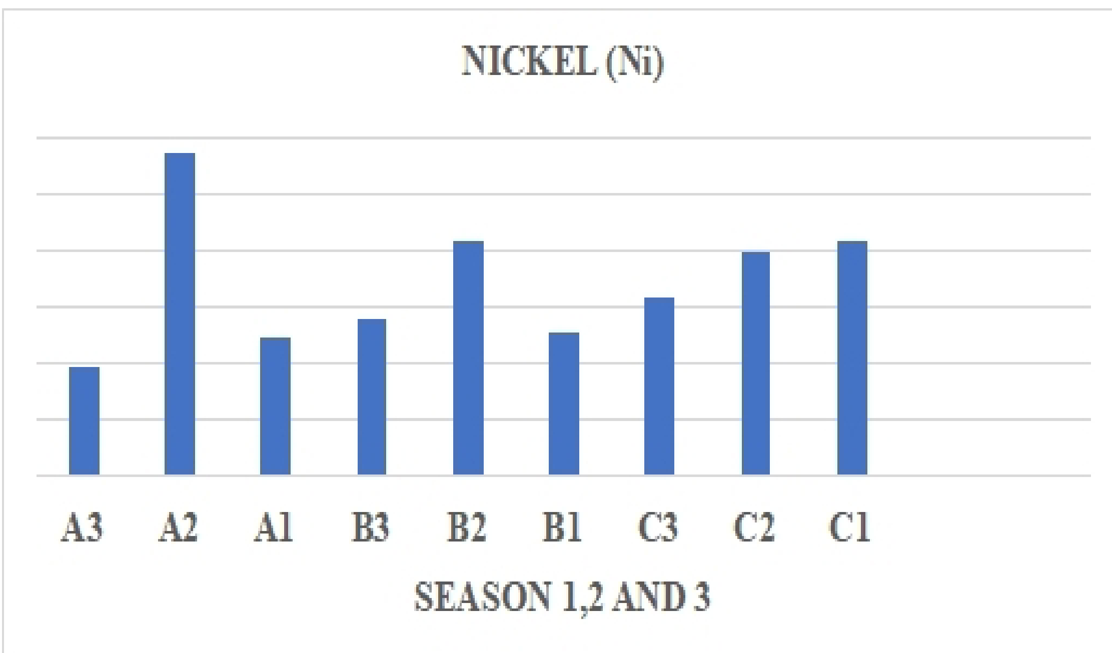

Figure 11. Bar Chart for Nickel (Ni)

Iron (Fe)

Figure 10 shows that Iron Fe was determined in all seasons but it shows highest percentage at C1 after which it was higher in A1. Table 4 shows that Fe was above permissible limit for drinking water across all the seasons and points with a value of0.14±0.05

Nickel (Ni)

Figure 10 shows that Nickel (Ni) was determined in all seasons but it shows highest percentage at A2 after which it was higher in C1. Table 4.2.1 shows that concentration of Ni across all the seasons and points was above permissible limit with value of 0.17±0.06.

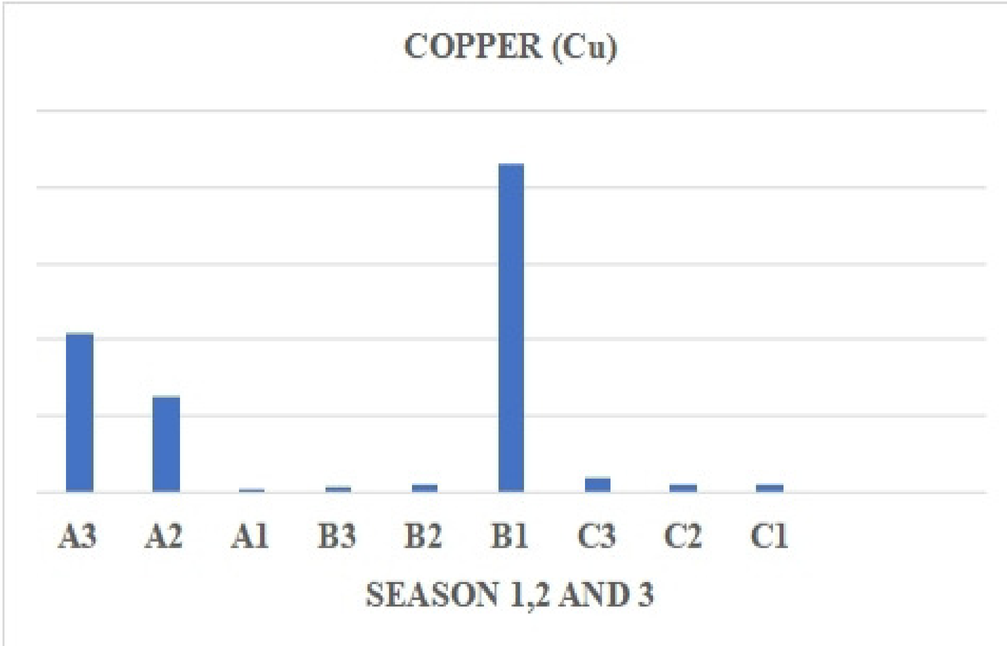

Figure 12. Bar Chart for Copper (Cu)

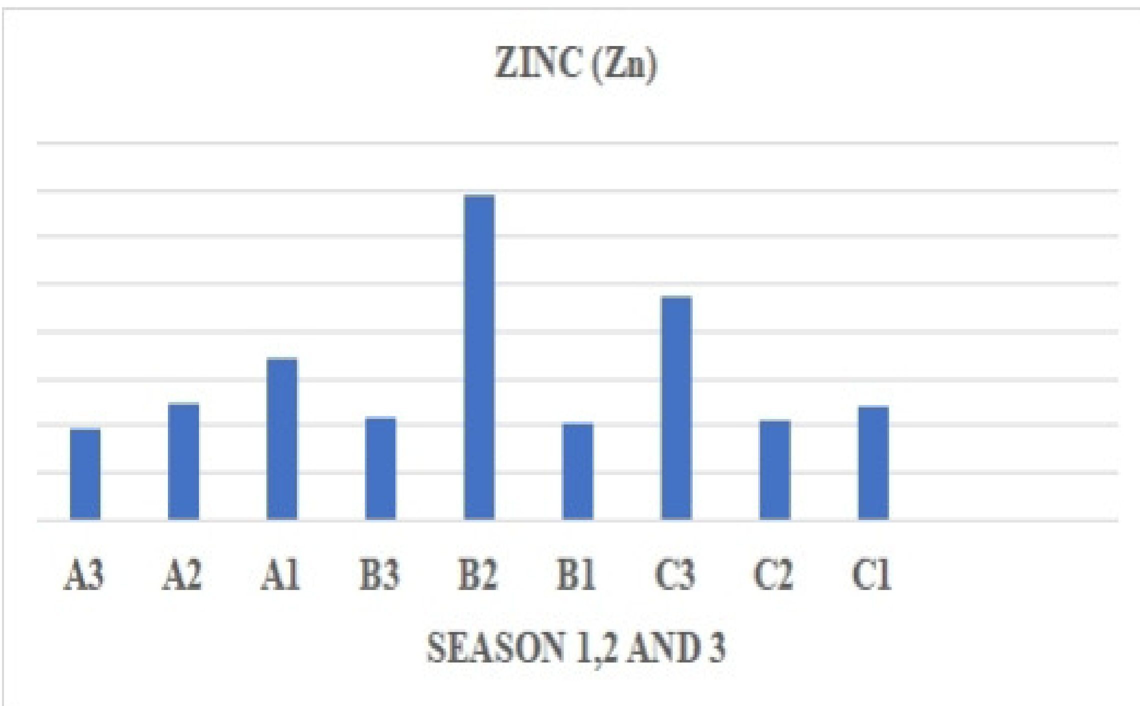

Figure 13. Bar Chart for Zinc (Zn)

Copper (Cu)

Figure 11 above shows that Cu was determined more in B1 (having the highest percentage), A3, A2 and it was minimal in the rest seasons. Table 4 shows concentrations of Cu across the three seasons and points was below permissible limit with value of 0.46±0.69.

Zinc (Zn)

Figure 13 shows that Zn was determined in all seasons but it shows highest percentage at B2 after which it was

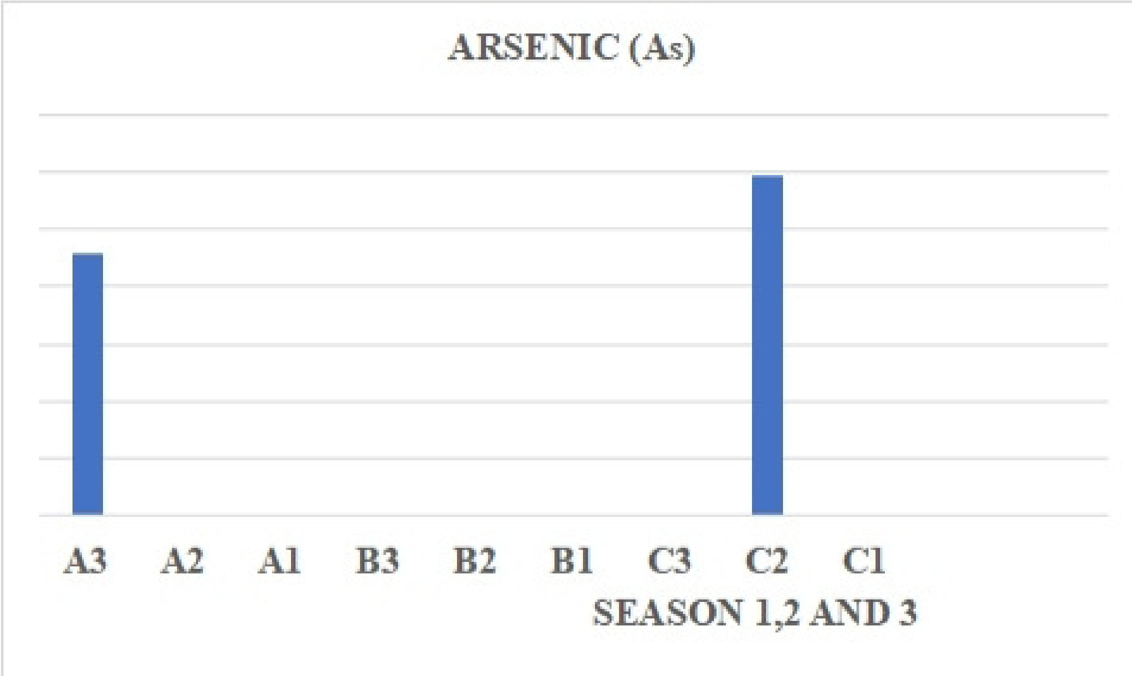

Figure 14. Bar Chart for Arsenic (As)

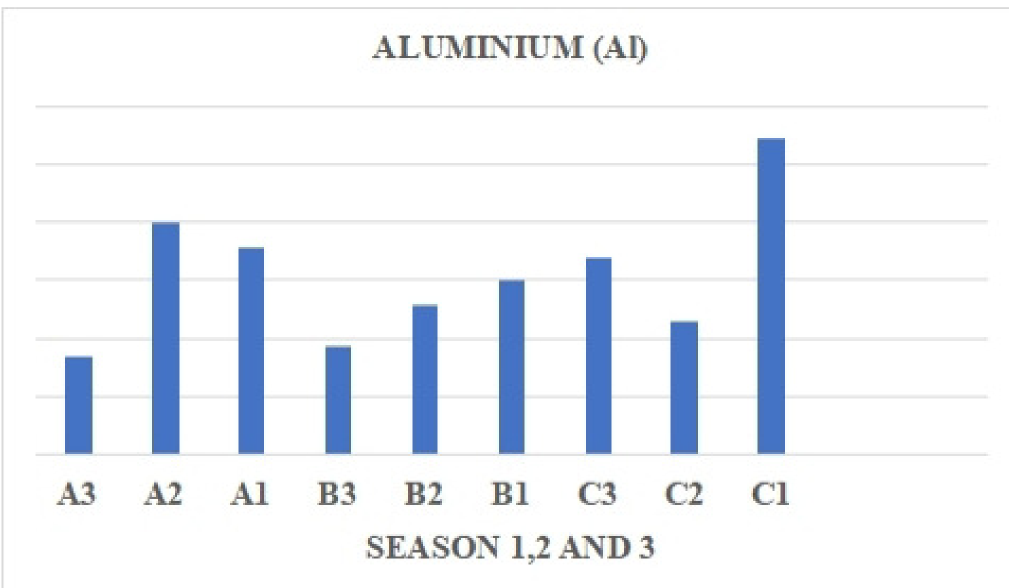

Figure 15. Bar Chart for Aluminium (Al)

higher in C3. Table 4 shows that Zn was below permissible limitacross the three seasons and points with value of 0.16±0.08.

Arsenic (As)

Figure 14 shows that As was determined in just two seasons at two different locations which are A3 and C2 but it shows highest percentage at point C2. The concentration of As across the three seasons and points was below permissible limit with value of 0.01±0.02 as shown in Table 4.

Aluminium(Al)

Figure 15 above shows that Al was determined in all

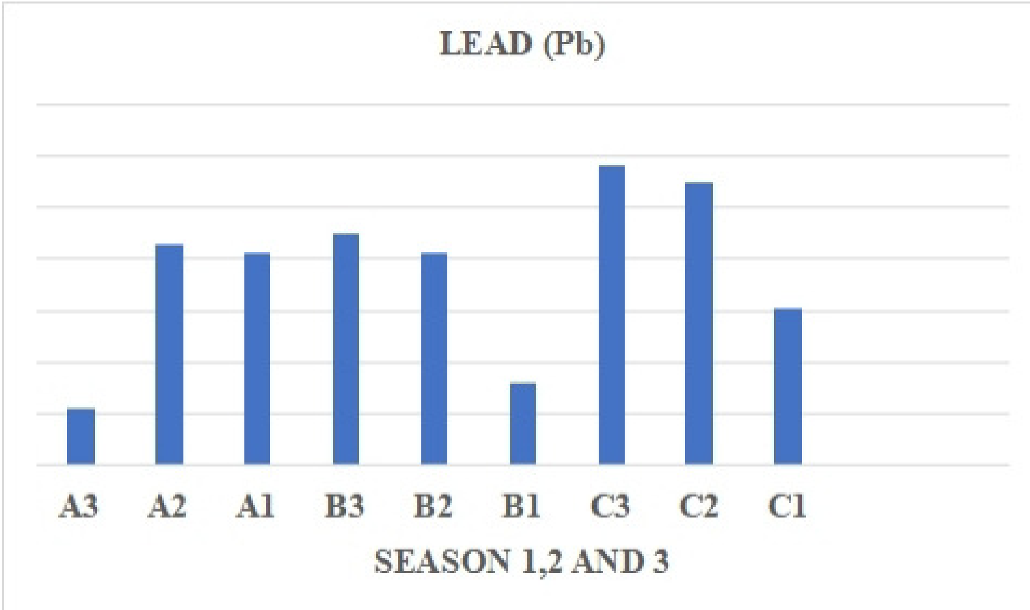

Figure 16. Bar Chart for Lead (Pb)

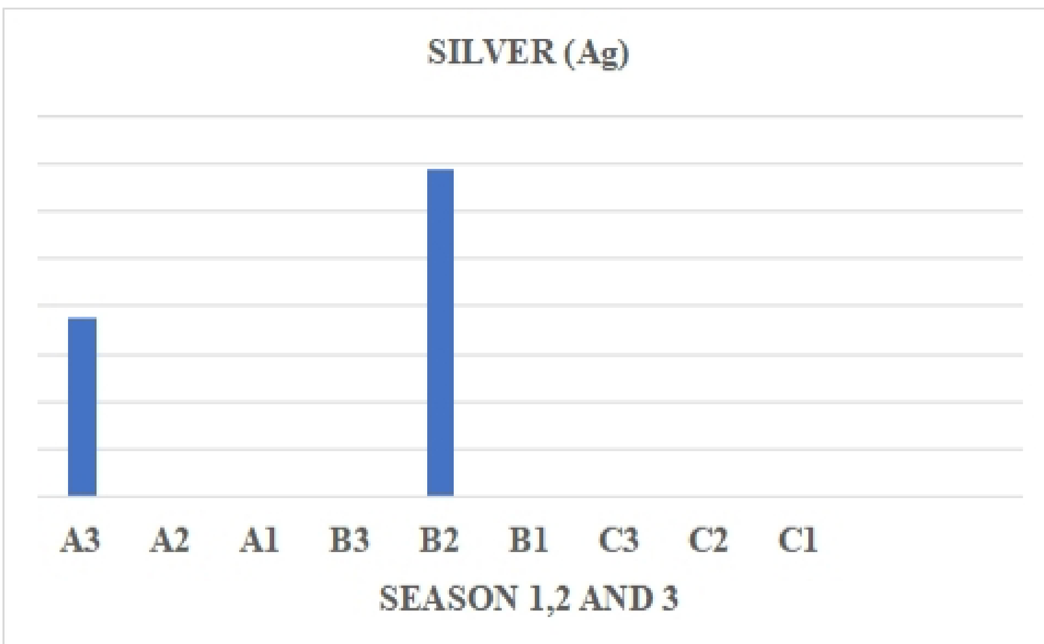

Figure 17. Bar Chart for Silver (Ag)

seasons but it shows highest percentage at C1 after which it was higher in A2. The concentration of Al across the three seasons and points was within permissible limit with value of 0.62±0.22 as shown in Table 4.

Lead (Pb)

Figure 16 above shows that Pb was determined in all seasons but it shows highest percentage at C3 after which it was higher in C2. The concentration of Pb across all seasons and points is within permissible limits with value of 0.08±0.03 as shown in Table 4.

Silver (Ag)

Figure 17 shows that Ag was determined in just two seasons at two different location which are A3 and B2 but it shows highest percentage at point B2 followed by A3.

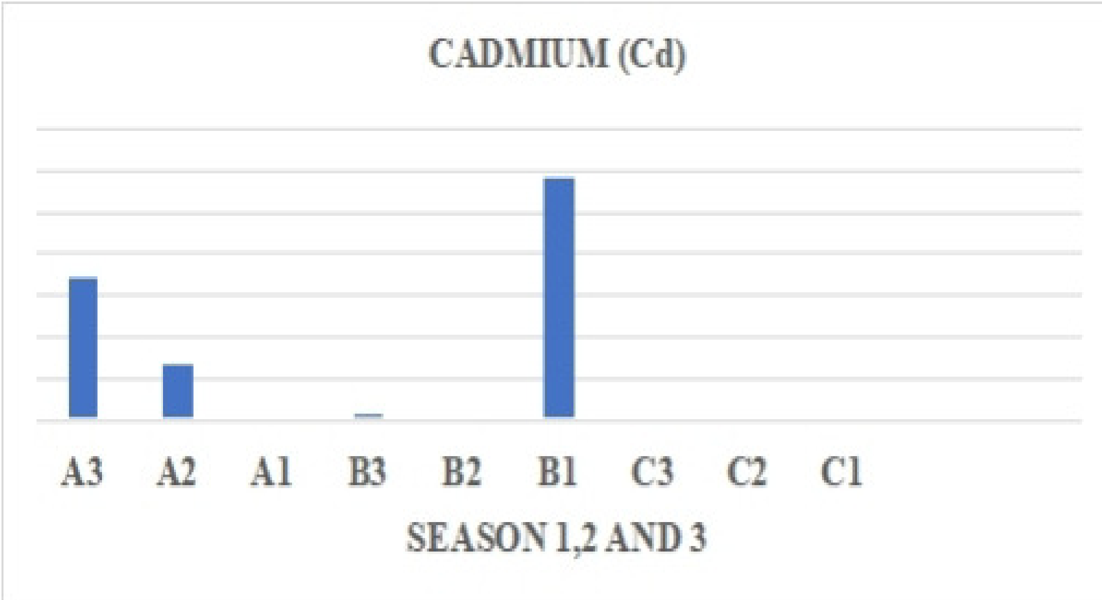

Figure 18. Bar Chart for Cadmium (Cd)

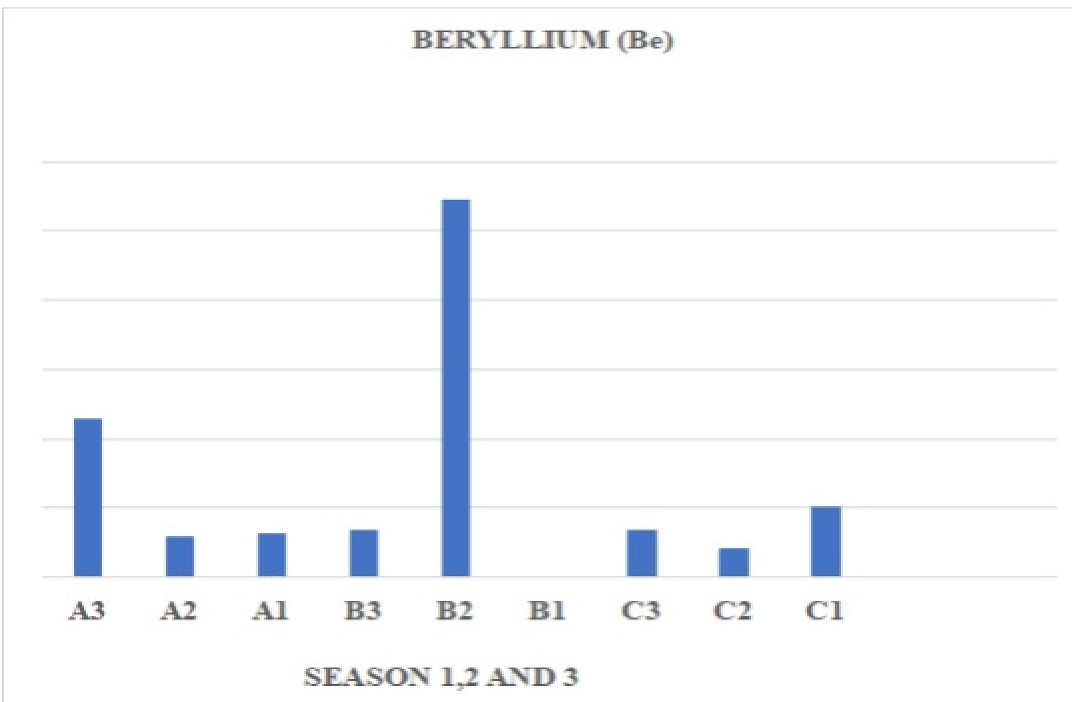

Figure 19. Bar Chart for Beryllium (Be)

The concentration of Ag across all seasons and points is below permissible limits with value of 0.01±0.01 as shown in Table 4.

Cadmium (Cd)

Figure 18 shows that Cd was determined morein three seasons and at two points which are B1 (having the highest percentage), A3, A2. It was minimal in A1, B3 and B2 and not detected in C3, C2 and C1. The concentration of Cd across all seasons and points is above permissible limits with value of 23.66±39.36 as shown in Table 4.

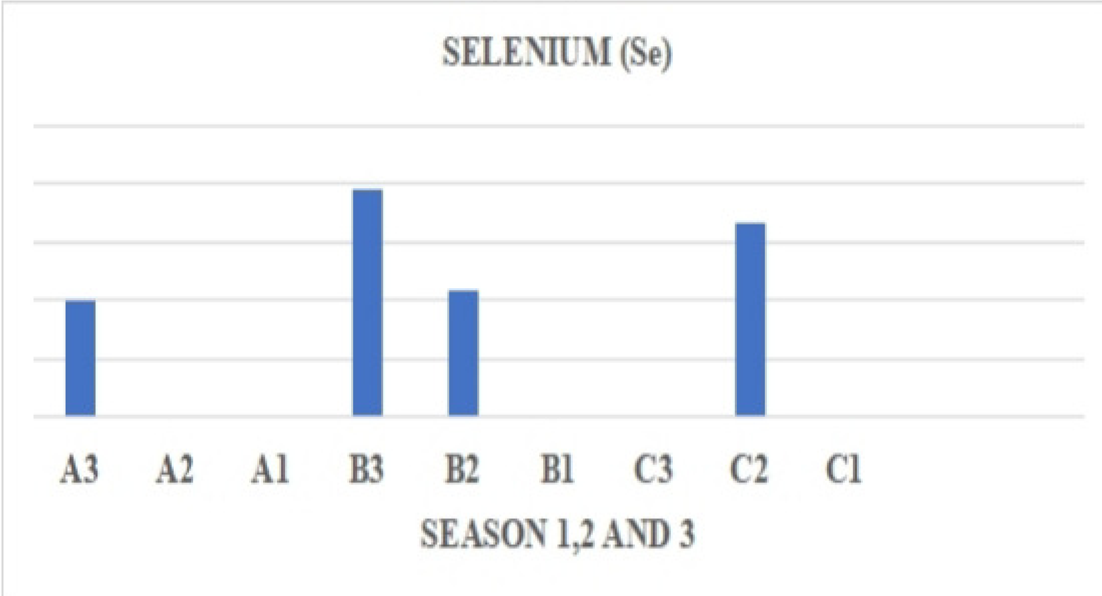

Figure 20. Bar-Chart for Selenium (Se)

Beryllium (Be)

Figure 19 shows that Be was determined in all seasons and points except B1 but it shows highest percentage at point B2 after which it was higher in A3.

Selenium (Se)

Figure 20 shows that Se was determined in just two seasons at the three locations which areA3, B2, B3 and C2 but it shows highest percentage at point B3. The concentration of Cd across all seasons and points is within permissible limits with value of 0.01±0.02 as shown in Table 4.

Essential nutrients that are frequently present in natural settings, such as Na, Mg, Ca, and K, are necessary for a variety of biological functions. The steady concentrations of Ca, Mg and K can be seen in all seasons and points although Ca , Mg, as well as Na was highest in point C after the rainy season (C3). Table 4 shows that sodium is more abundant in Osun river than others in order of Na>Ca>Mg>K which also agree with the findings of Sharma *et al*., 2023. The cause of the presence ofthese nutrients can be as a result of precipitation induced leaching through soils high in sodium, sewage effluent, leachate infiltration from landfills as well as less dilution as a result of no rainfall (Banerjee and Prasad, 2020).

Toxic elements like Cd, Pb, and As, on the other hand, exhibit greater variability with Cd>Pb>As suggesting possible sources of contamination and raising environmental concerns. These elements' large standard deviations point to potential variations in their input sources or outside influences on their distribution. Adebanjo and Oyebode (2019) discovered that Pb concentration in Osun river was relatively low (< 0.08mg/l) and mean concentration of Pb obtained in this study was 0.08 which indicate a rise in Pb concentration in Osun river overtime.

Cadmium (Cd) is a highly toxic heavy metal that occurs naturally in environmental media and as a contaminant emitted mainly from industrial sources, such as mining and metal smelting (Zamora *et al*., 2021). Cadmium is relatively more mobile than other heavy metals and Cd showed a mean concentration of 23.66±39.36 of which it is the highest heavy metal present in the river across all seasons and locations. Cd is recognized as an extremely significant contaminant as its high toxicity and large solubility in water (Xing *et al*., 2019) and Figure 18 shows that Cd concentration was highest in B1.

CONCLUSION

The pollution caused by heavy metals in Osunriver was determined using physicochemical parameter and ICP-OES technique. The effects are likely attributable to both anthropogenic and industrial discharges, contributing to the river's pollution. Elevated concentrations of heavy metals in BOD and conductivity surpassed acceptable thresholds, indicating widespread pollution across some of the sampling locations. However, parameters such as hardness, alkalinity, turbidity, TDS and temperature remained within acceptable limits. Moreover, the higher concentrations of heavy metals compared to regulatory standards signify a significant pollution problem in the river, potentially posing adverse effects on living organisms even in minute quantities. The findings underscore the necessity of educating people who on drinking the river water for the purpose of healing their ailments about the potential health risks. Cd, Fe, Cr, Mn, Ni, Al and Pb were above permissible limits across all seasons and points when compared with the permissive limits as shown in Table 4. Cd which was observed to be the highest heavy metal in Osun river at the time of this study has been observed to be associated with coronary heart disease, stroke, peripheral artery disease, as well as carcinogenic effects (Genchi *et al.,* 2020*).* Zn and Fe are known to be essential elements and generally non toxic but can cause health risks in high quantity such as gastrointestinal disorder, kidney and liver abnormal functioning, vomiting, diarrhea and abdominal pain and Pb causes serious effect on mental health (Alzhemiers' disease) and nervous system malfunction (Jyothi, 2020).

RECOMMENDATION

Inhabitants of Osogbo, Osun state and the general public who comes to the river during the Osun-Osogbo festival should be enlightened about the danger inherent in using this water for drinking. Remediation plans should be implemented by the government and measures should be introduced to guide against indiscriminate discharge of domestic wastes, industrial wastes as well as human waste into the water body. Further studiesshould also be carried out on the river from time to time to monitor the pollution levels and remediation plans should be effected.

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