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Chemometrics monitoring and characterization of heavy metals and physicochemical status of Chanchaga River and Tagwai dam in Minna, Nigeria

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Abstract

The deleterious seasonal variation of waterbodies content leaves so much concern for safety of environment. In this study, heavy metals: Pb, Ni, Mn, Zn, Cd, Cu and Cr, as well as physiocochemical parameters: pH, temperature, turbidity, silica, nitrite, nitrate, nitrite as nitrogen and ammonia were determined in 80 samples of sediments and water samples from Chanchaga River and Tagwai Dam in Minna metropolis during dry and rainy seasons. The mean concentrations of the heavy metals in water and sediment samples were ranged as follows respectively: Pb (ND ; ND), Mn (ND - 0.01 mg/dm^3;ND – 0.09 mg/dm^3), Zn (0.00 – 0.02 mg/dm^3 ; ND – 0.12 mg/dm^3), Cd (ND ; ND-0.03 mg/dm^3), Cu (ND – 0.01 mg/dm^3 ;ND – 0.03 mg/dm^3) and Cr (ND-0.02 mg/dm^3 ; ND-0.02 mg/dm^3) for rainy and dry seasons. The concentrations (mg/dm^3) of the physicochemical parameters were as follows: pH (6.35 – 7.46 ; 4.41-7.75), temperature (27.64 - 30.57^{0}C ; 25.35 – 27.91), silica (ND – 6.09 mg/dm^3 ; 1.97 -10.11 mg/dm^3) ammonia (0.41- 7.54 ; 4.50 - 14.33 mg/dm^3), turbidity (30.87 – 80.86 NTU ; 15.33-66.30 NTU), Conductivity (87.43-115.70 µS/cm ; 209.00 – 421.93 µS/cm), nitrite (ND – 0.12 mg/dm^3; 0.05 - 0.41 mg/dm^3), nitrite-nitrogen (0.01 – 0.03 mg/dm^3 ; 0.03 - 0.13 mg/dm^3) and nitrate (ND – 8.13 mg/dm^3 ; 2.80 - 21.62mg/dm^3). Cd, Zn, Mn, ammonia, turbidity, Cu, pH, and nitrite were above the WHO limit in water and sediment samples and in both seasons. The results of the analysis showed the pollution in Chanchaga River and Tagwai Dam to be above WHO permissible limit.. Principal Component Analysis of the datasets showed nitrite-nitrogen, turbidity and pH as the signature contaminants among the water samples, while nitrate, nitrite-nitrogen, Cd, silica and turbidity characterize the sediment samples. Hierarchical Cluster Analysis (HCA) of the water and sediment samples characterizes the pollution source types. Correlation analysis showed strong positive relationship among conductivity-temperature (0.839), nitrate - nitrite nitrogen (0.806), nitrite – nitrite nitrogen (0.999) in the water samples and strong positive correlation between temperature and silica (0.763mg/dm^3), conductivity (0.919µS/cm) and Zn (0.664mg/dm^3) in the sediment samples.

Keywords: Water quality; Heavy metals; Chemometrics; Pollution; Physiocochemical parameters; Chanchaga River; Tagwai Dam; Signature; Hydrogeological origin

1. Introduction

Pollution of the aquatic environment has become a significant problem due to industrialization and urbanization making it essential to monitor the presence of these toxic chemicals in the aquatic environment for the safety assessment of the environment. Over the past decades, human activities have led to ecological pressure in natural habitats thereby increasing the atmospheric deposition of heavy metals (Chukwuemeka *et al.,* 2020). Heavy metals are metallic chemical elements that have relatively high density greater than 5 g/cm3 and are toxic even at very low concentrations. Some of the toxic heavy metals include lead (Pb), cadmium (Cd), chromium (Cr), Mercury (Hg), Arsenic (As) and Thallium (Ti).

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Long term exposure of Heavy metals may cause cancer and can also result in degeneration of neurological, physical and muscular processes leading to diseases such as Alzheimer's disease, Pakinson's disease and muscular sclerosis. (Oguh *et a.l*, 2020). They enter into 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 (Venugopal *et al.,* 2019) or from industrial areas via discharge of untreated industrial effluent in the river (Singh *et al.,* 2008). The presence of heavy metals in surface and underground water at above background concentrations is undesirable (Adelekan *et al.,* 2016).

Heavy metal concentrations in aquatic ecosystems are monitored by measuring their concentrations in sediments and water, since for the normal metabolism of the aquatic life, metals are taken up from water, food or sediment (Bolawa *et al*., 2018). Investigations pertaining to the metals in sediments have enlarged in recent years; while previously sediments were only considered as pollutantreservoirs (Passos *et al*., 2017). A minor fraction (about 1%) of these pollutants remains dissolved in water whereas overwhelming concentrations (99%) are stored in sediments.

Water does contain different types of floating, dissolved, suspended and microbiological as well as bacteriological impurities. Some physical test should be performed for testing of its physical appearance such as temperature, color, odour, pH, turbidity, TDS etc, while chemical tests should be performed for its BOD, COD, dissolved oxygen, alkalinity, hardness and other characters (Muhammad *et al.,* 2018). Tagwai Dam and Chanchaga River are important aquatic ecosystems in Minna and are also major sources of water in Minna Metropolis, Niger State. Anthropogenic activities such as farming, fishing and irrigation are seen within and around the lake making it necessary to identify and evaluate the presence of heavy metals status and to comparatively determine if they are within or exceed the permissible limits.

Chemometric techniques are powerful tools for the evaluation and interpretation of river pollution data. Principal component analysis (PCA) is a dimension-reduction method that is used to convert a large number of related original variables into a smaller number of uncorrelated variables called principal components, which are linear combinations of the original variables. Among the statistical techniques, both principal component analysis (PCA) and cluster analysis (CA) are useful methods to discover common patterns in data distribution, leading to initial dimension reduction of datasets and helping its interpretation. PCA and CA assist to set up analyzed parameters in different factors/groups on the basis of contribution from their possible sources (Matthias *et al*., 2020).

Principal Component Analysis (PCA) has been widely used to expose variable redundancy and combine variables into single factors. Cluster Analysis (CA) is often coupled to PCA to provide groupings of individual variables according to distances or similarity indices (Han *et al.,* 2018). The explanation of the above data processing helps to identify pollution sources and allocate natural vs. anthropogenic contribution.

Although heavy metal pollution in Tagwai Dam and Chanchaga River has been investigated, assessing the contamination and ecological risks of heavy metals in the water bodies using multiple approaches that are based on multivariate analytical tools is meaningful. The assessment would help characterize the contamination sources in river and surface sediments and provide a tool for effectively protecting the river environment.

Thus, this study focused on the analysis of the physico-chemical quality and accumulation of selected heavy metals in water and sediment samples from Chanchaga River and Tagwai Dam, and application of chemometric techniques to the pollution data. Methods of multivariate data analysis were applied for the evaluation and interpretation of data. This analysis could be helpful for Nigerian Government to optimize the marine water monitoring plan and enhance their pollution control actions

1.1. Study Sites

The study was carried out in Minna, Niger State, located within longitude 6°33'E and latitude 9°37'N, covering a land area of 88 km2 (Fig 1). The area has a tropical climate with mean annual temperature, relative humidity and rainfall of 30°C, 61.00% and 1334.00 mm, respectively. The climate presents two distinct seasons, a rainy season (between April to October), and a dry season (between November and March). The vegetation in the area is typically grass-dominated savannah with scattered tree species.

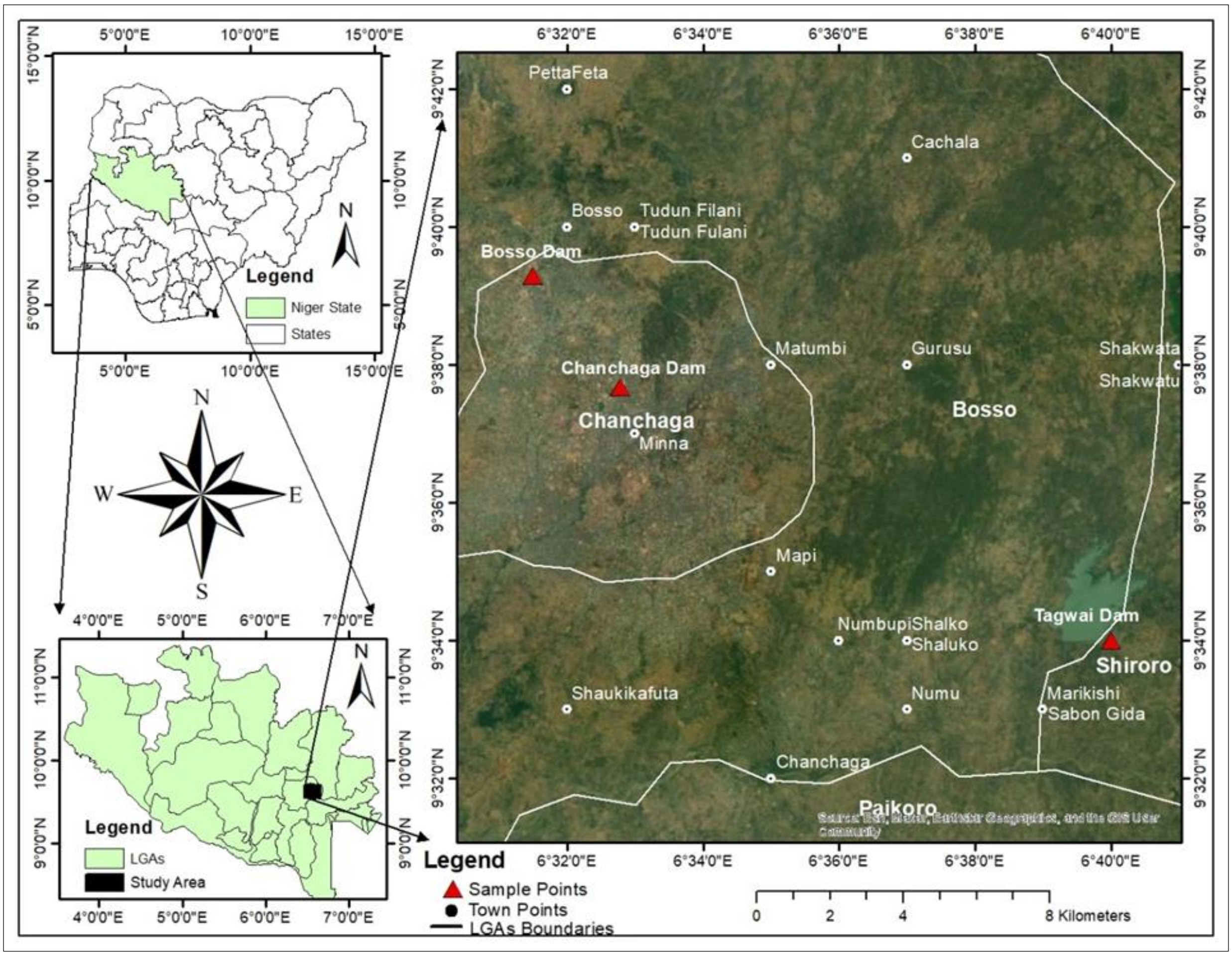

Figure 1 Map of Minna Showing the Study Areas

1.2. Tagwai Dam

Tagwai Dam is about 10 km away from Minna town. Mean maximum temperature remains high throughout the year having about 30°C, particularly in March and June. The vegetative cover is characterised by woodland and tall grasses inter spread with tall, dense species. In some areas, traces of rain forest species can be seen of Sudan Savannah alongside the plain of the River.

Tagwai Dam lies between Latitudes 09^o 37' N to 09^o 33' N of the equator and longitudes 06^o 39' E to 06^o 42' E of the Greenwich meridian of Nigerian sheet 142 North Western (Minna) Nigeria. It covers an area of 9 km^2. Most parts of the area are covered by vegetation. Some of the outcrops are not accessible due to thick vegetation. The river was constructed for the purpose of domestic water supply to Minna metropolis. Fishing in the area is dominated by artisanal fishermen that use manually operated wooden canoes, using mostly cast net, gill nets, drift net and traps for fishing.

1.3. Chanchaga River

Chanchaga River transverses Muya, Shiroro, Paikoro, Bosso, and Katcha Local Government Areas and can be located on Longitude 6^{0}33'E –longitude 6^{0}38'E and latitude 9^{0}32'N-latitude 9^{0}35'N.The total land area covered by the basin is 159,259 km. Chanchanga River plays very important role to many people because it serves many purposes ranging from irrigation farming, fishing and domesticwater supply sources to Minna city, and some towns along the river, (e.g. Gidan Kwano, Kateregi). The people of the area are predominantly farmers and a lot of farming activities are done on daily basis. Domestic wastes are dumped in the river and activities such as bathing, washing and defecation are done on the banks of the river (Nda, *et al*., 2019).

2. Material and method

2.1. Samples, Sampling and Pretreatment

2.1.1. Water

Each study site was divided into ten sections. Four hundred water samples were collected at different points in rainy and dry seasons and homogenized into 40 composite samples. Water samples were gently collected in clean plastic containers and were subjected to preliminarily acidification. This was done by adding 5cm^3 of nitric acid to each water sample, and then they were transported to the laboratory for storage awaiting digestion. Water samples were collected in rainy and dry seasons.

2.1.2. Sediments

Each study site was divided into ten sections. Four hundred water samples were collected at different points in rainy and dry seasons and homogenized into 40 composite samples.. Samples of sediment were collected with a PVC pipe which was pushed with pressure through the water to obtain sediment layer at a depth of approximately 15 cm. Sediment samples were packed in polythene bags and transported to the laboratory where they were dried at 105 ºC until there was no further change in weight. Dried sediments for each sampling station was mixed and crashed with a pestle and mortar to homogenize. The homogenized samples were sieved and packed in clean polythene bags and kept for digestion and measurement of the heavy metals. Sediment samples were collected in rainy season and dry season.

2.2. Analysis Procedure

Physicochemical measurements such as temperature, silica, pH, turbidity, conductivity, Nitrite, nitrite nitrogen, ammonia, copper, nitrate, zinc, manganese, cadmium, lead and chromium were analyzed.

On-site analyses of pH, conductivity, and turbidity were carried out at the site of sample collection following the standard protocols and methods of American Society for Testing and Materials (ASTM D3557-12) using different calibrated standard instruments. The pH of the water samples was measured by using a pH meter. The pH meter was calibrated, with three standard solutions (pH 4.0, 7.0, and 10.0), before taking the measurements. The value of each sample was taken after submerging the pH probe in the water sample and held for a couple of minutes to achieve a stabilized reading. After the measurement of each sample, the probe was be rinsed with deionized water to avoid cross contamination among different samples.

The conductivity of the samples was measured using a conductivity meter. The probe was calibrated using a standard solution with a known conductivity. The probe was submerged in the water sample and the reading was recorded after the disappearance of stability indicator. After the measurement of each sample, the probe was rinsed with deionized water to avoid cross contamination among different samples.

The turbidity of the water samples was measured using a turbidity meter. Each sample was poured in the sample holder and kept inside for a few minutes. After achieving the reading stability, the value was recorded.

Silica was determined using the Standard Test Method for Silica in Water as described byASTM D859-16.A test of the molybdenum-blue method was used for silica measurement. In each of a series of 100 ml flasks, 5mI of 5%ammonium molybdate and 3ml in hydrochloric acid was placed and 25mI of distilled or sea water containing known additions of silicon was added. After 10minutes, 5 ml of 35% v/v sulphuric acid was added, the solution was allowed to stand for 5 minutes and I ml 0.1N-stannouschloride was added. After a further 10 minutes, the extinction softhe solutions were measure dina I cm cuvette using red filters.

For nitrite-nitrogen determination, the Nitrate/Nitrite-N in Water and Biosolids by Manual Colorimetry method as described by U.S. Environmental Protection Agency (2011) was used. 2 mL of color reagent (prepared by adding 100 mL 85% phosphoric acid (H_3PO_4) and 10 g sulfanilamide was added to about 800 mL reagent water and mixed to completely dissolve the sulfanilamide. 1 g N-(1-naphthyl)-ethylenediamine dihydrochloride was added and mixed to dissolve. It was diluted to 1 L with reagent water and added to 50.0 mL of sample. It was allowed ten minutes for the color to develop, the absorbance of the sample was measure at 540 nm.

Ammonia was measured by Berthelot or indophenol method using a UV-VIS spectrophotometer Perkin Elmer Lambda 25 with double beam. The method is based on ammonium ion reaction with phenol and hypochlorite in alkaline medium to form indophenol blue. The blue color formed is intensified with sodium nitroprusside and the absorbance is measured at 655 nm.

Nitrates were analyzed by a standardized method of molecular absorption spectrometry based on the formation of a yellow compound through the reaction of nitrates with sulpho salicylic acid (2-hydroxy-5sulfobenzoic acid) under acidic conditions followed by treatment with an alkaline solution containing also the disodium salt of the etylen diaminetetra acetic acid (EDTANa2) to prevent the precipitation of calcium and magnesium salts (SR ISO 7890-3-1998). The absorbance of the resulted compound was measured at 415 nm with a UV-VIS spectrophotometer Perkin Elmer Lambda 25.

The analyses of six heavy metals such as Cu, Zn, Mg, Cd, Pb, Cr, was carried out based on ASTM standards (ASTM, 2012), which are approved by APHA (American Public Health Association) using Atomic Absorption. For analysis of Cd, Cr, and Pb, direct extraction/air-acetylene flame method was used. The standard solution for each tested element was prepared according to its concentration and used to calibrate the system before analyzing each water sample. The results were recorded automatically on a computer connected with the AAS system. The mean of the triplicate measurement was taken.

Analyzed data was subjected to multivariate analysis of PCA and HCA using Eigenvector Research Inc Solo software, stand-alone Chemometrics software powered by PLS_Toolbox for pattern recognition. Microsoft Excel 2014 (Multivariate Analysis Add-in) was used to carry out the descriptive statistics and correlation analysis.

3. Results and Discussion

3.1. Physiocochemical Parameters and Heavy Metals Concentration

3.1.1. Physiocochemical Parameters and Heavy Metals Concentration in Water

Table 1 Physico-chemical Parameters and Heavy Metal Concentration in Water Samples during Rainy and Dry Seasons

Parameters	Chanchaga Rainy Season	Chanchaga Dry Season	Tagwai Rainy Season	Tagwai Dry Season	WHO (2014)
pH	6.93 ± 0.01^{c}	7.46 ± 0.05^{d}	7.44 ± 0.01^{d}	6.35 ± 0.07^{a}	6.5-8.5(7.50^{d})
Temperature(°C)	27.67 ± 0.10^{b}	30.57 ± 0.01^{cd}	27.64 ± 0.01^{b}	30.48 ± 0.01^{c}	25^{a}
Silica(mg/l)	6.09 ± 0.01^{d}	ND^{a}	4.38 ± 0.01^{b}	ND^{a}	10.00^{e}
Turbidity(NTU)	80.86 ± 0.01^{f}	58.37 ± 0.0^{b}	76.25 ± 0.01^{g}	30.87 ± 0.01^{e}	5.00^{a}
Conductivity(μS/cm)	96.49 ± 0.29^{c}	115.70 ± 0.05^{f}	87.43 ± 0.01^{b}	115.06 ± 0.19^{e}	1000^{g}
Nitrite(mg/l)	0.07 ± 0.01^{d}	ND^{a}	$0.12 \pm {*0.01}^{e}$	$0.03 \pm {*0.01}^{c}$	3.00^{f}
Nitrite as N_2 (mg/l)	0.02 ± 0.01^{ab}	0.01 ± 0.00^{a}	$0.03 \pm {*0.01}^{bc}$	0.01 ± 0.00^{a}	0.04^{c}
Ammonia(mg/l)	0.41 ± 0.01^{a}	7.54 ± 0.01^{f}	6.49 ± 0.05^{e}	2.63 ± 0.01^{b}	0.40^{a}
Copper(mg/l)	0.01 ± 0.00^{b}	$*0.02 \pm 0.00^{c}$	$*0.40 \pm 0.00^{e}$	ND^{a}	0.01^{b}
Nitrate(mg/l)	7.16 ± 0.04^{e}	ND^{a}	8.13 ± 0.06^{f}	0.92 ± 0.05^{c}	10.00^{g}
Zinc(mg/l)	0.01 ± 0.00^{a}	0.02 ± 0.00^{b}	$*0.03 \pm {*0.01}^{c}$	$*0.02 \pm 0.00^{b}$	0.01^{a}
Manganese(mg/l)	0.01 ± 0.00^{b}	ND^{a}	ND^{a}	ND^{a}	0.10^{c}
Cadmium(mg/l)	ND^{a}	ND^{a}	ND^{a}	ND^{a}	0.03^{*c}
Lead(mg/l)	ND^{a}	ND^{a}	ND^{a}	ND^{a}	0.01^{b}
Chromium(mg/l)	0.02 ± 0.01^{bc}	ND^{a}	0.01 ± 0.00^{b}	$*0.04 \pm {*0.01}^{c}$	0.05^{d}

Values are reported as average mean ± standard error of triplicate determinations .Values along the rows with the different alphabetic superscripts are significantly different at $p \leq 0.05$ while values with the same alphabet are not significantly different ($p \leq 0.05$); * = 10-1 ; ND = Not Detected

The concentrations of Ph, temperature, turbidity, silica, nitrate, nitrite, nitrite-nitrogen, ammonia, conductivity, Cd, Zn, Cu, Pb, Cr and Mn in water samples for all sampling locations in dry and rainy seasons are shown in Table 1. The table represents the mean values for the determined elements during both seasons.

The average mean values of water temperature had significant seasonal variation between the locations. The lowest water temperature was 27.57°C in samples collected from Chanchaga River during rainy season while the highest water temperature was 30.57°C in samples collected from Tagwai Dam during dry season. The observed increased values could be attributed to turbidity and thermal inertia of the water bodies. Seasonal variation in temperature may be due to absorption of solar energy and subsequent release to the atmosphere. During rainy season, low values of temperature observed could be due to freshwater flow as stated bySaravanakumar *et al.*, 2018. One of the implications of increased temperature for water bodies is that metabolic rate and the reproductive activities of aquatic life are controlled by temperature. Metabolic activity increases with a rise in temperature, thus increasing the demand for oxygen by fish. However, an increase in river temperature also leads to decrease in dissolved oxygen, limiting the amount of oxygen available to these aquatic organisms. With a limited amount of dissolved oxygen, fishes in these water bodies may become stressed. (Kurnaz *et al.,* 2017). These results show that the obtained values were above the WHO threshold of 25^0C and the temperature of the water bodies were at the level that can affect the aquatic life negatively.

The average pH values of water samples in the study locations during rainy and dry seasons shown in Table 4.1 were found to be in the range of 6.35-7.46mg/l which complies with that of the World Health Organization (WHO) guideline value of 6.50 -8.50mg/l for water. These levels differ significantly ($p \leq 0.05$) for both the rainy and the dry seasons in each location. This implies that seasonal variations lead to considerable changes in pH. Fluctuations in pH values during different seasons of the year is attributed to factors like removal of CO_2 by photosynthesis through bicarbonate degradation, dilution of waterbodies by freshwater influx, reduction of salinity and temperature and decomposition of organic matter. It was observed that the pH of the water samples reduced during rainy season but increased during the dry season. The average mean concentration of the heavy metals also increased with increase in pH values. A reduction in pH may allow the release of toxic metals that would otherwise be adsorbed to sediment.

The mean values for turbidity recorded in all study locations were above recommended limit. The average mean turbidity values obtained increased during rainy season but decreased in dry season in each location. The highest turbidity value was observed in water sample collected from Chanchaga River (80.86NTU) in the rainy season while the lowest was observed in TagwaiDam (30.87NTU) during dry season. High turbidity is caused by waste discharge, algae growth and urban runoff (Popoola *et al.,* 2019). As recorded by the National Population Commission of Nigeria (web) and National Bureau of Statistics (web), Chanchaga area has increased population when compared to that of Tagwai area leading to increase in the quantity of wastes discharged into the river as well as elevated runoff during rainy season.

The average Conductivity values were in the range of 87.43 – 115.70µS/cm for water samples, with the values for the rainy (Chanchaga, 96.49 µS/cm; Tagwai, 87.43 µS/cm) and dry seasons (Chanchaga, 115.70 µS/cm ; Tagwai, 115.06 µS/cm) differing significantly ($p \leq 0.05$), indicating that seasonal variations have the potential to cause change in the conductivity. Increased conductivity values were obtained during the dry season and reduced during the rainy season in both water and sediment samples. The low values obtained during the rainy season may be due to dilution of the water by rainfall. Also, the lower values of conductivity obtained in the rainy season could be caused by dilution of dissolved salts due to rainfall (WHO, 2017). As rainfall decreases, the level of conductivity increases as a result of concentration of the ions due to evaporation in the river. Similar findings were reported in the literature (Agbaire, *et al.,* 2019). The values obtained in this study for both seasons were within the recommended guidelines of WHO (1000 µS/cm) for water bodies.

All samples in this study contained ammonia, significantly ($P \leq 0.05$) which are all above the WHO recommended value. There were increased ammonia concentration in the rainy season than in the dry season. This could be due to the increased agricultural activities in the study locations during rainy season. Elevated levels of ammonia in water bodies usually result from human activities such as overuse of chemical fertilizers and improper disposal of human and animal wastes as sources of nitrogen-containing compounds, which are converted in the soil. Also, elevated ammonia pollution levels are sustained in the rainy season because sludge deposits with high ammonia content become suspended in water and are washed into water bodies. This may explain the high levels of ammonia seen in rainy season when compared to dry season. Exposure to ammonia pollution can lead to health issues such as fever, difficulty breathing, chest pain and cough.

The average mean concentration of Zn in the water samples was observed at values ranging from 0.00 mg/l to 0.01mg/l which is above the recommended limit. Zn pollution in rivers has been reported to be introduced by discharge of waste materials, fertilizers that may leach into groundwater,refuse incinerationand effluent from residential and industrial area. The water bodies studied are in proximity to intensive agricultural activities and waste discharge is increased during rainy season, these could explain the observed Zn contamination in them. The increased value during rainy season could also be attributed to the increased leaching during the season. In a similar study, a higher Zn mean level of 76.25 mg/l than the 3.00 mg/l recommended limits was recorded from Forcados River while lower mean levels of 0.085 mg/l during dry season and 0.716 mg/l during rainy season from River Ganga's water and 1.0 mg/l from Nairobi River's water were recorded (Agatha, 2017). The observed Zn pollution in this study could be attributed to land use activities such as agricultural system.

3.1.2. Physiocochemical Parameters and Heavy Metals Concentrations in Sediments

Table 2 Physico-chemical Parameters and Heavy metal Concentration in Sediment Samples during Rainy and Dry Seasons in the Study Locations

Parameters	Chanchaga Rainy Season	Chanchaga Dry Season	Tagwai Rainy Season	Tagwai Dry Season	WHO (2014)
pH	4.41±0.01[a]	6.22±0.01[d]	5.58±0.03[c]	7.75±0.01[g]	6.5-8.5(7.50[f])
Temperature(°C)	25.35±0.01[b]	27.50±0.01[c]	27.91±0.01[f]	27.57±0.01[d]	25 [a]
Silica(mg/l)	8.57±0.01[d]	1.42±0.01[b]	10.11±0.01[f]	1.97±0.01[c]	10.00[e]
Turbidity(NTU)	27.90±0.01[b]	20.57±0.02[d]	66.30±0.01[e]	15.33±0.01[b]	5.00[a]
Conductivity(μS/cm)	412.80±0.01[d]	421.93±0.01[e]	209.00±0.01[f]	260.23±0.01[a]	1000[g]
Nitrite(mg/l)	0.05±0.01[ab]	0.05±0.02[ab]	0.41±0.04[d]	0.09±0.01[c]	3.00[e]
Nitrite as N_2 (mg/l)	0.12±0.01[c]	0.04±0.01[b]	0.13±0.01[c]	0.03±0.01[b]	0.04[b]
Ammonia(mg/l)	14.33±0.02[f]	4.50±0.01[b]	8.29±0.01[d]	7.97±0.01[c]	0.40[a]
Copper(mg/l)	0.03±0.01[c]	ND[a]	0.03±0.02[c]	0.01±0.01[ab]	0.01[b]
Nitrate(mg/l)	4.05±0.01[d]	2.80±0.01[a]	21.62±0.01[g]	3.49±0.01[b]	10.00[f]
Zinc(mg/l)	0.12±0.01[c]	ND[a]	ND[a]	ND[a]	0.01[b]
Manganese(mg/l)	ND[a]	*0.01±0.01[ab]	0.09±0.01[c]	0.02±0.01[b]	0.10[c]
Cadmium(mg/l)	0.02±0.01[bc]	ND[a]	0.03±0.01[c]	*0.03±0.01[c]	0.03*[c]
Lead(mg/l)	ND[a]	ND[a]	ND[a]	ND[a]	0.01[b]
Chromium(mg/l)	0.02±0.01[b]	*0.02±0.01[b]	0.02±0.01[b]	ND[a]	0.05[c]

Values are reported as average mean ± standard error of triplicate determinations.Values along the rows with the different alphabetic superscripts are significantly different at p≤0.05 while values with the same alphabet are not significantly different (p≤0.05); * = 10^{-1}; ND = Not Detected

The concentrations of Ph, temperature, turbidity, silica, nitrate, nitrite, nitrite-nitrogen, ammonia, conductivity, Cd, Zn, Cu, Pb, Cr and Mn in sediment samples for all sampling locations in dry and rainy seasons are shown in Table 2. The table represents the mean values for the determined elements during both seasons.

In Table 2, the pH values indicated acidic nature of the sediments in the study locations during rainy season. Although the average mean values are within the acidic range, the sediment pH was high in dry season and low during rainy season possibly due to redox changes in the sediments and water column apart from the influence of freshwater. The pH of sediment and the interstitial water affects metal retention by developing a pH-dependent charge at a weak acidic surface and determines the extent of ion-exchange reactions. Similarly, protons and hydroxide ions compete with absorbing cations and anions respectively. pH variation in sediments influences the release or adsorption of each metal into sediment fraction. High pH lowers desorption of metals and possesses high buffering capacity against acidic conditions that may be created as a result of wastes accumulation. Association of metals with the carbonate and organic fraction are affected by pH variations. Low pH is known to influence the sorption of heavy metals by organic fraction in sediments (Oshisanya *et al.,* 2021). In this study, the total extractable fraction of the metals in the sediment samples generally increased during rainy season with a relatively lower average pH. This may be due to increase in metals complexation.Acidic pH was obtained by Tukura, *et al*., (2017) in water and sediment samples from Lagos lagoon. Although their mean value (4.9) was higher than the mean values obtained in this study, it still falls within acidic range.

In sediment samples, the highest turbidity value was obtained from Chanchaga Diver during rainy season while the lowest value (1.93NTU) was obtained in Tagwai Dam during dry season. This maybe due to higher rainfall in rainy season than in the dry season. The mean values obtained during the sampling period for both seasons were higher than the WHO standards of ≤5.00 NTU. Seasonal variations in turbidity levels in various rivers in Nigeria have been reported by Ojelabi *et al.,* 2018. High turbidity increase water temperature due to the particles absorbing sunlight. This may be part of the reason for the increased temperature values recorded in this study.

Nitrate values varied from 0.63 to 21.62 mg/l respectively. The average value for sediment samples in other locations were within acceptable limit except in Bosso dam (1.62mg/l) during rainy season. The main source of nitrate contaminant in water is through run-off from farmlands. These water bodies are surrounded by farmlands and have increased agricultural activities surrounding them. Nitrate is a major ingredient of farm fertilizer and is necessary for crop production. Nitrate can also get into water bodies from leaking of wastewater (where latrines and septic tanks are poorly sited) or other organic wastes (from animals livestock, fish and birds) into groundwater. Nitrate in rivers also result from sewage disposal systems and livestock facilities. Considering the fact that the site with high nitrate contents are agrarian, the high nitrate observed is related to runoff from farmlands due to the wide scale use of nitrogenous fertilizer [nitrogen-phosphorus-potassium (N-P-K)].

In general the nitrate values were increased during rainy season and decreased during dry season. The highest nitrate value recorded during rainy season may be attributed to heavy rainfall and land runoff. Another possible way of nitrate entry is through oxidation of ammonia form of nitrogen to nitrite and then consequently to nitrate. The low values recorded during dry period may be due to utilization by phytoplankton. The higher value of nitrite recorded during rainy season may be due to various reasons including variation in phytoplankton excretion, oxidation of ammonia and reduction of nitrate and by recycling of nitrogen and bacterial decomposition of planktonic detritus present in the environment. The nitrite sources in waters are the organic matters, fertilizers, and some of minerals. Nda *et al.,* (2019) also observed elevated nitrate pollution values in Chanchaga River during rainy season. Nitrates are higher during rainy season but reduce towards dry season because rain flushes out deposited nitrate from the near surface (Nda *et al.,* 2019).

Ammonia was observed in the sediment samples at elevated levels above the permissible limit in all locations and in both seasons ranging from 4.50mg/l – 14.52mg/l. The concentration increased during rainy season and decreased during dry season. Ammonia can enter the aquatic environment via direct means such as municipal effluent discharges and the excretion of nitrogenous wastes from animals, and indirect means such as nitrogen fixation, air deposition, and runoff from agricultural lands. The study areas are surrounded by farmlands. The agricultural activities within the areas may contribute to ammonia pollution in the water bodies as both chemical fertilizers and human manure may leach from farmlands. The observed elevated values in rainy season may be due to increased runoffs during this season.

3.2. Chemometric Models

Principal Component Analysis tools such as Score plot, loading plot, biplot, Hotelling $T^{\wedge 2}$/Residual plot where applied to the datasets. HCA was also applied to the datasets.

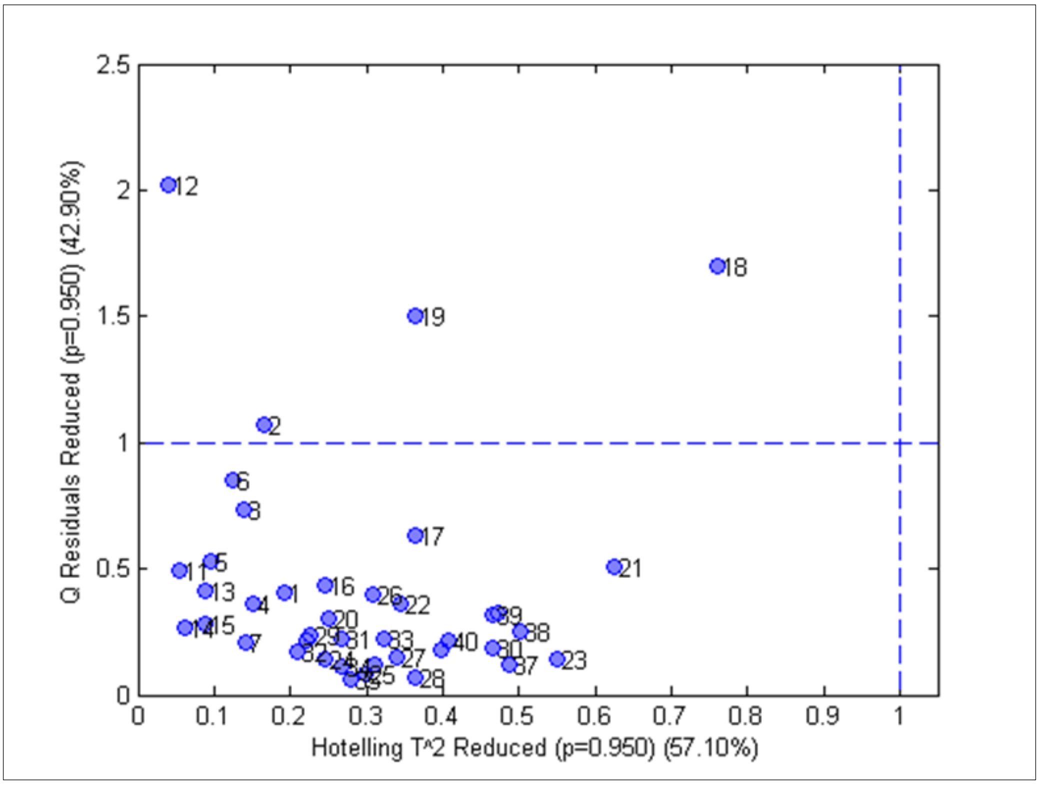

Figure 2 Hotelling T^2/Residual plot for water samples during rainy and dry seasons

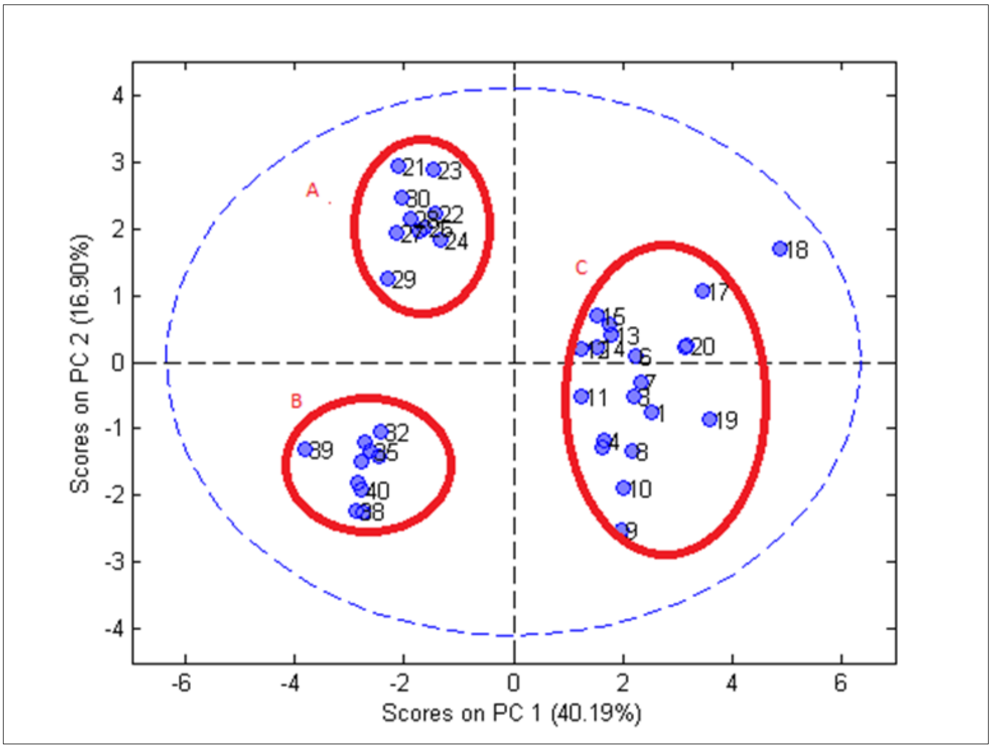

Figure 3 PCA Score plot for water samples during rainy and dry seasons

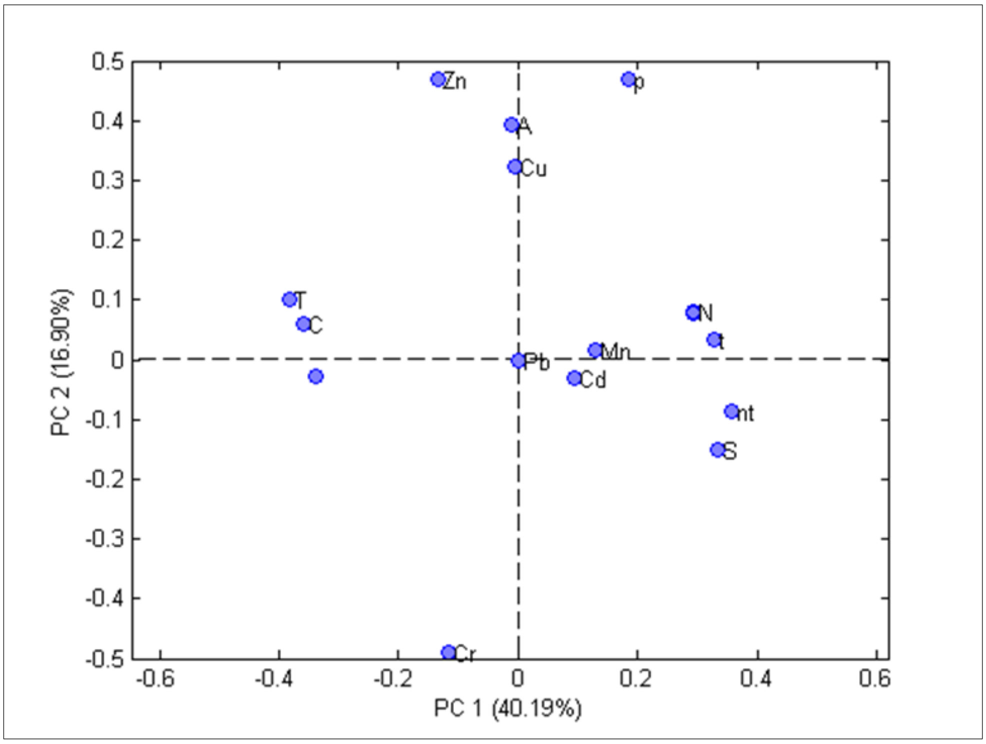

Figure 4 PCA Loadings plot for water samples during rainy and dry seasons

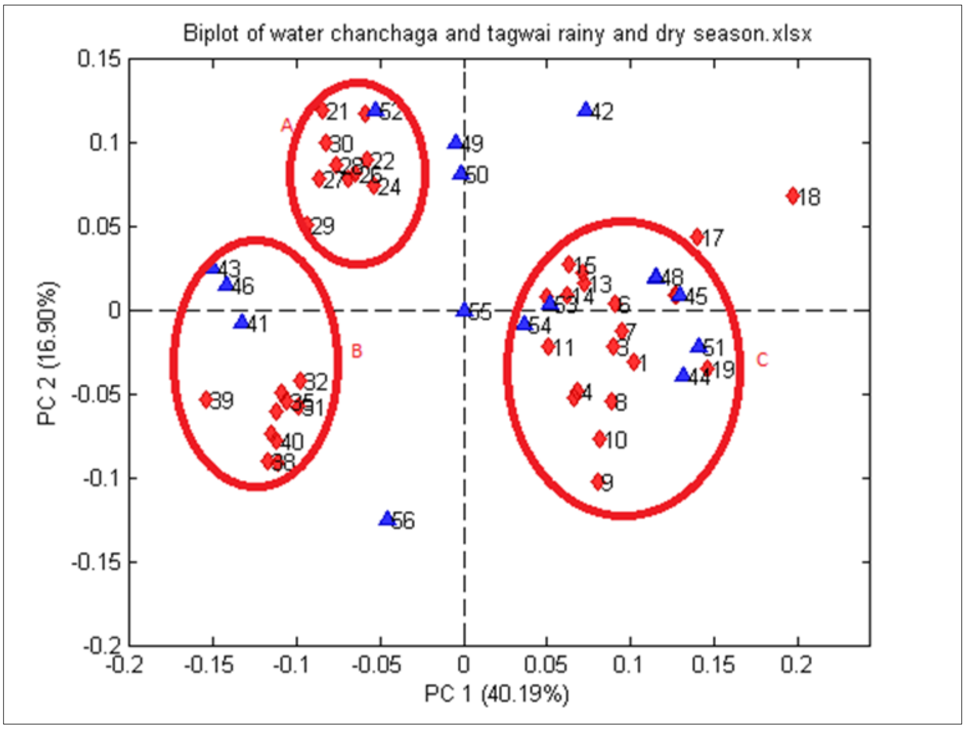

Figure 5 PCA Biplot for water samples during rainy and dry seasons

3.2.1. Principal Component Analysis (PCA) on Water Dataset

Two principal components (PCs) were selectedwhich accounted for 57.10% of the cumulative variance in the data set. The plots were obtained as follows.

The Hotelling $T^{\wedge 2}$/Residual plot shown in figure 2 is based on water samples data for water samples during rainy and dry seasons. Hotelling $T^{\wedge 2}$ enables us to visualize unusual or unique samples. Samples TWR2 (2), TWR8 (18), TWR9 (19) and CWR2 (2) were shown as unusual. They are considered as unusual because while other samples were gravitating towards (0,0) origin, TWR2 (2), TWR8 (18), TWR9 (19) and CWR2 (2) stood out. The water samples (12, 18, 19) were collected from Tagwai Dam during rainy while sample 2 was collected from Chanchaga River during rainy season. These samples have extreme levels of ammonia, nitrate and Cr concentration in them and that makes them unusual related to other samples. Sample 2 was the only sample from Chanchaga River with ammonia and Cr detected in it.

Score plot reveals groupings based on the samples hydrogeological origin (Salau *et al.,* 2020). Figure 3 shows the Scores plot for water samples, three clusters were identified for water samples during rainy and dry seasons. Group A comprises water samples of Chanchaga River hydrogeological origin during dry season. Group B comprised water samples of Tagwai Dam hydrogeological origin during dry season and they are characterized by Cr and nitrate pollution, and high conductivity values.Group C comprises samples collected from Chanchaga River and Tagwai Dam during rainy season. Samples in group C are characterized by elevated nitrate pollution. Zn and Cr were also detected in these samples.

Loadings plot shows the significance of the variables in differentiating the samples. It gives information of signature variable for study sample (Unaeze *et al.,* 2021). Loadings plot shown in Figure 4is for water samples during rainy and dry seasons. The plot shows pH, Cu, Mn, Nitrite-Nitrogen, ammonia and turbidity as the signature elements for the samples. The prominent variables are significant in differentiating the samples. Ammonia was not detected in samples from Chanchaga during rainy season but was detected at high concentration in Tagwai Dam. However, it decreased in Chanchaga River and increased in tagwai dam during dry season, this explains why it was selected as being prominent in differentiating the samples. Also, looking at the results, nitrate was not detected at in samples from Chanchaga River during rainy season but was recorded at high values in Tagwai Dam during both seasons. Similarly, Mn was detected only in Chanchaga during rainy season. PC1 accounts for 40.91% of the total variance and It showed a positive loading on silica, nitrate, nitrite as nitrogen, Mn, pH Cd and turbidity.pH and Ammonia were the prominent variable to PC1 because they had the highest component loading. Positive loading on nitrate, ammonia , turbidity, nitrite as nitrogen as shown indicates there presence in the samples and may be due to run-off from farmlands containing fertilizers used in agriculture. PC2 showed positive loadings for Zn, conductivity and temperature, and accounts for 16.90% of the total variability in the data set. Negative loading of Cr in PC 2 reflects their reduction due to dilution process during rainy season (Salau*et al.* 2020).

Biplot model, which is a simultaneous plot of both score and loadings, is shown in figure 5 for water samples during rainy and dry seasons. It shows three groups of samples with characterizing variables. Group A is characterised by preponderance of ammonia and Zn pollutants. Group B is characterised by considerable temperature values while group C is characterized by prominent nitrate and Cr concentration values. Similar observation was made from the scoresplot and dendogram.

3.2.2. Principal Component Analysis (PCA) in Sediment Dataset

Figure 6 is a curve showing theeigenvalue plot for sediment samples during rainy and dry seasons.Two principal components (PCs) were extracted which captured 22.21% of the total variation in data set.

Figure 7 represents the Hotelling $T^{\wedge 2}$/Residual plot for sediment samples during rainy and dry seasons. It revealed samples TSR1 (1), TSR 6 (6), CSR 1 (11), CSR2 (12), CSR3 (13) and TSR1 (21) as the outliers having unique pollution. Samples 1 and 6 were collected from Chanchaga River during rainy season. Samples 12, 13 and 11 were collected from Tagwai Dam during rainy season while sample 21 was collected from Chanchaga River during dry season. Samples 1, 6, 11, 12, and 13 all have extreme Cd, nitrate, nitrite and Mn pollution in them. Cr was also detected in the outliers except for samples 1 and 21. These samples were collected within the river bank with on-going irrigation farming. The observed increased pollutants level could be attributed to fertilizers, pesticides or other agrochemicals applied on the crops being washed directly into the water bodies.

Figure 8 shows the score plot for sediment samples collected in rainy and dry seasons. Two clusters were identified for sediment samples during rainy and dry seasons. Cluster A comprises water samples collected from Chanchaga River and Tagwai Dam during dry season. These samples are characterized by reduced conductivity, silica and nitrate levels.

Samples in cluster B were collected from both locations during rainy season. Cluster B samples also have elevated nitrate and ammonia levels. The samples in this cluster are characterized by acidic pH and extreme Cd concentration values ranging from 0.02-0.07mg/l which is much higher than the WHO threshold of 0.003mg/l. This may be due to sedimentation as suggested by Cotman *et al.,* (2019). Mohammad *et al.,* (2018) got similar result in Sokoto river. The discharge of heavy metals into rivers by domestic and industrial activities causes their rapid association with particulates and incorporation into sediments.

Figure 9 represents the loadings plot for sediment samples during rainy and dry seasons. The plot shows Nitrate, Nitrite as Nitrogen, Cd, silica and turbidity as the most prominent variables. PC1 accounts for 42.81% of the total variance and It showed a positive loading on Cd, Cr, Cu, Zn, conductivity, ammonia, silica and temperature. Positive loading on nitrate, nitrite as nitrogen as shown indicates there presence in the samples and may be due to run-off from farmlands containing fertilizers used in agriculture. PC2 showed positive loadings for Pb, Mn and pH, and accounts for 22.61% of the total variability in the data set. There was no negative loading for any of the variables.

Figure 10 is a Biplot for sediment samples during rainy and dry seasons with Principal Component 2 (PC2) at cumulative variance of 22.61% plotted on the x-axis and Principal Component 1 (PC1) at 42.81% cumulative variance on the y-axis. It shows two groups of samples with common variables or similar pollution status. The biplot shows group A to have Ph, nitrite, Mn and Pb in common. Group B is characterised by Cd, Cr, conductivity, temperature, turbidity, ammonia, nitrate, silica, Cu, Zn and nitrite-nitrogen as their common variable.

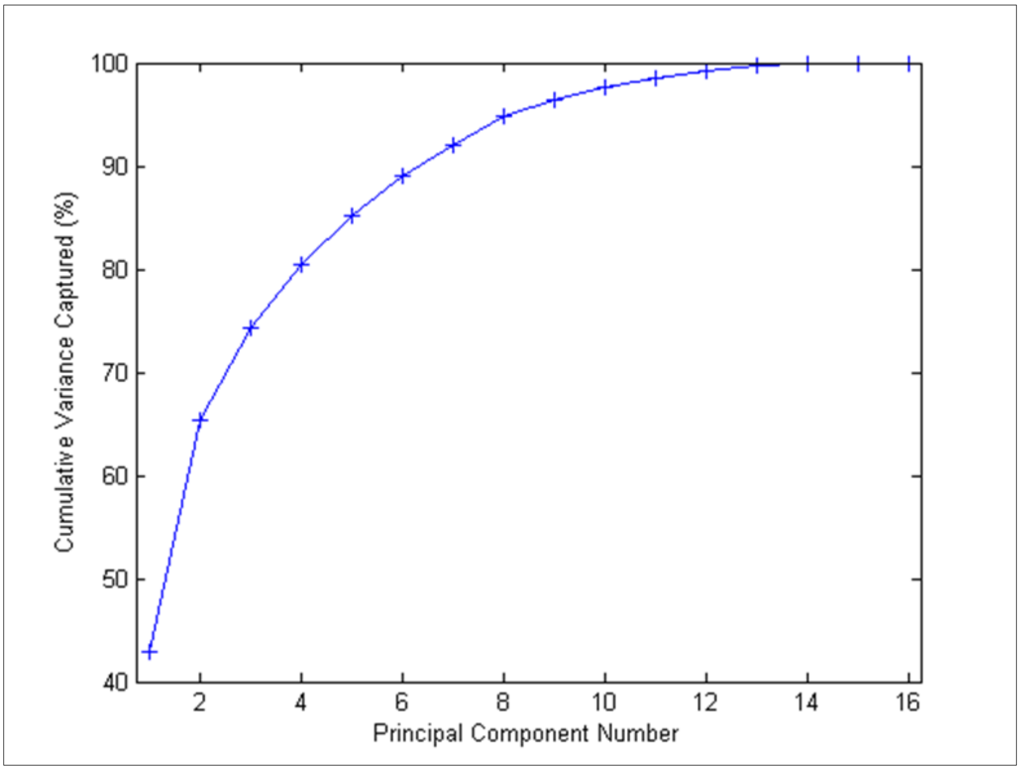

Figure 6 PCA Eigen value plot for sediment samples during rainy and dry seasons

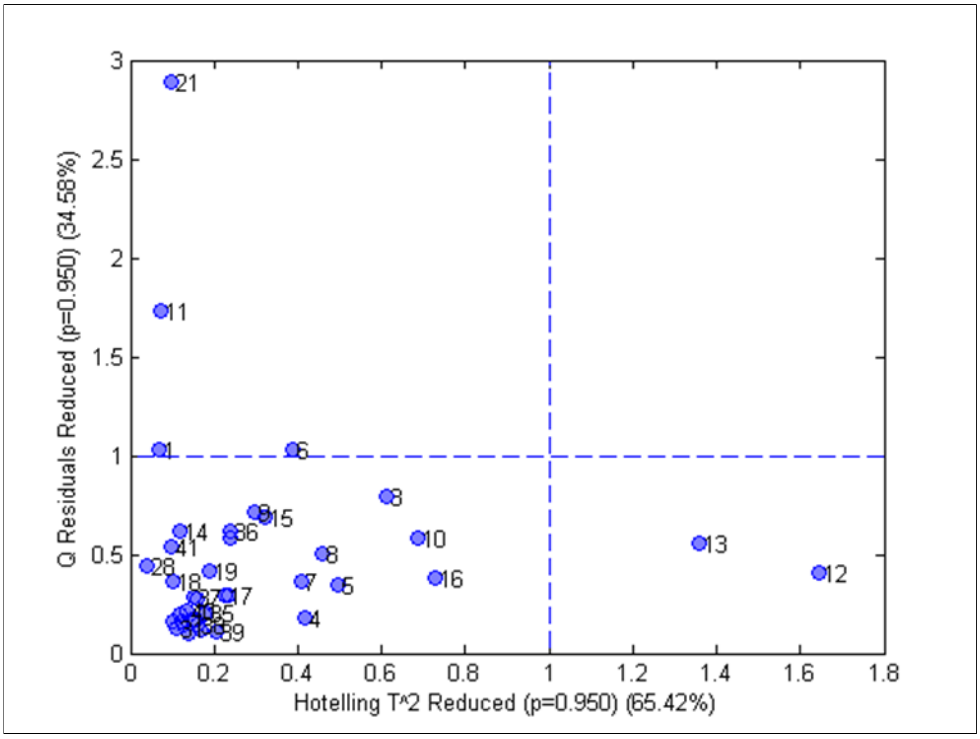

Figure 7 Hotelling T^2/Residual plot for sediment samples during rainy and dry seasons

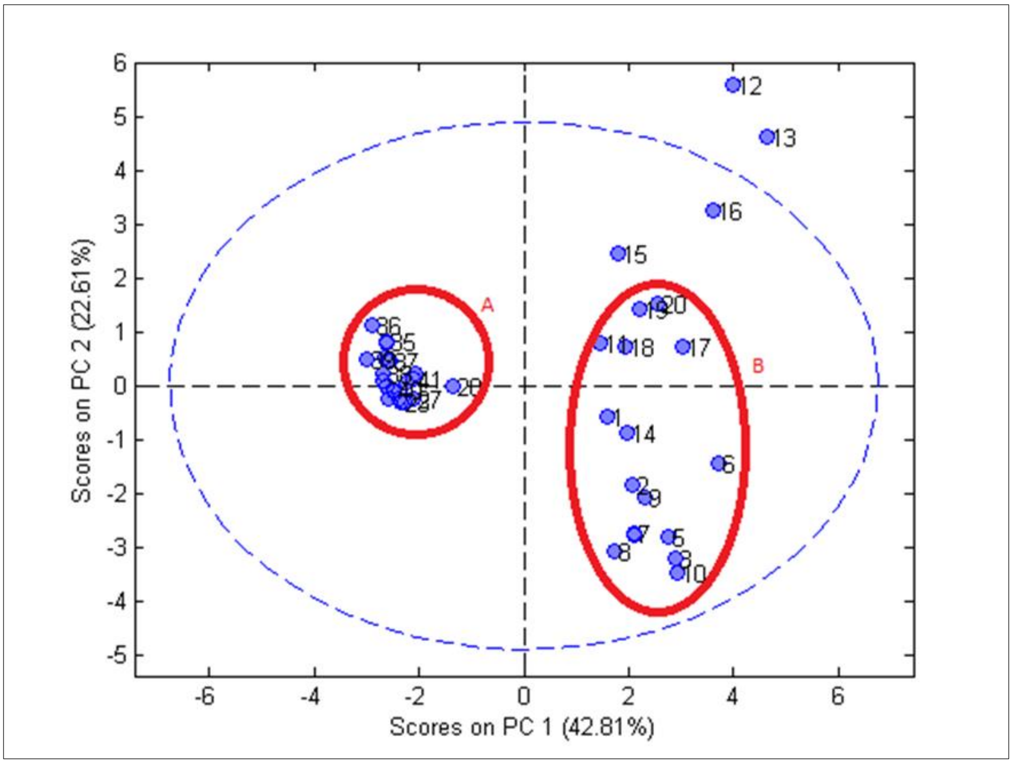

Figure 8 PCA Score plot for sediment samples during rainy and dry seasons

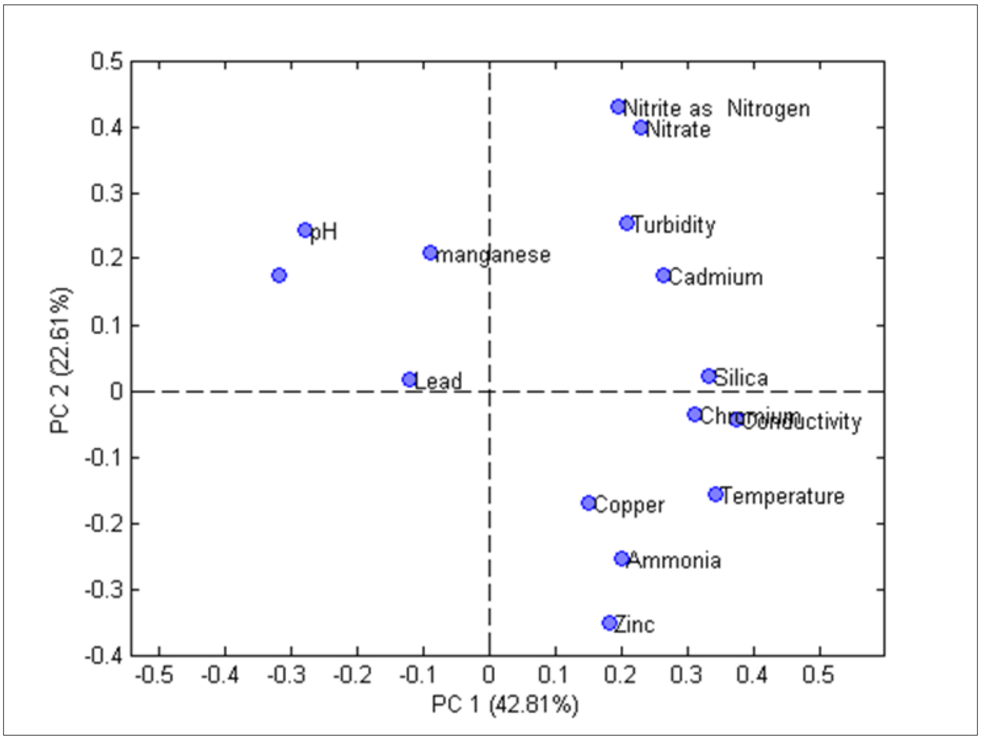

Figure 9 PCA Loadings plot for sediment samples during rainy and dry seasons

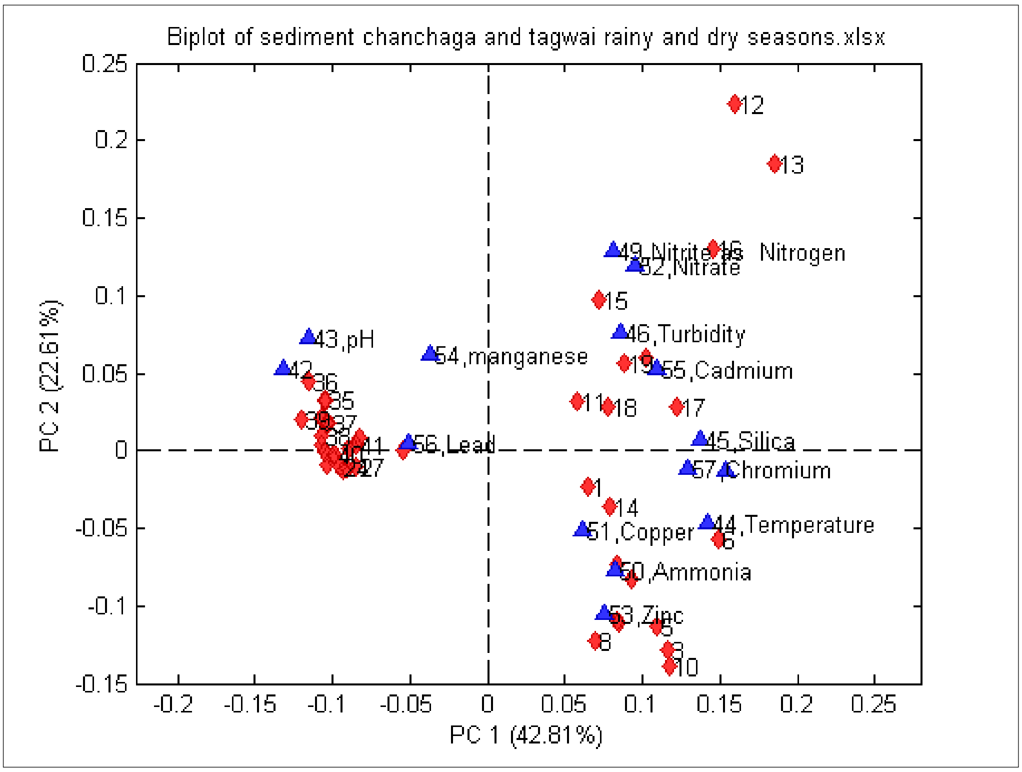

Figure 10 PCA Biplot for sediment samples during rainy and dry seasons

3.2.3. Hierarchical Cluster Analysis on Water and Sediment Data Set

Hierarchical Cluster Analysis groups samples based on their similarities and dissimilarities. Four samples groups were identified for the water samples data set while three groups were identified for sediment samples.

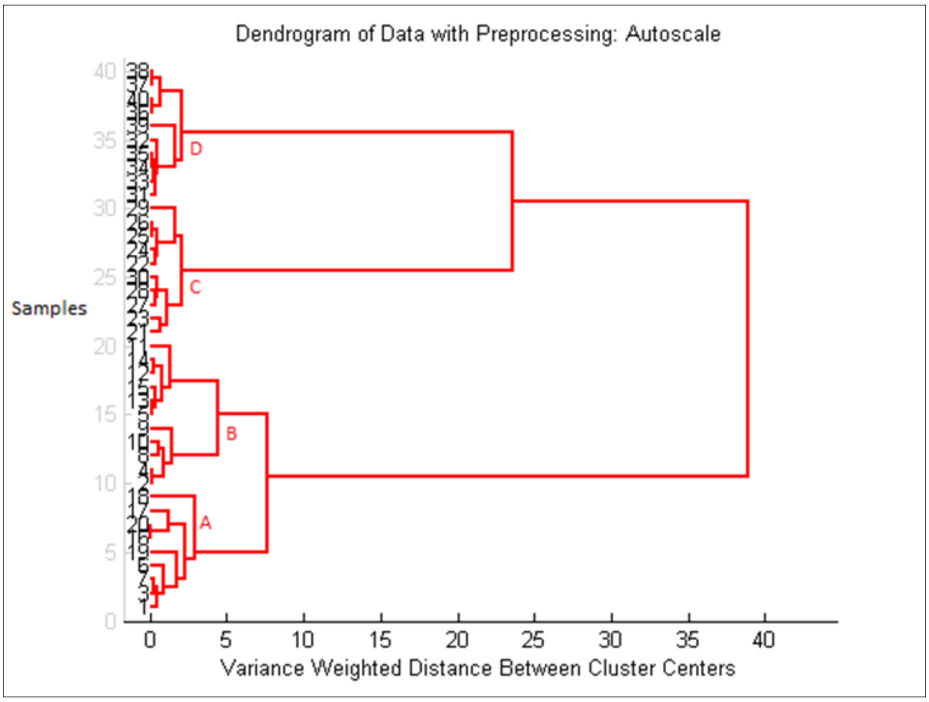

Figure 11 HCA Dendogram for water during rainy and dry seasons

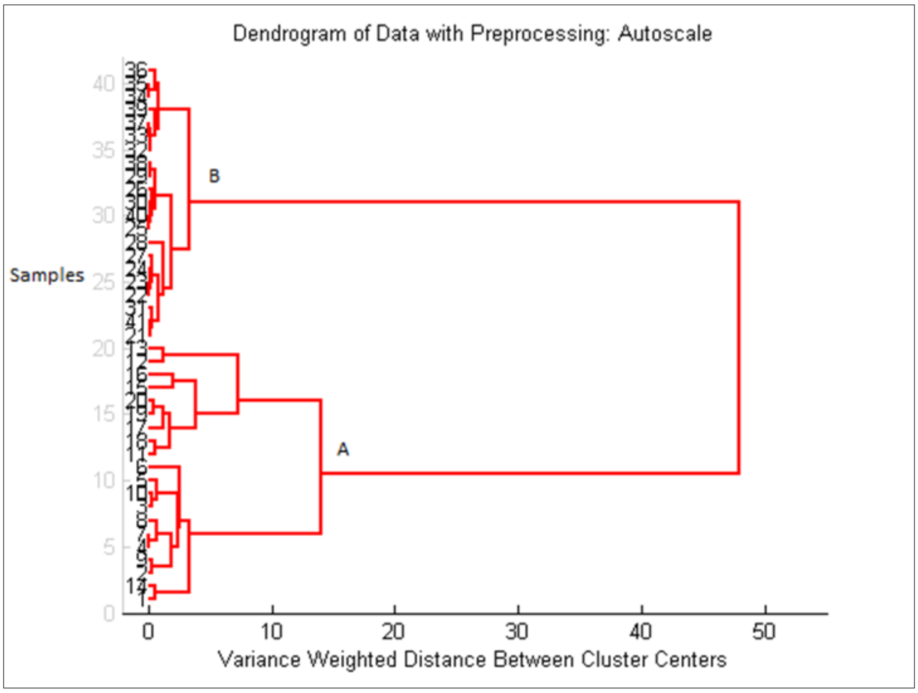

Figure 12 HCA Dendogram for sediment during rainy and dry seasons

Hierarchical Cluster Analysis (HCA) of Water Dataset

Figure 11 represents HCA Dendogram for water during rainy and dry seasonsshowing the fourty samples plotted on the x-axis and variance weighted distance between cluster centers on the y-axis. It shows different pairs or groups of samples with common variables or characteristics.

The clustering procedure highlighted groups in which the sites have similar characteristics and natural source types. The sample pairs in each of the groups had similar pollution status. Cluster A comprises pairs of samples from both study locations during rainy season and are considered as samples with elevated levels of nitrate and high turbidity values. Common source of pollution in these sites include waste water effluents and run off from agricultural lands and landfills. The nitrate sources in waters are the wastewaters, organic nitrogen and the fertilizers used in agriculture. Cluster B comprises sample pairs from tagwai during rainy season. Cr was detected in these samples. Cluster C contains sample pairs with increased conductivity values and also elevated levels of ammonia. These samples were collected from chanchaga river during dry season. They also showed Zn concentration in them. Cluster D contains pairs of samples from tagwai dam during dry season. These samples have increased Cr in them. Their conductivity values were also reduced.

Hierarchical Cluster Analysis (HCA) of Sediment Dataset

Figure 12 represents HCA Dendogram for sediment during rainy and dry seasonsshowing the fourty samples plotted on the x-axis and variance weighted distance between cluster centers on the y-axis. It shows different pairs or groups of samples with common characteristics.

For the sediment samples, the dendogram obtained by Ward's method is shown in Figure 12. The resulted dendogram grouped all 40 sediment samples into two (2) significant clusters. Group A contains samples with low pH values ranging from 3.80 – 5.70. Extreme Cd and nitrate pollution was also detected in group A samples. They also had Cr concentration in them at reduced level. The increased nitrate content of sediment during the rainy season can be considered an indication of increased pollution of from organic sources and increased agricultural activities during this period. Group B comprises samples with elevated Mn and Cu concentration. These samples were collected from Tagwai dam and chanchaga river during dry season.

3.2.4. Correlation Analysis of Water and Sediments Datasets

Correlation analysis is about the interdependence of the variables. It reveals how the presence or change in one variable affects the presence of another variable in the samples.

Table 3 Correlation Analysis of water samples during rainy and dry seasons

	p	**T**	**S**	**t**	**C**	**n**	**N**	**A**	**Cu**	**nt**	**Zn**	**Mn**	**Cd**	**Pb**	**Cr**
p	1														
T	-0.32384	1													
S	0.202572	-0.82719	1												
t	0.434742	-0.76342	**0.611365**	1											
C	-0.29148	**0.839014**	-0.70046	-0.68438	1										
n	0.350203	-0.53524	0.428222	0.356502	-0.60646	1									
N	0.359203	-0.54229	0.427846	0.365169	-0.60789	**0.999364**	1								
A	0.370009	0.191611	-0.30982	-0.07217	-0.09403	0.300643	0.302575	1							
Cu	0.350509	0.039342	-0.10435	-0.1948	-0.02437	0.04757	0.051687	0.230678	1						
nt	0.239448	-0.79421	**0.655775**	**0.582839**	-0.75358	**0.806177**	**0.806747**	-0.07972	-0.06189	1					
Zn	0.39957	0.405529	-0.34199	-0.07262	0.433649	-0.30903	-0.30712	0.221814	0.198911	-0.42539	1				
Mn	0.206821	-0.40843	0.424931	0.445071	-0.24856	-0.22347	-0.21748	-0.15654	0.003359	0.04787	0.092488	1			
Cd	0.140989	-0.21283	0.178886	0.168732	-0.2435	0.119022	0.125967	-0.04002	0.232907	0.05415	-0.22475	0.074125	1		
Pb	0.069012	0.5382	-1.42091	0.21682	0.33986	0.220197	0.10932	-0.83922	0.3274	0.13249	0.44271	-0.31974	**0.73921**	1	
Cr	-0.60196	0.160122	-0.12183	-0.31296	0.103182	-0.19457	-0.20118	-0.30448	-0.26662	-0.14132	-0.5508	-0.15633	0.057146	#DIV/0!	1

C =Conductivity; P = pH; t = Turbidity; S = Silica; N = Nitrite as N_2; A = Ammonia; nt = Nitrate; n = Nitrite; T = Temperature ;

Table 4 Correlation Analysis of sediment samples during rainy and dry seasons

	pH	**T**	**S**	**t**	**C**	**n**	**N**	**A**	**Cu**	**nt**	**Zn**	**Mn**	**Cd**	**Pb**	**Cr**
pH	1														
T	-0.77454	1													
S	-0.57961	0.763123	1												
t	-0.15017	0.330537	0.445564	1											
C	-0.77339	0.919742	0.841918	0.450189	1										
n	-0.00586	0.232199	0.397607	0.676513	0.424772	1									
N	-0.00644	0.232979	0.398169	0.674039	0.425512	0.99994	1								
A	-0.37124	0.56985	0.401221	0.136399	0.518513	-0.1604	-0.16213	1							
Cu	-0.22781	0.416249	0.299062	0.012346	0.36746	-0.03769	-0.0377	0.472154	1						
nt	-0.11238	0.313329	0.543002	0.627621	0.530318	0.927821	0.928193	-0.09807	-0.03036	1					
Zn	-0.61667	0.664151	0.238012	0.020887	0.519318	-0.21469	-0.21597	0.539649	0.340682	-0.19361	1				
Mn	0.555558	-0.34511	-0.13902	-0.11109	-0.19898	0.098469	0.097868	-0.01919	-0.00993	0.129118	-0.37102	1			
Cd	-0.31978	0.450448	0.604058	0.340496	0.621163	0.552477	0.551754	0.32965	0.257007	0.637645	-0.00687	0.21396	1		
Pb	0.236275	-0.32506	-0.34218	-0.16386	-0.34239	-0.11398	-0.11408	-0.12244	-0.0398	-0.13776	-0.17256	0.050435	-0.11578	1	
Cr	-0.57485	0.750039	0.720554	0.317668	0.776855	0.330214	0.332307	0.493364	0.343593	0.450727	0.399296	-0.11251	0.516138	-0.1041	1

Pearson correlation value at 95% confidence level or 0.05% significant level; C =Conductivity; P = pH; t = Turbidity; S = Silica; N = Nitrite as N2 ; A = Ammonia; nt = Nitrate; n = Nitrite; T = Temperature

Correlation Analysis of Water Dataset

Correlation analysis of the data was carried out using Microsoft Excel Add-ins. Table 3 represents the correlation output of the parameters determined in the water samples during rainy and dry seasons. The result shown in Table 3 suggests that most of the variables were negatively correlated. However, Strong positive relationship is found among conductivity-temperature, silica – turbidity and nitrate, nitrate – turbidity, nitrate – nitrite and nitrite as nitrogen, Cd - Pb which was also observed in PC2.pH showed weak negative correlation with temperature (-0.32384), conductivity (-0.29148) and Cr (-0.60196). This means that changes in pH of water are associated with those in temperature, conductivity and Cr concentrations. A negative correlation implies that a decrease in pH is related to an increase in temperature, conductivity and Cr levels in the water bodies and vice versa. It implies that as water becomes more acidic, more Cu and Cr are dissolved into it. A weak negative correlation between pH-temperature (- 0.365), pH-conductivity (-0.359) and pH-Cu (-0.249) were found by Daraigan *et al.* (2017). This is similar to the findings of this study which indicates a weak correlation instead.

Turbidity correlated positively with nitrate and silica. This implies that the presence of nitrate and silicais associated with turbidity of the water bodies. Temperature has a strong positive correlation with conductivity (0.832). This means that increase in temperature is associated with increased conductivity. Strong positive correlations were found between nitrite and nitrite as nitrogen (0.999) and nitrate and nitrite as nitrogen (0.807).

Correlation Analysis of Sediment Dataset

Table 4 represents correlation analysis of sediment samples during rainy and dry seasons. Temperature showed strong positive correlation for silica (0.763), conductivity (0.919), ammonia (0.569), Cr(0.750) and Zn (0.664). This means that changes in temperature of water are associated with those in silica, conductivity, and Zn concentrations. A positive correlation implies that an increase in temperature is related to an increase in silica, conductivity, and Zn levels in the water bodies and vice versa. Silica showed a strong positive correlation with conductivity (0.877), nitrate (0.543), Cr (0.720) and Cd (0.604). Turbidity strongly correlated positively with nitrate, nitrite and nitrite as nitrogen. This implies that increase in the concentration of nitrate, nitrite and nitrite-nitrogen increases the turbidity of the water bodies. Conductivity exhibited strong positive correlation with Cd. This also implies that the presence of Cd associated with the conductivity of the sediment samples. Nitrite strongly correlated positively with nitrate (0.919) and nitrite as nitrogen (0.999). This means that increased nitrite level leads to increase in nitrate and nitrite as nitrogen in the water bodies.

Table 5 Correlation Analysis of water samples during rainy and dry seasons

	pH	**T**	**S**	**t**	**C**	**n**	**N**	**A**	**Cu**	**nt**	**Zn**	**Mn**	**Cd**	**Pb**	**Cr**
pH	1														
T	-0.77454	1													
S	-0.57961	**0.763123**	1												
t	-0.15017	0.330537	0.445564	1											
C	-0.77339	**0.919742**	**0.841918**	0.450189	1										
n	-0.00586	0.232199	0.397607	**0.676513**	0.424772	1									
N	-0.00644	0.232979	0.398169	**0.674039**	0.425512	**0.99994**	1								
A	-0.37124	**0.56985**	0.401221	0.136399	**0.518513**	-0.1604	-0.16213	1							
Cu	-0.22781	0.416249	0.299062	0.012346	0.36746	-0.03769	-0.0377	0.472154	1						
nt	-0.11238	0.313329	**0.543002**	**0.627621**	**0.530318**	**0.927821**	**0.928193**	-0.09807	-0.03036	1					
Zn	-0.61667	**0.664151**	0.238012	0.020887	**0.519318**	-0.21469	-0.21597	**0.539649**	0.340682	-0.19361	1				
Mn	**0.555558**	-0.34511	-0.13902	-0.11109	-0.19898	0.098469	0.097868	-0.01919	-0.00993	0.129118	-0.37102	1			
Cd	-0.31978	0.450448	**0.604058**	0.340496	**0.621163**	**0.552477**	**0.551754**	0.32965	0.257007	**0.637645**	-0.00687	0.21396	1		
Pb	0.236275	-0.32506	-0.34218	-0.16386	-0.34239	-0.11398	-0.11408	-0.12244	-0.0398	-0.13776	-0.17256	0.050435	-0.11578	1	
Cr	-0.57485	**0.750039**	**0.720554**	0.317668	**0.776855**	0.330214	0.332307	0.493364	0.343593	0.450727	0.399296	-0.11251	**0.516138**	-0.1041	1

C =Conductivity; P = pH; t = Turbidity; S = Silica; N = Nitrite as N_2; A = Ammonia; nt = Nitrate; n = Nitrite; T = Temperature

4. Conclusion

This work was undertaken to evaluate the pollution status of Chanchaga River and Tagwai Dam. In this study, Cd concentration heightened in the sediment samples (0.02-0.03 mg/dm^3) during the rainy season. Increased Zn concentration (0.12 mg/dm^3)was recorded in Chanchaga River during rainy season in the sediment samples, and also during dry season (0.02 mg/dm^3) in the water samples.

The concentrations of ammonia (0.41-14.33 mg/dm^3), nitrate (21.62 mg/dm^3), nitrite-Nitrogen (0.04-0.13 mg/dm^3) and turbidity (15.33-80.86 mg/dm^3) were above the WHO limit (0.40, 10.00, 0.04 and 5.00 mg/dm^3respectively) in the water and sediment samples in the rainy and dry season.

The Hotelling $T^{\hat{}2}$/Residual plot unveiled samples TWR2 (2), TWR8 (18), TWR9 (19) and CWR2 (2), collected from Tagwai Dam and Chanchaga River during rainy season as the unusual water samples. Samples TSR1 (1), TSR 6 (6), CSR 1 (11), CSR2 (12), CSR3 (13) and TSR1 (21) were revealed as the unusual sediment samples. The Score plot showed three groups for the water samples based on their hydrogeological origin, and two groups for the sediment samples. The loadings plot showed pH, Cu, Mn, Nitrite-nitrogen, ammonia, turbidity, nitrate, Cd and silica as the signature variables in the water and sediment samples. The biplot showed three groups of samples with ammonia, Zn, nitrate, Cr and temperature as their characterising variables. The Hierarchical analysis disclosed that sample pairs from Tagwai Dam during rainyand dry seasons had elevated Cr concentration and reduced conductivity values while samples fromChanchaga River in the dry season had increased conductivity values, Zn and elevated levels of ammonia.

The correlation analysis of the water samples dataset showed that changes in pH of water are associated with those in temperature, conductivity and Cr concentrations. It also revealed that the presence of nitrate and silicais associated with turbidity of the water bodies. The increase in temperature also associated with increased conductivity. The correlation analysis of the sediment samples revealed that changes in temperature are associated with those in silica, conductivity, and Zn concentrations. Silica showed a strong positive correlation with conductivity (0.877), nitrate (0.543), Cr (0.720) and Cd (0.604). It was seen that increase in the concentration of nitrate, nitrite and nitrite-nitrogen increases the turbidity of the water bodies. Also, increased nitrite level leads to increase in nitrate and nitrite as nitrogen in the water bodies.

The present investigation clearly indicates that the water and sediments from Chanchaga River and TagwaiDam is contaminated with Cd, Cr, nitrate, ammonia, nitrite-nitrogen and Znthe water bodies were also highly turbid. The concentration of the recorded pollutants increased during rainy season. The result observed in this study suggests that agricultural activities and waste disposal are the major sources of pollution in the water bodies. Consequently, there is a dire need to reduce/regulate the anthropogenic sources of pollution in the study area

Compliance with ethical standards

Disclosure of conflict of interest

There is no conflict of interest to declare.

References

[1] Adelekan, B. & Abegunde, K. (2016). Heavy metal contamination of soil and ground water at automobile mechanic village in Ibadan, Nigeria. International Journal of the Physical Sciences. 6(5),1045-1058.

[2] Abliz, A., Shi, Q. & Keyimu, M. (2018). Spatial distribution, source, and risk assessment of soil toxic metals in the coal-mining region of northwestern China. Arab Journal of Geoscience,11,793

[3] Agatha, A. N. (2017). Levels of Some Heavy Metals in Tissues of Bonga Fish, Thmallosafimbriata from Forcados River, Journal of Applied Environmental Sciences.1: 44-47.

[4] Agbaire P.O. & Obi, C.G., (2009). Seasonal Variations of Some Physico-Chemical Properties of River Ethiope Water in Abraka, Nigeria. Journal of Applied Sciences and Environmental Management. 13, 10.4314/jasem.v13i1.55265

[5] Ahmad,F., Fakhruddin, A. N. M., Toufick M. D., Nasima K., Tanzir A., Mahfuzur R. & Abu T. M. A. (2018). Spatial distribution and source identification of heavy metal pollution in roadside surface soil. Ecological Processes. Springer Journal 5:2 DOI 10.1186/s13717-016-0045-5.

[6] Akan, J.C., Mohmoud, S., Yikala, B.S. & Ogugbuaja, V.O. (2018) Bioaccumulation of some heavy metals in fish samples from River Benue in Vinikilang, Adamawa State, Nigeria. American Journal of Analytical Chemistry. 3(11), 727-736

[7] Alexandra V. Kulinkina, Jeanine D. Plummer, Kenneth K.H. Chui, Karen C. Kosinski, Theodora Adomako-Adjei, Andrey I. Egorov, Elena N. (2018). Physicochemical parameters affecting the perception of borehole water quality in Ghana. *International Journal of Hygiene and Environmental Health,* 220, (6), 990-997

[8] Alfred, S. L., Khumoetsile, B.M. & Gilbert, K.G. (2018). Assessment of Heavy Metal Enrichment and Degree of Contamination around the Copper-Nickel Mine in the Selebi Phikwe Region, Eastern Botswana. Environmental and Ecology Research, 1, 32-40.

[9] Al-osman, M., Yang, F. & Massey, I.Y. (2019). Exposure routes and health effects of heavy metals on children. Biometals32, 563–573.

[10] Aminayanaba, O. A.&Lawal, O. (2017). Investigation of relationship between sediment characteristics and heavy metals across seasons in the lower Focardos River, Nigeria. Journal of Applied Science and Environmental Management 21(1):208–221

[11] Andréfouët, S., Eghbert, E. A.&Sylvain, O. (2018). Challenges in rendering Coral Triangle habitat richness in remotely sensed habitat maps: The case of Bunaken Island (Indonesia). Marine Pollution Bulletin. 131; 72-82

[12] Apexa, P. & Bharti P.(2015). Analysis of physicochemical parameters of salt pans at Newport and Nari situated around Bhavnagar Coas. Journal of Ecobiotechnology, 7:1-9.

[13] APHA, (2012). Standard Methods for the Examination of Water and Wastewater. American Public Health Association, Washington.

[14] ASTM (2012) D1688-12, Standard Test Methods for Copper in Water, ASTM International, West Conshohocken, Pa, USA.

[15] ASTM (2012) D1691-12, Standard Test Methods for Zinc in Water, ASTM International, West Conshohocken, Pa, USA.

[16] ASTM (2012) International, ASTM D1068-12, Standard Test Methods for Iron in Water, ASTM International, WestConshohocken, Pa,

[17] ASTM (2012) International, ASTM D3559-12, Standard Test Methods for Lead in Water, ASTM International, West Conshohocken, Pa, USA

[18] ASTM (2012). International, ASTM D3557-12, Standard Test Methods for Cadmium in Water, ASTM International, West Conshohocken.

[19] ASTM (2012). International,D1687-12, Standard Test Methods for Chromium in Water, ASTM International, West Conshohocken, Pa, USA.

[20] ASTM International, ASTM D3557-12, Standard Test Methods for Cadmium in Water, ASTM International, West Conshohocken, Pa, USA, 2012, http://www.astm.org/.

[21] Asuquo F. E. (2019). Physiocochemical characteristics of anthrogenic pollution sources of surface waters of Calabar river, Nigeria. Global J. Pure Appl. Sci. 5: 595-600

[22] Awofolu, O.R., Okedeyi, O.O. & Dube, S. (2017). Assessing the enrichment of heavy metals in surface soil and plant (*Digitaria eriantha*) around coal-fired power plants in South Africa. *Environmental Science Pollution Resolution*, 21,4686–4696

[23] Ayari, J., Agnan, Y. & Charef, A. (2017). Spatial assessment and source identification of trace metal pollution in stream sediments of Oued El Maadene basin, Northern Tunisia. Environmental Monitor Assessment 188:397.

[24] Baghed V. S., Gopal K., Dwivedi S. &Tripathi, R. D. (2019). Bacterial indicators of faecal contamination of the Gangetic river system right at its source. Ecological Indicators 5: 4- 56. Biological Oxygen Demand. Encyclopedia of Public Health. . Encyclopedia.com. 27 Aug. 2019 <https://www.encyclopedia.com>.

[25] Barone, G. Dambrosio, A., Storelli, A., Garofalo, R., Busco, V. P. &Storelli, M. M. (2018). Estimated Dietary Intake of Trace Metals from Swordfish Consumption: A Human Health Problem. Toxics 6, 22.

[26] Bartoli, G., Papa, S., Sagnella,E. &Fioretto, A. (2017). Heavy metal content in sediments along the Calore river: relationships with physical–chemical characteristics. Journal of Environmental Management, 1-6.

[27] Begum, F., Karamat, A. Muhammad, Z., K. Sultan, I., Haibat, A. Sher, A. &Sameena, M. (2018). Effect of landslide-induced flood on soil physico-chemical properties in the mountainous landscape, Northern Pakistan. Fresenius Environmental Bulletin. 27(12), 8128-8132.

[28] Benjamin, A. (2019). Impact Assessment of Human Activities and Seasonal Variation on River Benue, within Makurdi Metropolis, Available:https://www.academia.edu/4532319/Impact_Assessment_of_Human_Activities_and_Seasonal_Variation_on_River_Benue_within_Makurdi

[29] Biancolillo, A. & Lessandra, M. (2018). Chemometric Methods for Spectroscopy-Based Analysis. Frontiers in Chemistry. 6;576. DOI=10.3389/fchem.2018.00576

[30] Bleiziffer, R. (2017) Classical Chemometrics Methods Applied for Clinical Data Analysis. International Conference on Advancements of Medicine and Health Care through Technology, Cluj-Napoca, Romania. IFMBE Proceedings, 59. Springer, Chemistry

[31] Bojarczuk, A., Jelonkiewicz, Ł. & Lenart-Boroń, A. (2018). The effect of anthropogenic and natural factors on the prevalence of physicochemical parameters of water and bacterial water quality indicators along the river Białka, southern Poland. *Environmental Science Pollut Res*25,10102–10114. https://doi.org/10.1007/s11356-018-1212-2

[32] Bolawa, O. E.& Yusuff., A. F. (2019). Determination of heavy metals in imported frozen fish and local fresh fish obtained from different markets in Lagos State, Nigeria. *UNILAG Journal of Medicine, Science and Technology*, 6(1), 33-44.

[33] Chen, W., Wang, M., Liu, R.& Peng, C.(2017). Effects of urbanization on heavy metal accumulation in surface soils. Journal of Environmental Sciences. 64; DO - 10.1016/j.jes.2017.11.026

[34] Cherh, Y. M. &Jih-Gaw L., M. B. (2018). An Overview of the Effects of Heavy Metals Content in Wastewater on Anammox Bacteria. Advances in Environmental Studies. 2(1). 9-15.

[35] Chukwuemeka, V. I.,. Jimoh, E. A, Olajide, K. O., Auta, Y. I., Auta, H. S., &O. F. Erhabor. (2020). Spatio-Temporal Variation Level of Heavy Metals in Surface Water and Sediment in Tagwai Lake, Minna, Nigeria. Tropical Freshwater Biology, 29 (1) (2020) 123-131

[36] Cotman M; Zagorc-Koncan J. and Droic A. (2019). Study of impacts of treated wastewater to the Krka River, Slovenia. Water Science Technology; 44(6): 47-54.

[37] Cristian, A. D., Barbara, M. M. R., Alexandre, A., Enrique, A. C. &José, L. B.(2020). Trace elements in trophic webs from South Atlantic: The use of cetaceans as sentinels, Marine Pollution Bulletin, 10.1016/j.marpolbul.110674, 150, (110674).

[38] Dalu, T., Wasserman, R.J. &Wu, Q. (2018). River sediment metal and nutrient variations along an urban–agriculture gradient in an arid austral landscape: implications for environmental health. Environmental Science Pollution Resolution,25, 2842–2852

[39] Daniel, G.,Jânio, S.,Santos,G., Bruno, L., Ferreira,R. &Maggio, M. (2018).Use of principal component analysis and hierarchical cluster analysis (HCA) for multivariate association between bioactive compounds and functional properties in foods. *Trends in Food Science & Technology,*72, 83-90

[40] Daraigan, S. G., Ahmed, S. Wahdain, A. S., Ahmed, S. Bamosa, A. S. & Obid, M. H. (2017). Linear correlation analysis study of drinking water quality data for AlMukallan City, Hadhramout, Yemen. International Journal of Environmental Sciences, 1 (7), 1692- 1701.

[41] Davies, O. A., Allison, M.E, & Uyi, H. S., (2020). Bioaccumulation of heavy metals in water, sediment and periwinkle from the Elechi Creek, Niger Delta. African Journal of Biotechnology, 5(10), 968-973.

[42] Davis. D. A., Bruno V. M., Loza, L., Filler S. G. & Mitchell A. P. (2018). Candida albicans Mds3p, a conserved regulator of pH responses and virulence identified through insertional mutagenesis. Genetics 162(4), 73-81.

[43] Dedeke, G. A. Iwuchukwu, P. O., Aladesida, A. A. Afolabi, T. A. &Ayanda, I. O. (2018). Impact of heavy metal bioaccumulation on antioxidant activities and DNA profile in two earthworm species and freshwater prawn from Ogun River. Science of the Total Environment. 624, 576-585.

[44] Deming, H., Jinping, C., Xianfeng, H., Zhenyi, J., Lei, M., Hao, X.,Yuning, M., Xiaojia, C. &Heling, W. (2019). Spatial distribution, risk assessment and source identification of Heavy metals insediments of the Yangtze River Estuary, China. Marine Pollution Bulletin. MPB-08215; 8.

[45] Díaz, M., Galindo-Riano, M.D., Casanueva-Marenco, M.J., García-Vargas, M. & Kosore, C.M. (2018), Assessment of the metal pollution, potential toxicity and speciation of sediment from Algeciras Bay (South of Spain) using chemometric tools. *Journal of Hazard Materials*, 190, 177-187

[46] Edward, J. B., Idowu, E. O., Oso, J. A., Ibidapo, O. R. (2018). Determination of heavy metal concentration in fish samples, sediment and water from odo-ayo River in Ado-Ekiti, Omozokpia et al.; BJAST, 11(1): 1-13, 2015; Article no.BJAST.19001 12 Ekiti-State, Nigeria. International Journal of Environmental Monitoring Analysis. 1(1):27-33.

[47] Ernst, W. (2020). Ecophysiological Studies on Heavy Metal Plants in South Central Africa. Kirkia,8(2), 125-145.

[48] Ezemonye, L. I., Adebayo, P. O., Enuneku, A. A., Tongo, I.& Ogbomida, E. (2018). Potential health risk consequences of heavy metal concentrations in surface water, shrimp (Macrobrachium macrobrachion) and fish (Brycinus longipinnis) from Benin River, Nigeria. Toxicology reports, 6, 1–9. https://doi.org/10.1016/j.toxrep.2018.11.010

[49] Fondriest Environmental, Inc. (2014).“Water Temperature.” Fundamentals of Environmental Measurements. 7 February, Web. <https://www.fondriest.com/environmentalmeasurements/parameters/water-quality/water-temperature/ >.

[50] Franco-Uría, Rajkumar, H., Naik, P.K. & Rishi, M.S. (2019). Evaluation of heavy metal contamination in soil using geochemical indexing approaches and chemometric techniques. International Journal of Environmental Science Technology,16, 7467–7486.

[51] Ghori, N., Ghori, T., Hayat, M.Q. (2019). Heavy metal stress and responses in plants. International Journal of Environmental Science Technology,16, 1807–1828.

[52] Hamaidi, C. F. &Brahim, E., M. (2019). Water quality and physicochemical parameters of outgoing waters in a pharmaceutical plant. Applied Water Science,9, 165

[53] Han, L., Y., Ming, Z.&Jing-Jing, S. (2018). Automatic untargeted metabolic profiling analysis coupled with Chemometrics for improving metabolite identification quality to enhance geographical origin discrimination capability. Journal of Chromatography1541; 12-20

[54] Heltai, G., Percsich, K., Halasz, G., Jung, K. &Fekete, I. (2017). Estimation of ecotoxicological potential of contaminated sediments based on a sequential extraction procedure with supercritical CO2 and subcritical H2O solvents. Journal of Microchemical, 79, 231-237

[55] Hoang, V. D. & Marini, F. (2019). Chemometrics-based Spectroscopy for Pharmaceutical and Biomedical Analysis. Frontiers in Chemistry.7, 153

[56] Idowu, I.(2017). Evaluations of the Levels of Heavy Metals in River Water and Selected Species of Fish from Ogba River in Benin City, Nigeria. *Journal of Applied Sciences and Environmental Management.*21(6), 76-85.

[57] Ighariemu, V., Belonwu, D.C. & Wegwu, M.O. (2019). Levels of Some Heavy Metals and Health Risks Assessment of Three Different Species of Catfishes in Ikoli Creek, Bayelsa State, Nigeria. Biol Trace Elem Res189, 567–573.

[58] Igiri, B. E.,. Okoduwa, I. R., Idoko, G.O., Akabuogu, E.P., Adeyi, A.O. & Ejiogu, I. K. (2018). Toxicity and Bioremediation of Heavy Metals Contaminated Ecosystem from Tannery Wastewater. 2568038 16.

[59] Iqbal, M., Muhammad, S. &Shah H. (2018). Geochemical speciation, anthropogenic contamination, risk assessment and source identification of selected metals in freshwater sediments. Elsevier, B. V. https://doi.org/10.1016/j.enmm.2015.02.002.J.

[60] Isibor, P. O.,Imoobe, T.O.T., Izegaegbe, J. I.&Oluowo, E. F. (2019). Assessment of some heavy metals and total hydrocarbons in Clarias gariepinus fish of Osse River, Edo State, Nigeria.Journal of Environmental Science, Toxicology and Food Technology, 10 (9). 144-151. ISSN 2319-2402,p- ISSN: 2319-2399.

[61] Islam, M. S., Proshad, R. &Ahmed, S. (2018). Ecological risk of heavy metals in sediment of an urban river in Bangladesh. Human and Ecological Risk Assessment: An International Journal. 24; 699-720.

[62] Jiawei, W., Ruimin, L., Peipei, Z., Wenwen, Y., Zhenyao, S. & Chenghong, F. (2018). Spatial variation, environmental assessment and source identificationof heavy metals in sediments of the Yangtze River Estuary. Marine Pollution Bulletin 87, 364–373.

[63] Ju¨rgen W. E., Dirk T. & Olaf K. (2018). River Pollution Data Interpreted by Means of Chemometric Methods. Microchemical Journal, 58, 315–324.

[64] Kar, S. T., Denil, D. & Ransangan, J. (2020). Temporal and spatial variability of heavy metals in Marudu Bay, Malaysia. Oceanological and Hydrobiological Studies, 45(3), 353-367

[65] Kithiia, S.M. (2020). The effects of land use types on hydrology and water quality of Upper Athi River basin, Kenya. University of Nairobi.

[66] Kurnaz Ash , Ekrem Mutlu , Arzu Aydin . (2017). Determination of Water Quality Parameters and Heavy Metal Content in Surface Water of Çiğdem Pond (Kastamonu/Turkey). Turkish Journal of Agriculture - Food Science and Technology, 4(10): 907-913, 2017.

[67] Ling, L., Meihua, Z.& Yuhao, M. (2020). Heavy metals interfere with plasma metabolites, including lipids and amino acids, in patients with breast cancer.DOI: 10.3892/ol.2020.11402

[68] Manju, M. (2017). Effect of Heavy Metals on Human Health. International Journal of Research-Granthaalayah, 31, 1-7.

[69] Masindi, V. & Muedi, K. L. (2018). Environmental Contamination by Heavy Metals, Heavy Metals, Intech Open, DOI: 10.5772/intechopen.76082.

[70] Matthias, T., Filzmoser, P. & Reimann, C. (2020). Cluster analysis applied to regional geochemical data: Problems and possibilities. Applied Geochemistry. 23. 2198-2213.

[71] Mohammad,R., Kawser, A.&Muhammad, K.,(2017). Heavy metal pollution in surface water and sediment: A preliminary assessment of an urban river in a developing country. Ecological Indicators. 48, 282-291

[72] Muhammad, H.L., Shehu, R.A., Bilbis, L.S. &Dangoggo, S.M. (2018).Analyses of selected Heavy Metals and Mineral Elements in Pollution Prone Aquatic Environments of North-Western Region of Nigeria. Asian Journal of Biological Sciences, 7(6): 252-261.

[73] Musa, I. O. & Abubakar, I. A. (2019). Heavy Metals Contamination in the Tissues of Clarias gariepinus Obtained from Two Earthen Dams (Asa and University of Ilorin Dams) in Kwara State of Nigeria. Harran Üniv Vet Fak Derg. 8 (1): 26-32.

[74] Mwangi, J. M. (2018). Determination of Concentration of Selected Heavy Metals in Tilapia Fish, Sediments and Water from Mbagathi and Ruiru athi river tributaries, Kenya. School of Pure and Applied Sciences, Kenyatta University.

[75] Nda M., Jimoh O.D. & Adnan M.S. (2019) Estimation of Sediment Concentration of River Dagga, Chanchaga Basin, Niger State, Nigeria. Lecture Notes in Civil Engineering, 9. Springer, Singapore

[76] Nekoeinia, M., Mohajer, R.& Salehi, M.H. (2019).Multivariate statistical approach to identify metal contamination sources in agricultural soils around Pb–Zn mining area, Isfahan province, Iran. Environmental Earth Science,75, 760-772.

[77] Nemati, K., Abu, N.K., Abas, M.R., Sobhanzadeh, E.& Low, K.H. (2018), Comparison of unmodified and modified BCR sequential extraction schemes for the fractionation of heavy metals in shrimp aquaculture sludge from Selangor, MalaysiaEnviron. Monitoring Assessment, 176, 313-320.

[78] Nguyen, H.L., Braun, M., Baeyens, W., Van, R. & Leermakers, M. (2017), Tracing the metal pollution history of the Tisza River through the analysis of a sediment depth profile.Water Air Soil Pollution, 200, 119-132.

[79] Nwoke, H.U, Obi L.E. & Quakers I. I. (2019). Comparative Analysis of Water Quality of Water Stored in Concrete, Steel and Plastic Storage Facilities. International Journal of Scientific Engineering and Science. 3(6), 34-38.

[80] Ogbuneke, C. C. & Ezeibeanu, A. P. (2019). Comparative Assessment of Trace and Heavy Metals in Available Drinking Water From Different Sources in the Centre of Lagos and off Town (Ikorodu LGA) of Lagos State, Nigeria. *Advanced Journal of Chemistry-Section A, 2020*, 3(1), 94-104

[81] Ogueri C, Adebayo E.T. & Nwaiwu V.C. (2018). Assessment of heavy metals in fish species and some physico-chemical parameters of Oguta lake, Oguta, Imo state, Nigeria. *International Journal of Hydrology,* 2(2):121–124.

[82] Oguh, C. E., Osuji, C. A., Benjamin, E. C., Ugwu, C. V., Musa, A. D. (2020). Health Risk Assessment of Some Toxic Elements in Aquatic Bioindicator (Clarias gariepinus and Oreochromis niloticus) from Tagwai Reservoir Dam Minna, Niger State, Nigeria. *Scholars International Journal of Biochemistry,* 3(2): 12-21.

[83] Ogunlaja, A., Olumuyiwa, O., Dorcas, M. O.&Olajumoke,. A. (2019). Risk assessment and source identification of heavy metal contamination by multivariate and hazard index analyses of a pipeline vandalised area in Lagos State, Nigeria. *Science of The Total Environment.*651(2), 2943-2952.

[84] Ojelabi, E. A., Fasunwon, O. O., Badmus, B. S., Onabanjo, D. R. &Okubanjo, O. O. (2018). Geophysical and Chemical Analysis of Ground water, in AgoIwoye (South West Region in Nigeria). Africa Journal of Environmental Studies, 2(1):77- 80.

[85] Okafo, C.N., Yakubu, S.E., Ameh, J.B. & Okuofu, C.A. (2019). Heavy metal levels in some fish species harvested from River Kaduna, Nigeria. African Journal of Natural Sciences. 21, 9-16.

[86] Onjefu, S. A., Kgabi, N.A. & Taole, S.H. (2019). Heavy Metal Seasonal Distribution in Shore Sediment Samples along the Coastline of Erongo Region, Western Namibia. European. Journal of Scientific Research, 139, 49-63.

[87] Oshisanya, K.I., Unyimadu J.P., Shelle R.O.D., Nubi A.O, Ladigbolu, I.A., Oguguah N.M., Olumodeji,O.O., Adeleye A.O., Fashade, A.O. (2021). Seasonal Variation Of Heavy Metals In Sediment And Water Of Lagos Lagoon. Journal of American Science; 7(3):384-387]. (ISSN: 1545-1003).

[88] Osman, O. & Faust, S. (2018). Chemistry of Water Treatment. Boca Raton: CRC Press, https://doi.org/10.1201/9781315139265

[89] Passos, E.A., Alves, J.C., Santos, I .S., Alves, J.P., Garcia, C.A.B. &Costa, A.C.S. (2017). Assessment of trace metals contamination in estuarine sediments using a sequential extraction technique and principal component analysis. Microchem. J., 96 pp. 50-57

[90] Paul, S.K. Masafumi, F.&Daisaku, S. (2017). Heavy metal contamination of coastal lagoon sediments: Chemosphere. Volume 95, January 2014, Pages 628-634

[91] Popoola, L.T., Yusuff, A.S. & Aderibigbe, T.A. (2019). Assessment of natural groundwater physico-chemical properties in major industrial and residential locations of Lagos metropolis. Applied Water Science,9,191.

[92] Prabhat, K., Sang, S.,Ming, Z.,Yiu, F.&Ki-Hyun, K. (2019). Heavy metals in food crops: Health risks, fate, mechanisms, and management. Environment International. 125; 365-385

[93] Prasanna, M. V., Praveena, S. M., Chidambaram, S. Nagarajan, R., & Elayaraja, A. (2017). Evaluation of water quality pollution indices for heavy metal contamination monitoring: a case study from Curtin Lake, Miri City, East Malaysia. Environmental Earth Sciences. 67(7), 1987–2001.

[94] Razic, S. & Dogo, S. (2016). Determination of chromium in Mentha piperita L. and soil by graphite furnace atomic absorption spectrometry after sequential extraction and microwave-assisted acid digestion to assess potential bioavailability. Chemosphere, 78, 451-456

[95] Rehman, Q., F., Zhang, F.& Pant, R. (2018). Spatial variation, source identification, and quality assessment of surface water geochemical composition in the Indus River Basin, Pakistan. Environ Sci Pollut Res25, 12749–12763.

[96] Roberts, D.A. (2017). Causes and ecological effects of resuspended contaminated sediments (RCS) in marine environments. Environmental International. 40, 230–243, 10.1016/j.envint.2011.11.013

[97] Roseburrough, R. R. & Wang, X. (2019). Chromium Distribution in Water and Sediments in the Mobile River and Bay, Alabama. Gulf and Caribbean Research 30 (1): SC33-SC37. Retrieved from https://aquila.usm.edu/gcr/vol30/iss1/13

[98] Salau, RB, Bisiriyu, MT, Zalihat, A, Alheri, A, Aremu, MO, Olusola, AL, Mohammed, AK. (2020). Evaluation and Chemometric Analysis of the Mineral Profile of Locally Prepared Soups in Minna, Niger State. Journal of Chemical Society of Nigeria, 45 (1), 21 - 28

[99] Sanayei Y., Norli Y., Talebi S. (2019). Determination of heavy metals in river. World Applied Sci. J. 2019; 6: 1209-1214

[100] Santos, G. Ignacio, F., Ángel, I., Frédéric, L. & Dominique, C. (2016). Estimating airborne heavy metal concentrations in Dunkerque (northern France). Arab J Geosci 9: 231 DOI 10.1007/s12517-015-2225-5

[101] Saracoglu, S., Soylak,M. &Elci, L. (2019). Extractable trace metals contents of dusts of air filters from vehicles by sequential extraction procedure. J. AOAC Int., 92, pp. 1196-1202

[102] Saravanakumar, A., Rajkumar, M., Sesh, J. & Thivakaran, G. (2018). Seasonal variations in physico-chemical characteristics of water, sediment and soil texture in arid zone mangroves of Kachchh-Gujarat. Journal of Environmental Biology. 29(5): 725-732

[103] Selvam, S., Antony R. A.& Venkatramanan, S. (2017). Assessment of heavy metal and bacterial pollution in coastal aquifers from SIPCOT industrial zones, Gulf of Mannar, South Coast of Tamil Nadu, India. Appl Water Sci7, 897–913.

[104] Shabalala A.N., Combrinck L. & McCrindle R., (2013). Effect of farming activities on seasonal variation of water quality of Bonsma Dam, KwaZulu-Natal. South Afr. J. Sci., 109, p. 7, 10.1590/sajs.2013/20120052.

[105] Shawai, S. (2019). Status of Water Used for Drinking and Irrigation in Kano: A Critical Review on Physicochemical and Heavy Metals Concentration. American Journal of Biomedical Science and Research, 5(3), 235–242. doi:10.34297/ajbsr.2019.05.000918

[106] Singh, K., Rathore, A. Bhushan, N. & Hadpe, S. (2019). Chemometrics Applications in Biotech Processes: A Review. Biotechnology progress. 27. 307-15. 10.1002/btpr.561.

[107] Sivakumar, R.& Xiaoyu, Li. (2018). Bioaccumulation of heavy metals in fish species from the Meiliang Bay, Taihu Lake, China. Toxicology Reports. 5: 288–295.

[108] Solache, R. M. Linares, H. I. Vázquez, M. G. Fonseca,M., Fuentes, R., R. M. Martínez, M. V. Esquivel,M. J. (2019). Estimation and impact of carbon dioxide capture on drinking water: Tillmans equilibrium diagram. Journal of Water and Climate Change, jwc2019038, doi.org/10.2166/wcc.2019.038

[109] Stewart, B. W., & Kliehues, P. (2018). World Cancer Report. Lyon; IARC press, Lyon.

[110] Thomas, R. C. (2019). Analysis of oceanic waters and sediments.CRC Press. International Standard Book Number-13: 978-1-4987-0153-2.

[111] Tscheikner-Gratl, F., Bellos, V., Schellart, A., Moreno-Rodenas, A., Muthusamy, M., Langeveld, J., Clemens, F., Benedetti, L., Rico-Ramirez, M.A., de Carvalho, R.F., Breuer, L., Shucksmith, J., Heuvelink, G.B.M., Tait, S., 2019. Recent insights on uncertainties present in integrated catchment water quality modelling. Water Resources, 150, 368e379.

[112] Tukura, B. W., Kagbu, J. A. & Gimba, C. E. (2007). Effects of pH and Total Organic Carbon (TOC) on the Distribution of Trace Metals in Kubanni dam Sediments, Zaria, Nigeria. Science World Journal, 2 (3): 1-6

[113] Türkmen, M. & Ciminli, C. (2007). Determination of metals in fish and mussel species by Inductively Coupled Plasma-atomic emission spectrometry. Food Chemistry, 103:670-675.

[114] Unaeze, C.H., Salau R. B., Jacob J. O. and Ndamitso, M. M., Mohammed, A. K. (2021) Chemometrics in Water Quality Criteria and Appraisal. International Journal of Research Innovation in Applied Science. VI (X), 43 - 51

[115] Vink, J.P.M. (2019). The origin of speciation: trace metal kinetics over natural water/sediment interfaces and the consequences for bioaccumulation. Environmental Pollution, 157, 519-527

[116] Vu Dang, H.& Marini, F. (2019). Editorial: Chemometrics-based Spectroscopy for Pharmaceutical and Biomedical Analysis. Frontiers in chemistry, 7, 153.

[117] Wachira, D. N., Obiewa, J. O.& Kariuki, D. K., (2019).Assimilation of Pollution Loading on Sosiani River in Eldoret Municipality, Kenya: As a Wastewater Management Strategy.American Journal of Water Resources. 7(4), 155-162

[118] WHO/FAO. (2016). Joint FAO/WHO Food Standard Programme Codex Alimentarius Commission 10th Session. Working document for information and use in discussions related to contaminants and toxins in the gsctff (Prepared by Japan and the Netherlands) 4 - 8 April 2016.

[119] World Health Organization WHO. (2018). Heavy Metals in drinking-water. Background document for preparation of WHO Guidelines for drinking-water quality, Geneva.

[120] World Health Organization, WHO (2017). Guidelines for drinking-water quality, fourth edition. In: WHO [Internet].[cited 13 Apr 2017], http://www.who.int/water_sanitation_health/publications/2011/dwq_guidelines/en/

[121] Xiaoling, M.,Mengjing, T.,Liyang, Z.,Xuening, Z.&Xinyuan, C. (2017). Assessment of heavy metals contamination in sediments from three adjacent regions of the Yellow River using metal chemical fractions and multivariate analysis techniques. Chemosphere. 144, 264-272.

[122] Xuan, H. (2018). "Research and development of feature dimensionality reduction," Computer Science, 45(1), 12-18.

[123] Yahaya, I., Ezeh, G., Musa, Y. &Mohammad, S. (2019). Analysis of heavy metals concentration in road sides soil in Yauri, Nigeria. African Journal of Pure and Applied Chemistry. 12, 45-51.

[124] Yun, R.,Chiu, W.Chih, F.C., Xiang,Y. C.&Cheng, D. (2017). Assessment of heavy metals in aquaculture fishes collected from southwest coast of Taiwan and human consumption risk.International Biodeterioration & Biodegradation; 124; 314-325

[125] Yunqian, W., Liyuan, Y., Linghao, K., Enfeng, L., Longfeng, W. & Jingru, Z. (2019). Spatial distribution, ecological risk assessment and source identificationfor heavy metals in surface sediments from Dongping Lake, Shandong, East China. Catena 125. 200–205.

[126] Zamir, R. Islam, N. Rahman, M. A. & Rahman, M. S. (2019). Daily exposure assessment of as, Ni, Hg, Al and Mn in anti diabetic herbal preparations (ADHPs). PharmacologyOnLine, SILAE, Italy, 2(2), 282–293.

[127] Zhou, Q., Yang, N., Li, Y., Ren, B., Ding, X., Bian, H., & Yao, X. (2020). Total concentrations and sources of heavy metal pollution in global river and lake water bodies from 1972 to 2017. *Global Ecology and Conservation, e00925.* doi:10.1016/j.gecco.2020.e00925 10.1016/j.gecco.2020.e00925

[128] Zolfaghari. F., Khosravi, H., Shahriyari, A., Jabbari, M. &Abolhasani, A. (2019) Hierarchical cluster analysis to identify the homogeneous desertification management units. *PLoS ONE* 14(12): e0226355. https://doi.org/10.1371/journal.pone.0226355