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DETERMINATION AND MODELING OF HEAVY METAL CONCENTRATIONS IN RIVER RUTU AND DOMA DAM IN DOMA LGA, NASARAWA STATE.

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ABSTRACT

River Rutu and Doma dam in Doma LGA of Nasarawa state were analyzed for their physicochemical parameters and heavy metal concentrations. This was to ascertain the level of contamination and develop models for predictive purposes. Water samples were collected from each river in dry season twice (January & March) and same in the wet season (July & August). Physicochemical analyses were obtained using standard procedures while heavy metal concentrations were obtained using Atomic absorption spectrophotometer (AAS). Results showed that all physicochemical parameters analyzed were below the maximum tolerable limit by Nigerian Standard for Drinking Water Quality and the World Health Organization. Heavy metals analysed showed a general increase in concentration in the dry season with the exception of copper which showed a high concentration in the wet season in both study areas. Ni concentration in river Rutu was low and was not detected in Doma dam in the dry season. Data from physicochemical parameters and concentrations of respective heavy metals were inputted into the Minitab 18 statistical computer software for model development. The models developed for each heavy metal, Pb, Zn; Fe; Cu; Co; Cr and Mn were all multivariate in nature and noted to be statistically reliable at 95 % confidence limit. R^2 values for all the models ranged from 65 to 98 %, implying that the developed models can be relied on in predicting the concentration of the respective heavy metals by measuring the physicochemical parameters and evaluating using each model.

Key Words: Heavy Metal, Modeling, Physicochemical, Rivers, Seasons.

1.0 Introduction

It is a well-known fact that water remains one of the most indispensable resources for the existence of man and other organisms. However, the demand for this precious resource keeps increasing day in day out due to the pollutions threat it receives from both anthropogenic and natural sources. It has been reported that the earth's surface is made up of 70% water including lakes, seas, rivers, oceans, streams and groundwater, all of which are very important to the sustenance of life (Arimiens *et al.*, 2014). It has been noted that of the 70% of water that covers the earth's surface, only 3% is regarded as fresh water (Aniyikaiye *et al.*, 2019) and approximately 5% of the entire global water is readily accessible for beneficial purposes yet it keeps receiving pollution threat (Usharani *et al*., 2010; Adano *et al*., 2022). Surface water is used for many purposes, which include drinking, irrigation farming, recreation and serves as habitat to numerous organisms, (Amos *et al*., 2014). One of the issues of great concern is that the quality of this surface water which many depend on is being threatened or tempered with by many natural and anthropogenic activities which pollute these water sources (Joshua et al., 2015; Obaje *et al*., 2020).

(Kerketta *et al*., 2013; Edokpayi *et al*., 2014) stated some desirable properties of water to include; moderate temperature, adequate dissolved oxygen, pH near neutrality, and free from excessive amount of toxic substances and minerals as well as infectious agent. The ease at which wastes are thrown or discharged on water channels or directly on water bodies has increased the rate of surface water pollution. Some authors (Agbaire and Obi 2009; APHA 1999; Aremu *et al*., 2017) documented that 80 percent of global wastewater are released untreated into water bodies, these ranges from human waste to highly toxic industrial discharges. It is no longer a new thing that the disposal of untreated wastewater, sewage as well as refuse in Nigerian water bodies has reached an alarming stage. Majority of the people living in the world still do not have access to potable water and therefore, depend on well, streams and river water for domestic use. Researchers (Kerketta *et al*., 2013; Vergas *et al*., 2014) reported that heavy metals are the most persistent group of water pollutants for a very long time, posing danger to aquatic organisms and humans, even at trace concentrations. Once water is contaminated, it's very tedious, expensive, and in some cases difficult to remove the pollutants. Therefore, it has become imperative to continue to monitor the quality of water in order to save man and his environment.

In order to monitor the water quality, frequent sampling and analysis of the water quality would have to be made at selected periods and seasons over time. This will invariably cost a lot of money, time and sampling may not always be expedient. The development of mathematical models (multivariate in nature) for each heavy metal using few measurable physicochemical parameters of the water samples for predictive purposes is what this research work seeks to accomplish.

2.0 Materials and Methods

2.1 Study Area

Doma and its suburban lie between latitude 8˚32′35.0″N and Longitude 8˚21′19.58″E in the guinea savannah region of Northern Nigeria with an area of 2,714km^2 and a population of 139,607 (2006 Census). It shares a boundary with Lafia, Nasarawa state capital and some parts of Benue state and is situated at elevation of 179 meters above sea level. The State is within the Guinea Savannah region of Nigeria and is characterized by dry season from the month of November to March and a rainy season from the month of April to October. The people of Doma are commonly known with farming and fishing activities for those that settled close to water bodies.

2.2 Sample collections

Water samples were collected by the method described by (Nure *et al*., 2019) in pre-cleaned 1L plastic bottles with screw caps. The samples containers were washed thoroughly with detergent, and afterward soaked in a 5% HNO_3 for the period of 24 hours after which they were rinsed properly. Surface water samples were collected at 3 different portions from each of the 2 different rivers twice in each season (the month of March and August). The samples were labeled as R1, R2 and R3 for the 3 different portions in river Rutu while D1, D2 and D3 were used to represent the 3 different portions in Doma dam. Each sample container was rinsed out

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three times with water that is to be sampled before the bottles were plunged neck downward at about 15 cm below the surface of the water in these rivers. Determination of temperature in all the sites was done immediately while other samples were stored at a room temperature prior to other analysis

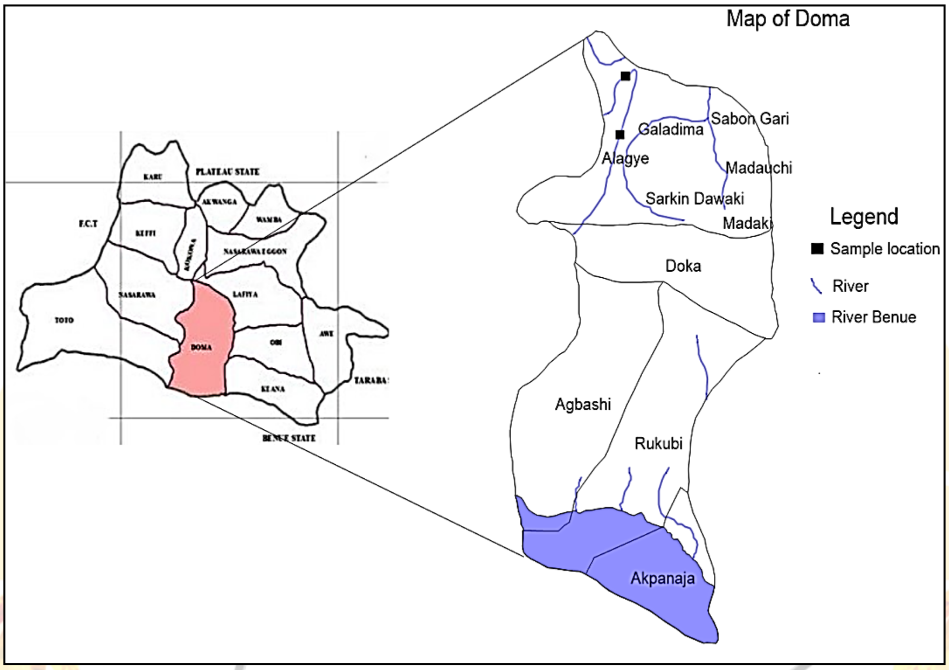

Figure 1: Map of Doma showing the Study Areas

2.3 Determination of physicochemical parameters

24 samples were analyzed in the wet season and 25 in the dry season. pH was analyzed with the aid of pH meter, temperature was analyzed at the point of sample collection using a calibrated thermometer, electrical conductivity using a conductivity meter, total dissolve solids and total suspended solids were both determined by gravimetric method. All analysis was carried out in triplicates and their mean presented.

2.4 Heavy metal analysis

One hundred milliliters (100 ml) of the water sample was transferred into a conical flask, 5 ml of Concentrated HNO_3 acid solution was added and heated slowly and allowed to evaporate to 20 ml in a fume cupboard. Heating continued with the addition of concentrated HNO_3 until a light colored clear solution was observed. The beaker wall was rinsed down with deionized water followed by filtration. The filtrate was transferred into 100 ml volumetric flask, allowed to cooled and made up to mark with deionized water (Adefemi and Awokunmi 2010). The heavy metals; Pb, Zn, Fe, As and Cu were then analyzed using Atomic Absorption Spectrophotometer AAS after calibration with appropriate standards.

2.5 Modeling and Statistical Analysis

Modeling and statistical analysis was done using the Minitab 18 statistical software including developing the models for each heavy metal. The physicochemical parameters of the water samples from river Ruto and Doma Dam (pH, temperature, electrical conductivity, total dissolved solids and total suspended solids) previously measured were inputted into their respective columns in worksheet of the Minitab 18 statistical programme, as the independent variables. Concentrations of the heavy metals analyzed in the water samples (Pb, Zn, Fe, As and Cu were also inputted into a separate column for the dependent variables. Thus, each heavy metal and the physicochemical parameters were inputted on a worksheet, making a total of five worksheets. The computer was then asked to model the data between the physicochemical parameters and each heavy metal concentration. The model was developed and recorded as a chart including all the model diagnostics for better interpretation.

3.0 Results and Discussion

In river Ruto and Doma dam, pH had a mean value of 6.90±0.251 and 6.60±0.160 while doma dam had mean values of 7.30±0.373 and 7.10±0.218 in the wet and dry seasons respectively. These values were within the safety limit of 6.5 – 8.5 stipulated by the regulatory standards for river water by the Nigerian Standard for drinking water quality as well as the world health organization.

Table 1: Mean Values of Physicochemical Parameters and Heavy Metal Concentrations in water samples of River Ruto and Doma Dam

Parameters	Wet season	Dry season	Wet season	Dry season	Standards	
	R	R	D	D	NSDWQ	WHO
pH	6.90±0.251	6.60±0.160	7.30±0.373	7.10±0.218	6.5-8.5	6.5-8.5
Temp	26.50± 0.05	2750±0.017	27.10± 0.361	27.5± 0.10	Ambient	15-28
EC (µS/cm	20.12±1.606	50.00±1.153	5.00 ± 0.328	42.0± 0.344	1000	1000
TDS (mg/L)	35.58 ±1.509	32.91±1.728	30.00±2.241	28.10±0.995	500	500
TSS (mg/L)	0.96± 0.156	0.65±0.087	0.75± 0.03	0.61± 0.017	200	200
Pb	0.82± 0.017	1.86± 0.002	0.583± 0.085	0.77±0.139	0.01	0.01
Zn	0.040± 0.018	0.67± 0.183	0.33± 0.107	0.365±0.179	5.0	3.0
Fe	0.19± 0.026	0.94± 0.795	0.261± 0.024	0.49± 0.194	0.3	0.3
As	0.885± 0.026	1.13± 0.177	1.22± 0.208	1.57 ± 0.432	0.01	0.01
Cu	2.432± 0.216	0.247±0.047	3.58± 0.972	0.86± 0.303	1.0	1.0

Key: R = River Ruto, D = Doma Dam, NSDWQ = Nigerian Standard for drinking water quality WHO = World health organization

The same trend was seen with the other physicochemical parameters of EC, TDS and TSS, where their respective values for both seasons and in both water samples were below the values quoted by both regulatory standards as seen in the table above. Temperature was the only variant whose mean values were higher than those of the regulatory or monitoring standards. The reason for the deviation in temperature may not be unconnected to the higher atmospheric temperature of Doma due to climatic or environmental disposition.

With regards to the concentration of heavy metals in both rivers, Lead (Pb) and Arsenic (As) had their mean values to be higher than those of the regulatory standards. The concentration of Zinc (Zn) in both sampled water and in both seasons were however lower than those of the regulatory standards. Mean Copper (Cu) values in the wet season for both rivers were observed

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to be higher than values of the regulatory standards while during the dry season, values were below the threshold limit while the converse is the case with iron (Fe) in both rivers.

3.1: Results for Modeling Heavy Metal Concentrations

$$Pb = 0.6247 - 0.001096\ EC \quad \text{.......................................} \quad (1)$$

Above is the model equation for estimating the concentration of Pb. as modeled by the Minitab statistical programme (Equation 1).

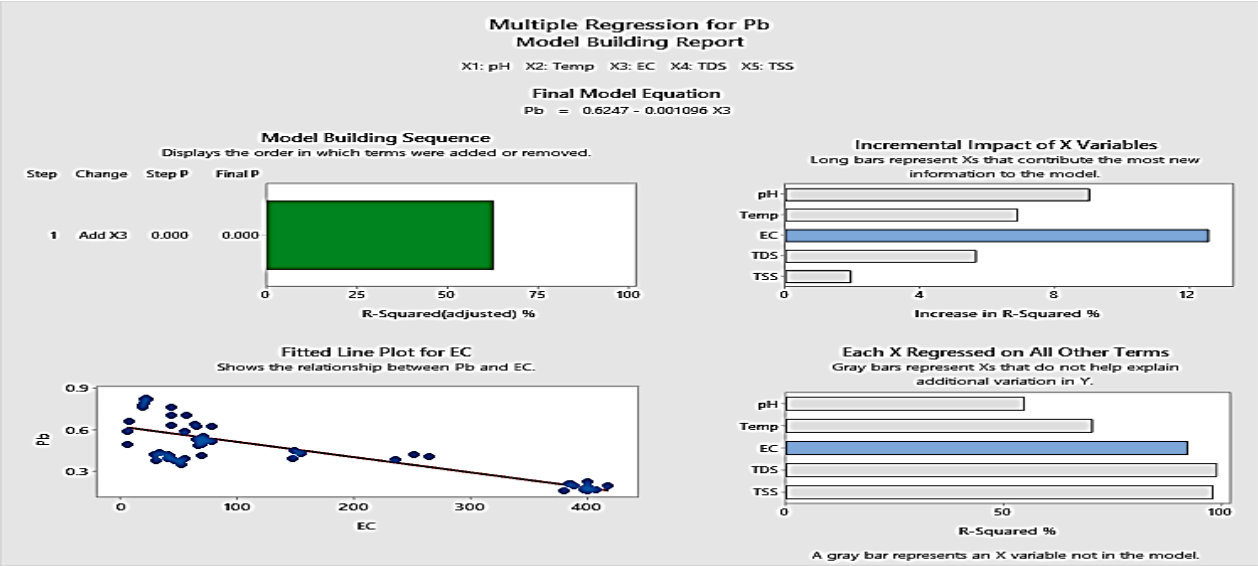

Figure 2: Model Diagnostic Report for Lead (Pb)

The model showed that only EC was correlating with the concentration of the heavy metal (Pb). The diagnostic report also revealed that about 96 % of the heavy metal concentration was dependent on the electrical conductivity measurements only. This observation corroborated with the findings of (Aremu *et al*., 2011; Vergas *et al*., 2014; Ajegena *et al*., 2020) who reported a strong relationship between metals such as Pb and EC since EC also measures the presence of heavy metals in dissolved form. The model equation of Pb = 0.6247 – 0.001096 EC and can be used to predict the concentration of Pb at any time provided that the EC values are measured.

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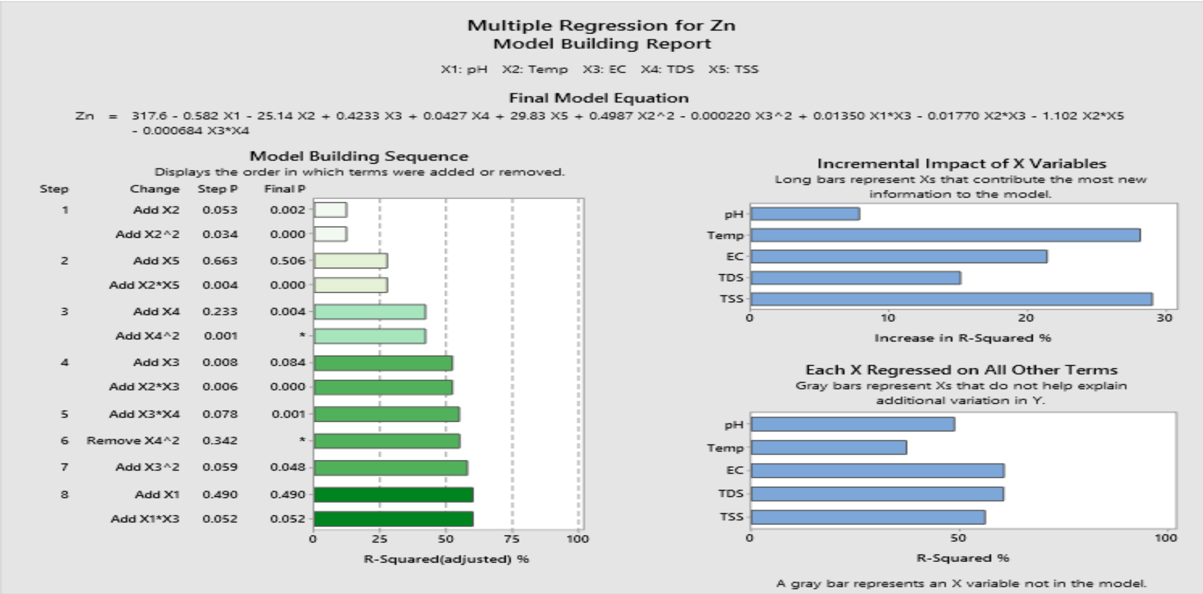

Figure 3: Model Diagnostic Report for Zinc (Zn)

$$Zn = 317.69(pH) - 25.14(temp) + 0.4233(EC) + 0.0427(TDS) + 29.83(TSS) + 0.4987(Tem)^2 - 0.000220(EC)^2 + 0.01350\,(pH)(EC) - 0.01770\,(Temp)(EC) - 1.102\,(Temp)(TSS) \quad \text{...... (Eqn 2)}$$

Equation 2 above is the model for predicting the concentration of zinc. It shows that all the physicochemical parameters of pH, temperature, EC, TDS and TSS all correlated with the concentration of Zn and the percentage variation in the heavy metal concentration by these physicochemical parameters was found to be 69.3 % and was also noted to be statistically significant ($P< 0.001$), see model diagnostic report for Zn (Figure 3) The model for Zn is in strong agreement with reports of (Vergas *et al*., 2014; Dapam *et al*., 2016; Makwe and Chup 2013) which opined that the concentration of heavy metals like Zn was depended on pH, temperature, EC and TDS.

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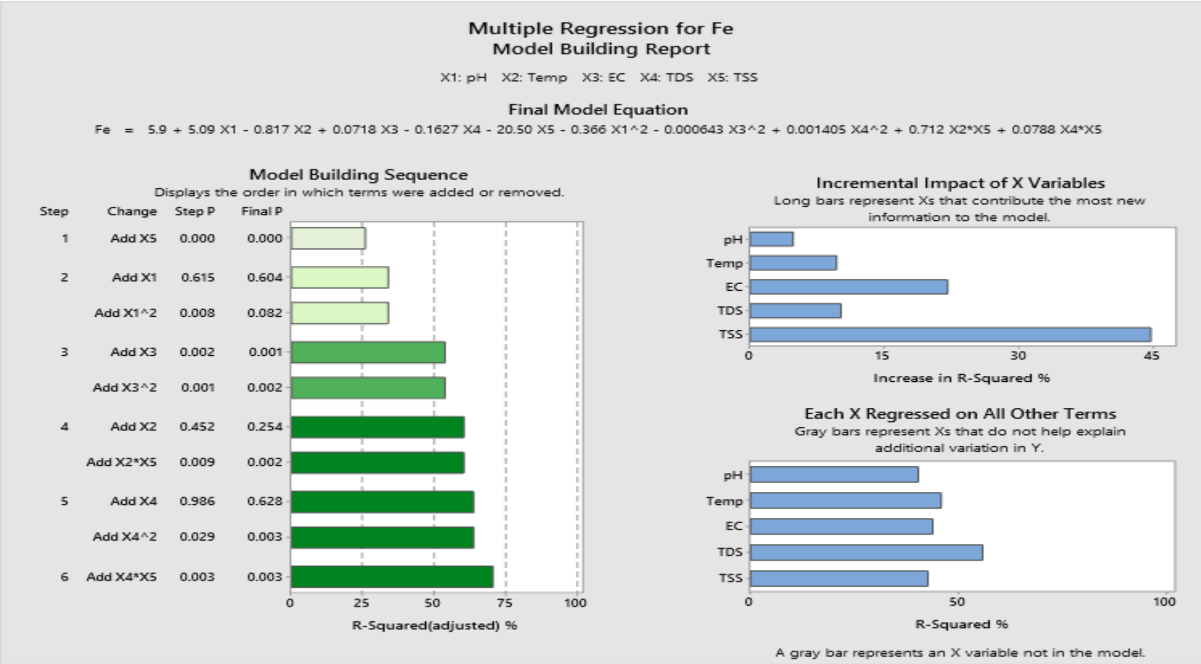

Figure 4: Model Diagnostic Report for Iron

Fe = 5.9 + 5.09(pH) - 0.817(temp) + 0.0718(EC) – 0.1627(TDS) – 20.50(TSS) – 0.366(pH)^2 – 0.000643 (EC)^2+0.0001405(TDS)^2+0.712(TSS) + 0.0788(TDS) (TSS) ……………. (Eqn. 3)

In Figure 4, the modeled variables correlated highly with the concentration of the heavy metal (Fe) and are statistically significant ($P< 0.001$). Furthermore, the percentage (%) variation showed by the model revealed that 76.65 % of the variation in the concentration of Fe can be explained by this regression model or the values of the physicochemical parameters of pH, EC, TDS and TSS. [14, 22, 23, 24] stated that pH and temperature plays a significant role in the release of heavy metal which may be the reason for their presence in the model.

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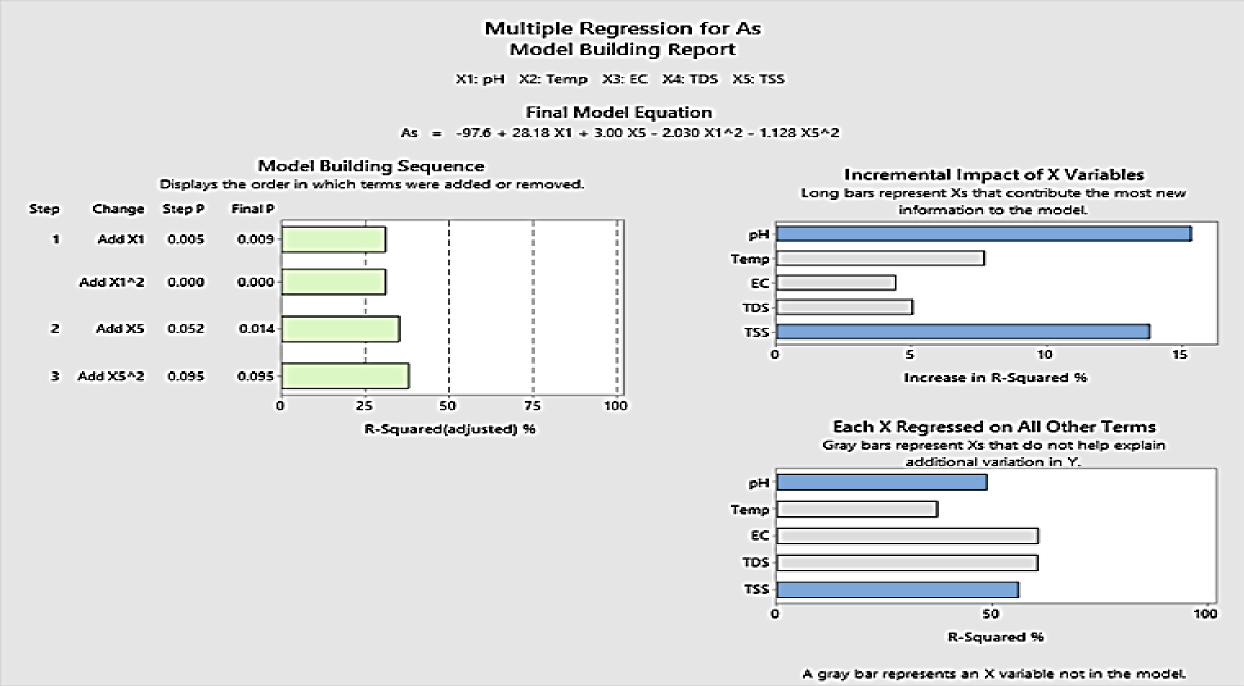

Figure 5: Model Diagnostic Report for Arsenic

$$As = 97.6 + 28.18\ pH + 3.00\ TSS - 2.030\ pH^2 - 1.128\ TSS^2 \quad \text{(Eqn. 4)}$$

Equation 4 represents the model developed for arsenic (As). This model shows that only two variables (pH and TSS) fitted adequately to estimate the concentration of (As) in the rivers. Statistically, the relationship between the metal concentration and the two physicochemical parameters as contained in the model were noted to be statistically significant ($P < 0.001$). However, a further look into the model's diagnostic report revealed that the predictability of arsenic concentration by the two physicochemical parameters at best, was only 43 % ($R^2 = 43.04$). The presence of many points with large residuals which are not fitted in the model (as seen in the diagnostic report) may be the reason for the low value of R^2.

$$Cu = 310 - 24.67\ Temp + 1.377\ EC - 1.099\ TDS + 1.89\ TSS + 0.493\ (Temp)^2 + 0.002283\ (EC)^2 - 1.16\ (TSS)^2 - 0.0580\ Temp(EC) + 0.0434\ Temp\ (TDS) - 0.001848\ EC(TDS) \quad \text{(Eqn. 5)}$$

Equation 5 above is the developed model which relates the concentration of Cu and some physicochemical parameters (temp, EC, TDS and TSS). Out of the five physicochemical parameters inputted into the statistical programme, only pH was left out of the model which showed no correlation. The relationship between Cu and some physicochemical parameters in the model is statistically significant ($P < 0.001$) and the model showed a high percentage variation ($R^2 = 83.92$) as shown in the diagnostic report for the metal. This is an indication that prediction of this heavy metal concentration using this model will be about 84 % correct. Though the model showed the presence of some unusual data points which may have a strong influence in the model, it is suggested that the high variation in the concentration of copper between the two seasons (rainy and dry) could be the reason for the unusual data points.

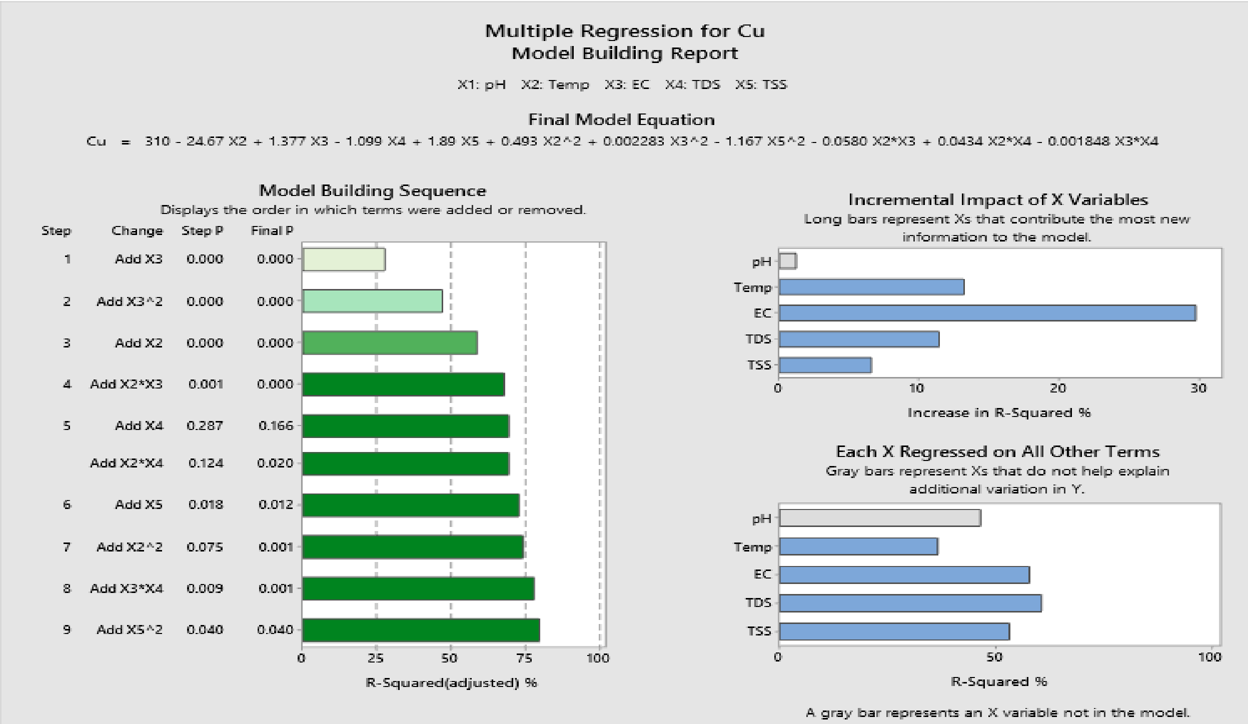

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Figure 6: Diagnostic Report for Copper

4.0 Conclusion

Results from this research revealed that the mean values of all the physicochemical parameters (pH, temp, EC, TDS and TSS) in river Ruto and Doma dam were within the acceptable limit set by NSDWQ and WHO. All the heavy metals analyzed showed a general increase in concentrations in the dry season with the exception of copper which showed a higher concentration in the wet season than the dry season in both study areas. Concentrations of Pb, Zn, and As were above the permissible limit in both study areas and in all seasons, while Fe was within the permissible limit in the wet season and above it in dry season and conversely the case with Cu. All heavy metal concentrations (Pb, Zn, As, Fe and Cu) were successfully modeled for predictive reasons. All the models were multivariate in nature except for Pb which was univariate. Additionally, all the models were statistically significant ($P < 0.001$) and R^2 ranged from 67.3 to 96 %. The only exception was (As) which was 43.04 %. Thus, the models would indeed be very useful in the future prediction of the concentrations of these respective heavy metals in any river by measuring the physicochemical parameters and evaluating the metal concentrations using the appropriate model.

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Conflict of Interest

Authors aver that there is no conflict of interest between them.

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