Simulating The Concentration Of Some Heavy Metals In Mista-Ali River (Mining Pond) In Jos Nigeria

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ABSTRACT: The Concentrations of five dissolved heavy metals, viz; Iron (Fe), Zinc (Zn), Cadmium (Cd), Copper (Cu) and Lead (Pb) in Mista-Ali River were determined using the atomic absorption spectrometry. With the aid of Minitab computer software, these concentrations were then modelled into quadratic time-series model \( Y = \beta_0 + \beta_1 t + \beta_2 t^2 + \beta_3 \text{P} + \beta_4 \text{pH} + \beta_5 \text{pH}^2 + \beta_6 \text{T} + \epsilon \) for each metal. These models gave insights on the forecast and predictability and the bioaccumulation or reduction of these metals in the river.

Key Words: Simulation, forecasting, Concentration, modelling, data input

INTRODUCTION
Forecasting or predicting the concentration of chemical systems is only possible after the development of appropriate model(s) through chemo-metrical means. Chemo-metrics is the science of extracting information from chemical systems by data-driven means. It is a highly interferential discipline, using methods frequently employed in core-analytical disciplines such as multivariate statistics, applied mathematics and computer science, in order to address problems in biochemistry, chemistry, medicine, biology and chemical engineering, (elsevier.com). After the development of appropriate models, simulations that would yield many useful results for better understanding of the system under study are then carried out. Simulation is therefore, defined as the process of designing a model of a real system and conducting experiments with these models for the purpose of understanding the behaviour of the system or of evaluating various strategies for the operation of the system, Yucesan et al (2002). Simulation has also been defined as a broad collection of methods used to study and analyze the behaviour and performance of the actual or theoretical systems, McGraw-Hill, (2002). Regardless of how it is expressed; a simulation model usually contains the model inputs and model outputs. The model outputs are the independent variables. These variables may contain one or two physico-chemical properties of the system under study such as pH, temperature, pressure, flow rate etc. While the model output would be the dependent variable being investigated or measured such as concentration, (Hartman, 2005). As stated earlier, simulation analysis is usually carried out on a computer using any of the three methods or techniques below:

1. Regression or Least square methods
2. Monte Carlo method and
3. Monte-Carlo optimization method.

In statistics, regression analysis includes any technique used for modelling and analyzing several variables when the focus is on the relationship between a dependent variable and one or more independent variables.

This is in the form of a linear regression or method of least square. In linear regression, the model specification is that the dependent Variable \( y_i \) is a linear combination of parameters but not necessarily linear in the independent variables. According to Tofallis, (2009) a multiple regression model with "p" independent variables takes the form:

\[ Y_i = \beta_0 + \beta_1 X_{i1} + \ldots + \beta_p X_{ip} + \epsilon_i \]

A regression model once established, will usually be accompanied by a regression diagnostic. This is to verify whether the model could be relied on. The usual practice is to use ANOVAs table of F-test, t-test or statistical significance, Meade and Islam, (1995). Some of the soft ware's commonly used to carry out simulations based on this method are; Minitab, Dreg and SPSS. Minitab is used at over 5000 Cities including over 2000 schools in 60 countries. It has long been recognized as a leading developer of easy-to-use statistical software. At a glance, Minitab offers a Comprehensive and statistical Capabilities, such as exploratory variance, multivariate analysis, non-parameters, time-series, cross tabulations, simulations and distribution (Minitab 11, 2006). The Monte Carlo simulation method relies on a random sampling of values for uncertain variables that are "plugged into" the simulation model and used to calculate outcomes of interest with the aid of software's such as Microsoft excel, Mat lab, Risk solver etc, to obtain statistics and view charts and graphs of the results (Douglas, 2009). Monte Carlo simulation methods are chiefly used in studying systems with a large number of coupled degrees of freedom such as fluids, disordered materials, strongly coupled solids and cellular structures, Rubinstein and Kroese, (2007). The Monte Carlo optimization method is based on random walks. Essentially, the program would move around a maker in a multi-dimensional space, tending to move in directions that lead to a lower function but sometimes moving against the gradient, Robert and Casella, (2004). The application of Monte Carlo simulation is quite vast and virtually in all areas such as graphics for ray tracing, modelling light transport, biological tissue finance and reliability engineering (Radojevic and Bashkin, 1999).

METHODOLOGY
Water sampling was carried out quarterly from July 2010 to April 2012. The samples were collected in plastic bottles previously washed, soaked in 10% HNO₃ over night and rinsed with de-ionized water before use. During sampling, sample bottles were rinsed three times with the sampled water and then filled at a depth of between 0-20cm. The
samples were labelled and taken to the Chemistry Laboratory, University of Jos, and stored, prior to analysis.

SAMPLE PREPARATION AND ANALYSIS
All reagents used were of analytical grade and distilled water was used for all the preparations. Water samples were filtered using Whitman No. 41 filter paper to remove any suspended particles. 100cm$^3$ of the filtrate (as collected water sample) was transferred into a beaker and 5cm$^3$ concentrated HNO$_3$ was added. The beaker with the content was placed on a hot plate and evaporated down to about 20cm$^3$. The beaker was covered with a watch glass and returned to the hot plate. The heating was continued, and then small portion of HNO$_3$ was added until the solution appeared light colored and clear. The beaker wall and glass were washed with distilled water and the sample was filtered to remove any insoluble material. The volume was adjusted to 100cm$^3$ with distilled water, Floyd and Hezekiah, (2008). This was the final solution for the analysis. Finally, 100cm$^3$ of distilled water was transferred in to a beaker and 5cm$^3$ was added. The beaker was covered with a watch glass and placed on a hot plate about 20cm$^3$. The beaker with the solution was covered with a watch glass and returned to the hot plate. The heating was continued, and then small portion of HNO$_3$ was added until the solution appeared light colored and clear. The beaker wall and glass were washed with distilled water and the sample was filtered to remove any insoluble material. The volume was adjusted to 100cm$^3$ with distilled water, Floyd and Hezekiah, (2008). This was the final solution for the analysis. Finally, 100cm$^3$ of distilled water was transferred in to a beaker and digested as above. This was the blank sample used for blank corrections. Determination of heavy metals (Fe, Zn, Cd, Cu and Pb) in triplicate was made directly on each final solution using the Perkin-Elmer Analyst 400 Atomic Absorption Spectroscopy (AAS) as reported by Papafilippaki, et al (2008). The temperature and pH measurements of water samples was also taken in triplicates at the time of sampling using the Ertco thermometer model 063FBLSC and the sper pH meter model 840087, respectively. The mean and standard deviations of these measurements were recorded.

RESULTS / DISCUSSION

<table>
<thead>
<tr>
<th>Time (Quarterly)</th>
<th>pH</th>
<th>Temperature ($^\circ$C)</th>
<th>Mean Concentration of Heavy Metal (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Fe</td>
</tr>
<tr>
<td>Q1</td>
<td>8.61±1.31</td>
<td>22.14±0.45</td>
<td>840±5.02</td>
</tr>
<tr>
<td>Q2</td>
<td>8.32±0.34</td>
<td>25.11±0.47</td>
<td>940±3.61</td>
</tr>
<tr>
<td>Q3</td>
<td>9.94±2.13</td>
<td>30.24±1.01</td>
<td>1225±7.2</td>
</tr>
<tr>
<td>Q4</td>
<td>10.13±0.6</td>
<td>24.34±1.01</td>
<td>1205±4.11</td>
</tr>
<tr>
<td>Q5</td>
<td>8.42±0.34</td>
<td>23.32±1.24</td>
<td>831±7.61</td>
</tr>
<tr>
<td>Q6</td>
<td>8.12±0.22</td>
<td>28.13±1.25</td>
<td>898±9.22</td>
</tr>
<tr>
<td>Q7</td>
<td>8.83±0.41</td>
<td>31.28±2.12</td>
<td>1228±4.68</td>
</tr>
<tr>
<td>Q8</td>
<td>9.68±0.52</td>
<td>26.19±0.45</td>
<td>1193±23.5</td>
</tr>
</tbody>
</table>

Figure 1 highlights vividly, the initially increasing trend in the concentration of Fe with time in the next few years and a subsequent decrease thereafter in the river. Generally, there was an increase in the concentration of the metal from the first quarter to the second quarter. This concentration then increased further from the second to third and finally a decrease in the fourth quarter. The fifth to the eighth quarter also showed a similar trend. And these are representing the seasonal variations in the metal concentrations in the river. Papafilippaki, et al (2008) With the aid of Minitab, these concentrations were then modelled giving a time-series equation, $Y_t = 894.679 + 38.4643t - 0.892857t^{2}$ and a pH and temperature dependent model, $Fe$ (mg/l) $= -1212 + 168pH + 28.1 T (^{\circ}$C) for predicting the concentrations of Fe in the river at any desired time or period. Furthermore, the pH and temperature-dependent
models would give the metal concentration at any time their values in the water sample was measured and evaluated, a process that would avoid elaborate experimentation thereby saving time and money. On the validity of the model, statistical analysis showed that the model was statistically significant (p < 0.05) and the variables were highly correlated (R² = 0.875).

Here, the concentration of Cd increased from the first to the third quarter but decreased slightly from the third to the fourth quarter. The trend was replicated in the second year, that is, the fifth to the eight quarter. The overall trend showed that the concentration of the metal was decreasing with time. The models developed for forecasting its concentration were

\[
Y_t = 0.496964 + 0.166488t - 4.7E-03t^{**}2
\]

and

\[
Cd (mg/l) = - 7.32 + 0.607 pH + 0.113 T (^\circ C)
\]

respectively. These models were also found to be statistically significant and its variables highly correlated.

**Figure 2:** Time-series plot for Zn

Figure 2 shows the time-series plot for Zn in the river. The general trend revealed a Zn concentration that was increasing gradually from the first to second quarter and then very sharply from the second to the third and a sharp decrease from the third to the fourth. However, from the fifth to the eighth quarter, the seasonal variation was quite the same except for the huge difference from the sixth to seventh quarter, which was a far departure from the corresponding period (second to third quarter) of the first year of measurement. The software, Minitab, therefore developed the time-series and the independent variables-based models for predicting the concentrations of Zn in the river as

\[
Y_t = 145.036 + 140.571t
\]

and

\[
Zn (mg/l) = - 2833 + 207 pH + 47.3 T (^\circ C)
\]

Unfortunately, these models were not statistically valid because the variables were poorly correlated (R² = 0.212) and the statistical significance was poor (p = 0.272). The failure of the model may not be unconnected to the unusually high value of the concentration at the second to the third quarter measurement (an outlier) as seen at the point of inflection in the figure.

**Figure 3:** Time-series plot for Cd

**Figure 4:** Time-series plot for Cu

**Figure 5:** Time-series plot for Pb

Figures, four and five represents the time-series plots for the concentrations of Cu and Pb respectively in the river. The general trend showed that the concentration of both metals was increasing as time was also increasing. The developed models for forecasting the metal concentration were expressed as:

\[
Y_t = 13.9018 + 1.93512t - 0.174405t^{**}2
\]

and

\[
Cu (mg/l) = - 29.1 + 2.93 pH + 0.793 T (^\circ C)
\]

for Cu and

\[
Y_t = 4.20179 + 0.407738t
\]

and

\[
Pb (mg/l) = - 5.18 + 0.599 pH + 0.192 T (^\circ C)
\]

respectively. These models were all found to be statistically significant and their variables highly correlated, hence their validity.
CONCLUSION
Various mathematical models were developed for forecasting the mean concentration of Fe, Zn, Cd, Cu and Pb in Mista-Ali River. These models were statistically significant except those for Zn and they were quadratic in nature. These models were also indicative of the pollution activities going on at the river specifically and in its neighbourhood at large. By simulation using the obtained models, the concentrations of the respective metals in 2013 and 2015 were evaluated to be 1228-130.8, 1.818-1.905, 12.01-17.16 and 4.70-8.196 mg/l respectively. Thus, residents who drink from or eat fruits and vegetables from farmlands irrigated by this river stand the chance of accumulating particularly Cu and Cd, whose concentrations were simulated to be increasing over this period, and may get to toxic levels in their bodies. The government, through its agencies like the Federal Environmental Protection Agency (FEPA), could adopt this method for monitoring and forecasting pollution activities in the environment in order to alert the citizenry in the event of an impending danger, enact appropriate laws, and control measures to protect the populace.

REFERENCES