ANALYTICAL STUDIES ON HEAVY METAL CONTAMINATION OF IMO RIVER

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ABSTRACT

In river systems, surface water has been widely used as environmental indicators and their chemical analysis can provide significant information on the assessment of anthropogenic activities. The paper evaluates the pollution status of the Imo River with reference to heavy metal enrichment. The mean concentration of the ten metals used in this study was slightly higher than the recommended maximum permissible limit by the Nigerian Standard for Drinking Water Quality except zinc. The results of the metal pollution index revealed that the river is slightly to moderately polluted with metals. The application of factor analysis on the data-set identified three factors which imply that these metals enter the river through three possible sources. Factor one comprises of pH, nickel, lead, iron and cadmium and accounts for 34.46% of the total variance. Factor two has a moderate loading of 25.89% of the total variance with arsenic, mercury, chromium and manganese as contributors. Factor three had the least loading from copper and zinc which constitutes a total variance of 16.64%. The pH of the river water has a mean value of 6.10 which signifies an acidic condition and is traceable to acid-rain ravaging the entire region caused by several years of continuous gas flaring. Aquatic organisms rarely survive under low pH and it also precipitates mobility of metals. The climate, local geology and hydrogeology of the area enhance the release and migration of these metals into the river system. The enrichment of these heavy metals in the river may be attributed to the dumping of waste into the river as well as the discharge of untreated industrial effluent into the river. The prohibition of dumping of waste into the river is strongly advocated. The present study demonstrated application of metal pollution index and factor analysis in understanding the quality of river water and appeared to be promising in the field of water quality management.

Keywords: Assessment, Metals Pollution Index, Factor Analysis, Imo River, Southeastern Nigeria

1.0 Introduction

River running through urban areas has also been faced water quality issues due to discharge of untreated domestic sewage, municipal wastes and industrial effluents into then leading to increase the metallic toxicity in the river waters [1]. Heavy metals are persistent in surface waters in the form of colloidal, particulate and dissolved forms and rivers are known as the dominant pathway for the transport of metals. Heavy metals are easily influenced by environmental factor such as runoff, groundwater, dissolution from sediment, deposition from atmosphere and anthropogenic pollutants. Metals are parts of the earth crust and are contained in rocks and minerals but become potentially toxic when dissolved in water [2].

Globally, there is an increasing awareness that water will be one of the most critical natural resources in future. Water is an important and life-sustaining substance to both plants and animals. It is an essential requirement of human and industrial development and it's the most delicate part of the environment. Water pollution by trace metals is an important factor in both geochemical cycling of metal and in environmental health. Trace amounts of heavy metals are always present in fresh waters from terrigenous sources such as weathering of rocks resulting into geo-chemical recycling of heavy metal elements in these ecosystems [3]. Therefore, a continuous monitoring of water quality is very essential to determine state of pollution in our rivers hence the need for the present study.

2.0 Objectives of the Research

Water is an essential requirement of human and industrial developments and it is one the most delicate part of the environment. There has been a tremendous increase in the demand for freshwater due to rapid growth of population and the accelerated pace of industrialization. The present study evaluates the level of contamination of Imo River by heavy metal in view of the enormous human activities domiciled in the region.

3.0 Statement of Problem

Rivers passing through urban cities are usually deteriorated due to the impact of population, urbanization and industrialization. Imo River is of particular importance in the study of surface water because it passes through highly populated and industrialized cities of Owerri, Aba and Port-Harcourt. Effluents from industries, municipal sewage, agricultural and urban run-off are discharged into river bringing about considerable change in the water quality. These anthropogenic activities on Imo River pose a serious threat not only to organisms in the river but also the downstream water users and once surface water is contaminated, its quality cannot be restored by stopping the pollutants from the source. It therefore becomes imperative to evaluate the quality of the water and to device ways and means to protect it.

4.0 Research Methodology

Ten sampling stations were established along the river course in order to give a comprehensive idea of overall quality of the river (Fig. 1). This was monitored for a period of one year by taking the sample once in every month. Water samples were collected from the water surface.

4.1 Laboratory analysis

Collected samples were subjected to filtration prior to chemical analysis while pH was determined in the field. The water samples were then analyzed for heavy metals using standard procedures of analysis [4].

4.2 Statistical analysis:

The factor and correlation analyses were done using SPSS 16:0. Metal pollution index was calculated from the point of view of suitability of the water for human consumption.

5.0 Review of Physiography, Geology and Hydrogeology of the Study Area

The name Imo State was coined from Imo River in 1976 and it is the main river separating Imo from Abia and Rivers States. It lies between latitude 4°40N to 6°30N and longitude 5°00'E to

7°30E (Fig. 1). The area is low lying and is drained by Imo River and its tributaries. The topography is under the influence of tides which results in flooding especially during the rainy season [5]. The prevalent climatic condition in the area comprises of the rainy (April to October) and dry (November to March) seasons and are characterized by high relative humidity throughout the year. The is underlain by the coastal plain sands also known as the Benin Formation which consists of fine to coarse grained sand with intercalation of clay lenses which are discontinuous (Fig. 1). The petrographic study on several thin sections shows that quartz makes up of 95% and feldspar has remaining 5% [6]. Furthermore, the area is underlain by thick unconfined aquifer of regional extent (Fig. 1). The depth to water table is below 15 m while the hydraulic conductivity (K) ranged from 5.0 to 44.0 m/d with a mean value of 20.0 m/day [7].

The aquifer transmissivity (T) are more than 500 m^2/day and an average porosity of 30.0%. The hydraulic gradients vary from 0.0007 in the recharge area to 0.005 in the discharge area while the linear groundwater velocity is in the range of 40.0 to 400.0 m/year. Recharge into the unconfined aquifer is through direct infiltration of rain water. The annual groundwater recharge ranges from 24.0 to 31.0 % of the annual rainfall of about 2500 mm [8]. The information on aquifer properties is necessary for the understanding of the dynamics and interaction between surface and groundwater since both overlap and the degree of mixing cannot be overemphasized.

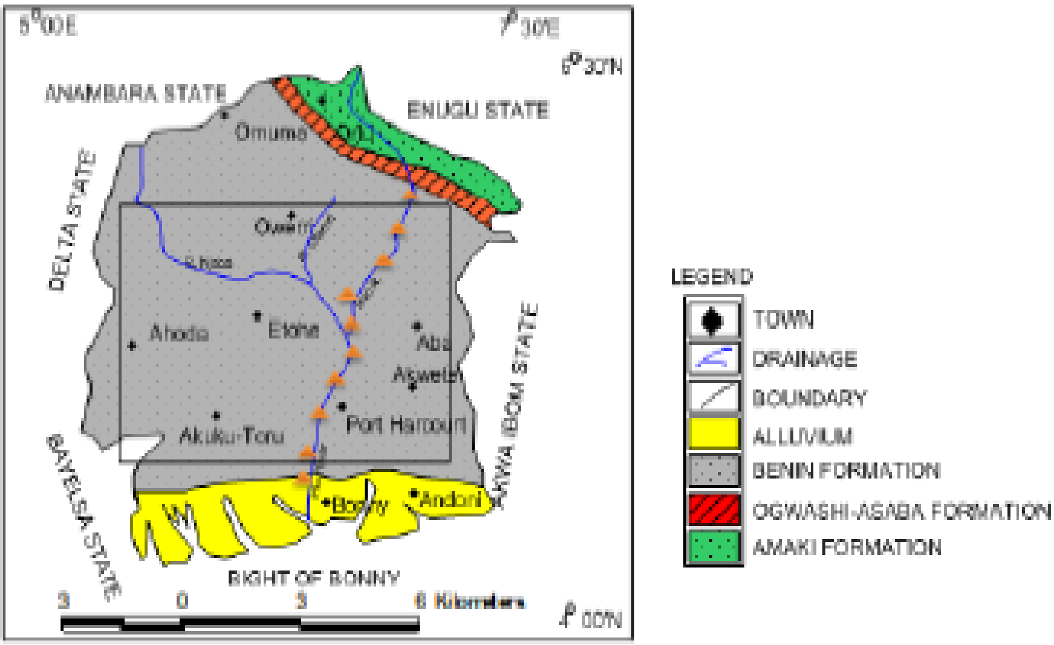

Fig. 1: Geology map of the area showing Imo River with the sampled stations

6.0 Results and Discussion

Contaminants in river system are investigated by analyzing the water and the result of the water analyses are contained in Table 1. The results of the analysis revealed that the Imo River is slightly to moderately polluted by heavy metals in the order of Ni > Fe > Cd > Pb > Mn > As > Hg > Cr > Cu > Zn. The metallic enrichment of the river may be attributed to the various anthropogenic activities such as dumping of solid waste along river channel (Plate 1), gas flaring in the vicinity of Imo River bank (Plate 2), flow stations, discharge of untreated industrial effluent from food, textile, paint, pharmaceutical, soap and detergent industries located along the river especially at the Aba and Port-Harcourt end.

Heavy metals are components of the rocks that make up the Earth crust and are released into the river by natural means such as weathering, run-off, dissolution and leaching as well as anthropogenic interference through mining, municipal wastes, industrial effluent and agro-chemicals [9]. The pH value ranged from 5.32 to 7. 30 with a mean value of 6.10 (Table 1) as against the acceptable range of 6.5 to 8.5 [10]. The values imply that the water is predominantly acidic and such water is likely to precipitate the mobility of metals and have a cohesive effect on materials. The concentration of iron ranged between 0.01 to 2.46 mg/L with an average value of 1.02 mg/L (Table 1). These values exceed the maximum permissible limit of 0.3 mg/L recommended by the Nigerian Standard for Drinking Water Quality. The implication of the high iron content is that the water from the river will have taste, colour and other aesthetic problems such as hemochromatosis.
The concentration of manganese varied from 0.01 to 0.09 mg/L with a mean value of 0.05 mg/L and these values are below the recommended value of 0.2 mg/L (Table 1) which implies no contamination. Manganese is a naturally occurring element in the environment. It comprises about 0.1% of the earth's crust. Manganese is an essential micronutrient for plants and animals. It is a functional component of nitrate assimilation and an essential catalyst of numerous enzyme systems in animals, plants and bacteria [11]. The concentration of dissolved manganese is influenced by changes in redox potential, dissolved oxygen, pH and organic matter. Manganese in surface water can be oxidized or adsorbed to sediment particles and settle to the bottom. Manganese in soil can migrate as a particulate matter to air or water, while the soluble manganese compounds can be leached from the soil. Manganese does not occur naturally as a base metal but is a component of more than 100 minerals, including various sulfides, oxides, carbonates, silicates, phosphates, and borates. It is found in rock, soil, water, and food [11]. Thus, all humans are exposed to manganese and it is a normal component of the human body. Manganese is released to air mainly as particulate matter, and the fate and transport of the particles depend on their size and density and on wind speed and direction. Some manganese compounds are readily soluble in water, so significant exposures can also occur by ingestion of contaminated drinking water. Chronic inhalation exposure to manganese affects negatively on lungs, nervous system, and reproductive system, although effects on other organ systems [12].

Table 1: Statistical Summary of the analyzed water samples

Parameters (mg/L)	Range	Mean	NSDWQ, (2007)
pH	5.32–7.30	6.10	6.5-8.5
Fe	0.01–2.46	1.02	0.3
Mn	0.01–0.09	0.05	0.2
Zn	0.02–2.80	1.65	3.0
Cu	0.03–1.48	1.02	1.0
Cr	0.02–0.16	0.07	0.05
Cd	0.001–0.023	0.01	0.003
Ni	0.01–0.13	0.07	0.02
Pb	0.01–0.12	0.03	0.01
Hg	0.001–0.005	0.002	0.001
As	0.001–0.045	0.021	0.01

NSDWQ = Nigerian Standard for Drinking Water Quality

The zinc content varied from 0.02 to 2.80 mg/L with a mean value of 1.65 mg/L which are lower than the [10] permissible value of 3.0 mg/L thereby suggesting no pollution. In most waters, the zinc (II) as oxidation state of zinc is toxic to aquatic organisms at relatively low concentrations. The greatest dissolved zinc concentration occurs in low pH, low alkalinity and high ionic strength solutions. Zinc is a very common environmental contaminant and it is commonly found in association with lead and cadmium. The major sources of zinc in the aquatic environment are the discharge of domestic waste waters; coal-burning power plants and manufacturing processes involving metals [13].

The concentration of copper varied between 0.03 to 1.48 mg/L with an average value of 1.02 mg/L as against the recommended value of 1.02 mg/L (Table 1). Copper is an essential substance to human life, but in high concentration, it can cause anemia, liver and kidney damage, stomach and intestinal irritation. Copper normally occurs in drinking water from copper pipes, weathering of products made from copper as well as from additives used to control weed. The values in some locations were high than the maximum permissible value which suggest possible contamination. The enrichment may be attributed to dumping of abandoned metallic objects and insecticides along the river as well as discharge of effluents from the neighboring industries into the river system. High concentration of copper in the body causes nausea, vomiting, and abdominal pain, breakdown of red blood cells and Wilson's disease in children [14].

The concentration of chromium ranged from 0.02 to 0.16 mg/L with a mean value of 0.07 mg/L as against the allowable limit of 0.05 mg/L (Table 1). The values of chromium in some locations are slightly higher than the recommended value and it can be attributed leachates from wastes in the vicinity of the river. The concentration of cadmium varied from 0.01 to 0.023 with an average value of 0.01 mg/L as against the acceptable value of 0.003 mg/L (Table 1). Discharge of used batteries, PVC plastics, paint, motor oil, insecticides and agrochemicals into the river may be responsible for the observed values. This is the challenge of any river that passes through developed cities because it receives wastes more than the river passing through villages. Cadmium is a few of elements spread in nature and can be considered as trace elements in view of the lack of focus in rocks, sediments, water and air, and notes an increase in concentration only in the case of a human activity or agricultural population or industrial. Cadmium is a common impurity as complex oxides, sulfides, and carbonates in zinc, lead and copper ores, and it is most often isolated during the production of zinc [15].

The sources of cadmium in the aquatic environment are from natural weathering processes, mining, metal smelters, industries, agricultural use of sludges, fertilizers and pesticides, burning of fossil fuels, and the deterioration of galvanized materials and cadmium-plated containers. Cadmium reaches into the blood stream by eating and drinking cadmium-contaminated food or water and by breathing cadmium contaminated air. The major effects of cadmium poisoning are experienced in the lungs, kidneys and bones. Acute effects of inhalation are bronchitis and toxemia in the liver. Chronic inhalation of cadmium compounds as fumes or dust produce pulmonary emphysema, where the small air sacs of the lungs become distended and eventually destroyed reducing lung efficiency [16]. High accumulation of cadmium in the body also damages the liver, placenta, brain and bones.

Plate 1: Refuse dumps along Imo River channel

Plate 2: Gas flaring stations along the Imo River course

The value of lead in surface water ranged between 0.01 to 1.2 mg/L with a mean value of 0.03 mg/L as against the permissible value of 0.01 mg/l [10]. Lead is potentially hazardous to most form of life and is considered toxic to organisms. Low lead concentration can affect fish by causing the formation of coagulated mucous over the gills and subsequently over the entire body and thus cause the death of fish due to suffocation. Lead is bio-accumulated by benthic foraminifera, freshwater plants, invertebrates and fish. The chronic effect of lead on man includes neurological disorders, especially in the fetus and in children, synthesis of hemoglobin, gastrointestinal tract, kidney diseases and impaired performance in IQ test. Lead is however used in batteries, petrol additives, alloys, cable sheathing, pigments, rolled and extruded products [14].

The concentration of nickel varied from 0.01 to 0.13 mg/L with a mean value of 0.07 mg/L as against the recommended value of 0.02 mg/L (Table 1). The elevated values may be due to leachate arising from smelting activities, nickel-cadmium batteries, lead-nickel batteries, nickel plating as well as leachate and effluent discharge into the river as a result of urbanization and industrialization. The concentration of arsenic varied from 0.001 to 0.045 mg/L with a mean value of 0.021 mg/L as against the allowable value of 0.01 mg/L (Table 1). The dumping and subsequent decomposition of chemicals used in making paints, rat poisoning, fungicides and wood preservation may led to the enrichment of the river with arsenic [17]. High concentration of arsenic in human body causes cancer and damage to the organs. The concentration of mercury ranged from 0.001 to 0.005 mg/L with an average value of 0.002 mg/L while the NSDWQ value is 0.001 mg/L. High concentration of mercury causes brain and kidney damage, anxiety, deafness and depression.

6.1 Metal Pollution Index

Heavy metal refers to any metallic chemical element that has a relatively high density and toxic or poisonous at low concentrations. They cannot be degraded or destroyed and can enter our bodies through food, drinking water and air. Heavy metals are dangerous because they tend to bioaccumulate. Bioaccumulation is an increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment.

Metal pollution index is a method of rating that shows the composite influence of individual parameters on the overall quality of water. The rating is a value between zero and one, reflecting the relative importance individual quality considerations. The higher the concentration of a metal compared to its maximum allowable concentration, the worse the quality of the water. It is also a combined physio-chemical and microbial index which makes it possible to compare the water quality of various water bodies [18, 19]. It has wide application and it is used as the indicator of the quality of sea and river water as well as drinking water [19, 20]. The MPI is the sum of the ratio of the analyzed parameters and their corresponding national water standard.

$$MPI = \sum_{i=1}^{n} \left[\frac{Ci}{(MAC)i}\right]$$

where: *Ci*: concentration of each element

MAC: maximum allowable concentration

The results of the computed metal pollution index are shown in Table 2. It can be observed from Table 2 that the degree of metallic contamination in the river is within the range of slightly polluted to moderately polluted. The polluting metals in their order of enrichment are: Ni > Fe > Cd > Pb > Mn > As > Hg > Cr > Cu > Zn. The poor sanitary condition within and around the river coupled with the high rate of urbanization and industrialization of the region through which the river passes are responsible for the poor river quality. The leachate arising the various human activities within the river banks poses a threat to the river quality.

Table 2: Calculated Heavy Metal Pollution Index for the Groundwater in the Area

Parameters (mg/L)	HMPI Value	Rating
Arsenic	2.10	Moderately polluted
Cadmium	3.33	Moderately polluted
Chromium	1.40	Moderately polluted
Copper	1.02	Moderately polluted
Iron	3.40	Moderately polluted
Lead	3.00	Moderately polluted
Manganese	2.50	Moderately polluted
Mercury	2.00	Moderately polluted
Nickel	3.50	Moderately polluted
Zinc	0.55	lightly polluted

< 0.01 = Very lightly polluted; 0.01-0.99 = Lightly polluted; 1.0-4.99 = Moderately polluted; 5.0-10.0 = Highly polluted; > 10.0 = Very highly polluted

6.2 Factor Analysis

Factor analysis is a grostatistical technique that focuses on data reduction in order to identify a small number of factors that are used to interpret the variations observed in the larger dataset. It attempts to identify new underlying factors that give a better understanding of the pattern of correlation within a set of observed variables [22, 22]. The objective of factor analysis is to interpret the structure within the variance-covariance matrix of a multivariate data collection. It uses the extraction of the eigenvalues and eigenvectors from the matrix of correlation or covariance. The information gained about the interdependencies between observed variables can be used later to reduce the set of variables in a dataset [23, 24].

Factor analysis has been used with remarkable success as a tool in the study of groundwater chemistry. The factor analysis has the potentials to unravel hidden inter-variable relationships and allows the use of virtually limitless number of variables, thereby allowing heavy metals to be used in surface water studies. Several researchers have used multivariate analyses to understand hydrogeological characteristics and contamination of regional surface water [25, 26].

Factor analysis extracts the multivariate influence to understand the causes of major factors affecting water quality and acquires information on the strength of the influence. It has also been adopted as an important analytical tool to describe and map the spatial variability of hydrochemical parameters [27]. The characteristics of surface water quality are closely related to environmental variability. SPSS-window-20 version was the statistical software used to perform factor analysis on the datasets.

Table 3: Factor loading of the dataset after varimax rotation

Parameters (mg/L)	Factor-1	Factor-2	Factor-3
Arsenic	.002	**.517**	.216
Cadmium	**.502**	.301	.116
Mercury	.235	**.505**	.149
Chromium	.360	**.517**	.334
Copper	.134	-.005	**.549**
Iron	**.850**	.391	.288
Lead	**.520**	.353	.091
Manganese	.002	**.659**	.114
Nickel	**.531**	.142	.336
Zinc	.257	.056	**.520**
pH	**.705**	.380	.345
Eigenvalues	2.446	1.832	1.106
% of Variance	34.459	25.890	16.638
Cumulative %	34.459	60.349	76.987

Factor analysis was applied to dataset and it generated three main factors with Eigenvalues greater than one. The three factors accounts for a total of 76.99% of the variance in datasets and it implies three different sources of contamination to the river. The first factor consists of cadmium, iron, lead, nickel and pH and these explained the 34.46% of the total variance (Table 3). Their presence may be attributed to anthropogenic activities such as gas flaring, discharge of industrial effluent and dumping of solid waste along the river course. The low pH can be attributed to the gas flaring in the region.

Factor 2 explains 25.89% of the total variance and the contributors are arsenic, mercury, chromium and manganese. The use of agrochemicals for farming along the river banks as well as leachate from decomposing wastes may be responsible for their enrichment. Factor 3 is a moderate loading copper and zinc and account for 16.64% of the total variance. Dumping and gradual decay of used metals and electronic gadgets such as computers, phones, cars, fans, refrigerator, television, metallic chairs and tables may have constituted to their presence in the surface water. High precipitation and relative humidity of the area coupled with porosity and permeability of the underlying lithology encourages rapid chemical weathering and infiltration of leachate into the rivers as well as the shallow water table. Furthermore a correlation analysis was done among the metals analyzed (Table 4) and a strong positive alignment exist between arsenic and lead, iron and nickel as well as copper and zinc.

Table 4: Pearson Correlation Coefficient Matrix for Heavy Metals in Soils from the Dumpsite

	As	Cd	Hg	Cu	Cr	Fe	Mn	Ni	Pb	Zn
As	1.000									
Cd	0.281	1.000								
Hg	0.117	-0.364	1.000							
Cu	0.135	0.185	0.275	1.000						
Cr	0.251	0.422	0.098	0.329	1.000					
Fe	0.075	-0.353	0.153	0.154	0.458	1.000				
Mn	0.128	0.223	0.351	0.042	-0.615	0.154	1.000			
Ni	0.319	0.176	0.113	-0.356	0.309	0.462*	0.254	1.000		
Pb	0.564*	0.212	0.435	0.423	0.121	0.324	0.465	0.127	1.000	
Zn	0.248	-0.387	0.258	0.657*	0.430	0.372	0.050	0.085	0.101	1.000

7.0 Conclusion and Recommendation

The application of MPI has clearly revealed that Imo River is slightly to moderately contaminated by heavy metals in the order of Ni > Fe > Cd > Pb > Mn > As > Hg > Cr > Cu > Zn. Human activities domiciled in the area are the major sources of these metals. The high porosity, permeability, hydraulic conductivity and transmissivity that characterize the aquifer geometry encouraged mobility of these metals with the aquiferous zone. The mobility of these metals between the surface water and stream sediment are enhanced by the low pH which is caused by long term gas-flaring in the area. This has led to death of aquatic organism and damage to the mangrove vegetation. The prohibition of dumping of waste along river banks is strongly advocated.

8.0 Reference

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