DOI: https://dx.doi.org/10.4314/gjpas.v29i1.11

GLOBAL JOURNAL OF PURE AND APPLIED SCIENCES VOL. 29, 2023: 91-97
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APPLICATION OF INVERSE MODELLING FOR PREDICTION OF THE SURFACE WATER CHEMISTRY OF THE EKULU RIVER IN ENUGU, SOUTHEASTERN NIGERIA

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(Received 11 April 2023; Revision Accepted 15 May 2023)

ABSTRACT

Surface water chemistry evolution of Ekulu River was conducted by inverse geochemical modelling using the PHREEQC computer program. In this study, samples were collected from the Ekulu river at 100m intervals, and were taken to the laboratory for major anions and cations, heavy metal and bacterial content analyses. Inverse geochemical modelling results reveal that the river evolved as a result of dissolution of siderite, quartz, gypsum, galena, sphalerite, pyrolusite and precipitation of goethite and pyrite. The Piper diagram indicates Calcium-Chloride water type, with high Ca^{2+} + Mg^{+} and Cl^{-} + SO_4^{2} contents, which is typical of water originated from gypsum dissolution and mine drainage. The results of the analyses show that the water cannot be recommended for drinking because the E. coli and coliform contents are higher than the permissible limits. The water chemistry of Ekulu river is as a result of secondary minerals dissolution and mine drainage from Onyeama coal mine whereas the microbial content resulted from pollution from recent faeces.

KEYWORDS: Ekulu River, Heavy metal, Hydrogeologic facies, Inverse modelling, PHREEQC,

INTRODUCTION

The final composition of water depends on rock types, land use (agricultural or industrial), presence of diffuse or conduit flow path, infiltration rate, climatic conditions, residence time and mechanism of recharge. Reconstruction of the processes that gave rise to any water quality requires inverse modelling with known solution and mineral phases. This involves combination of mineral phases, initial and final solution to explain chemical changes such as precipitation and dissolution.

Researchers have used inverse modelling to identify pollution sources in both groundwater and surface water using complex real-life scenarios to quantify uncertainties at reduced cost (Sharif et al., 2007; Younes, 2012; Peikam and Jalali, 2016; Moghaddan, et al, 2021).

For example, the result from modelling Mississippi River, USA, revealed Fe oxyhydroxide, fluorite, pyrite, calcite, halite, organic matter, H_2S (gas), siderite, and vivianite as the potential phases (Sharif et al., 2007). Peikam and Jalali (2016) used multivariate analysis and inverse modelling to study evolution of surface water chemistry in a watershed and found that changes of water chemistry along the flow path happened as a result of precipitation of feldspars and andalusite as well as dissolution of sylvite and kaolinite. Younes (2012) investigated the evolution of groundwater in Southeastern China with PHREEQC and found the minerals that dissolved to give rise to the water chemistry, through chemical processes such as dissolution, dedolomization and ion exchange. Accurate identification of sources of contaminant using modelling of spatial concentration data from observation points depends on the

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methodology used, as well as their application to real world cases (Moghaddan, et al, 2021). Jamshidi et al, 2020 presented a new method of identification of history and location of groundwater contaminant source using inverse model with combination of optimization algorithm and forward model. Therefore, application of inverse modelling to Ekulu river will give insight to the evolution and pollution sources.

Previous researches reveal that Ekulu river and other rivers in Enugu are highly contaminated (Osuinde and Eneuzie, 1999; Aniebone, 2014; Ugochukwu et. al, 2019; Chinedu et al., 2021; Ken-Onukuba et. al., 2021). Concentration of all the heavy metals in Abakpa River, Iva valley river and Ekulu River exceeded the different drinking water limits except zinc (Chinedu et al., 2021). Lead and cadmium are major contaminants in the Ekulu river (Ugochukwu et. al., 2019). In addition, this stream is used as a “natural lavatory”, as evidenced by high deposits of human excrement along the river banks in Abakpa area. Aniebone (2014) carried out research to determine the bacterial contaminant in surface water around Enugu metropolis, and found high concentrations of heavy metals and pathogens with colonies ranging between 10 to over 200. High coliform count in Ekulu River may be an indication that the water sources were faecal contamination (Osuinde and Eneuzie, 1999). Ekulu River has low pH, high turbidity, high iron content and coliform. Both Ekulu and Asata rivers in Enugu Areas are not generally suitable for domestic/industrial purposes because of low pH, high turbidity and coliform, nitrate, iron and chromium contents above the World Health Organization (WHO) and Federal Ministry of Environment (FMENV) Drinking Water Quality Standards (Ken-Onukuba, 2021). Therefore, re-evaluation of the current pollution status of Ekulu River is crucial for the determination of its evolution and suggestion of the remediation strategy.

Many authors have suggested different sources of heavy metal and microbial contamination of the Ekulu river (Ude, 2001; Ken-Onukuba et. al., 2021). Coal mining activities and disposal of industrial and domestic waste have been suggested as the sources of contamination of Ekulu river (Ken-Onukuba et. al., 2021). Sources of pollution of these streams in Enugu urban are water drained from fertilized agricultural land and uncultivated land (Ude, 2001). Therefore, employing geostatistical tools is required for assessment and determination of the pollution point sources of Ekulu river, which were lacking in literature.

The aim of this work was to determine the evolution and pollution point sources of Ekulu river through inverse modelling, using PHREEQC (PH Redox Equilibrium by C language) computer code.

GEOLOGIC SETTING

The study area covers Abakpa Nike and its environs in Enugu East L.G.A of Enugu State, south eastern Nigeria. The area lies between latitudes 6^{o} 28’N and 6^{o}33’N and longitudes of 7^{o} 29’E and 7^{o}33’E. Two lithological units were delineated; Unit A is dominated with shale belonging to the Enugu Shale, and Unit B consists of lateritic overburden with an intercalation of ironstone and sandstone, clay, siltstone and alluvial sandstone belonging to the Manu Formation (Figure 1). The ironstone is laterally extensive, well bedded with cracks and fractures. The sandstone is medium to coarse grained and reddish to brown colour. The clay is moderately consolidated and the siltstone is milkish white in colour. Siltstone is milkish to purple colour. Sedimentary structures include joint, cracks, bioturbation, ripple marks, ophiomorpha burrow, lamination and cross beds. The beds strike 85^{o}NW with dip: amount of 3^{o} in south western direction.

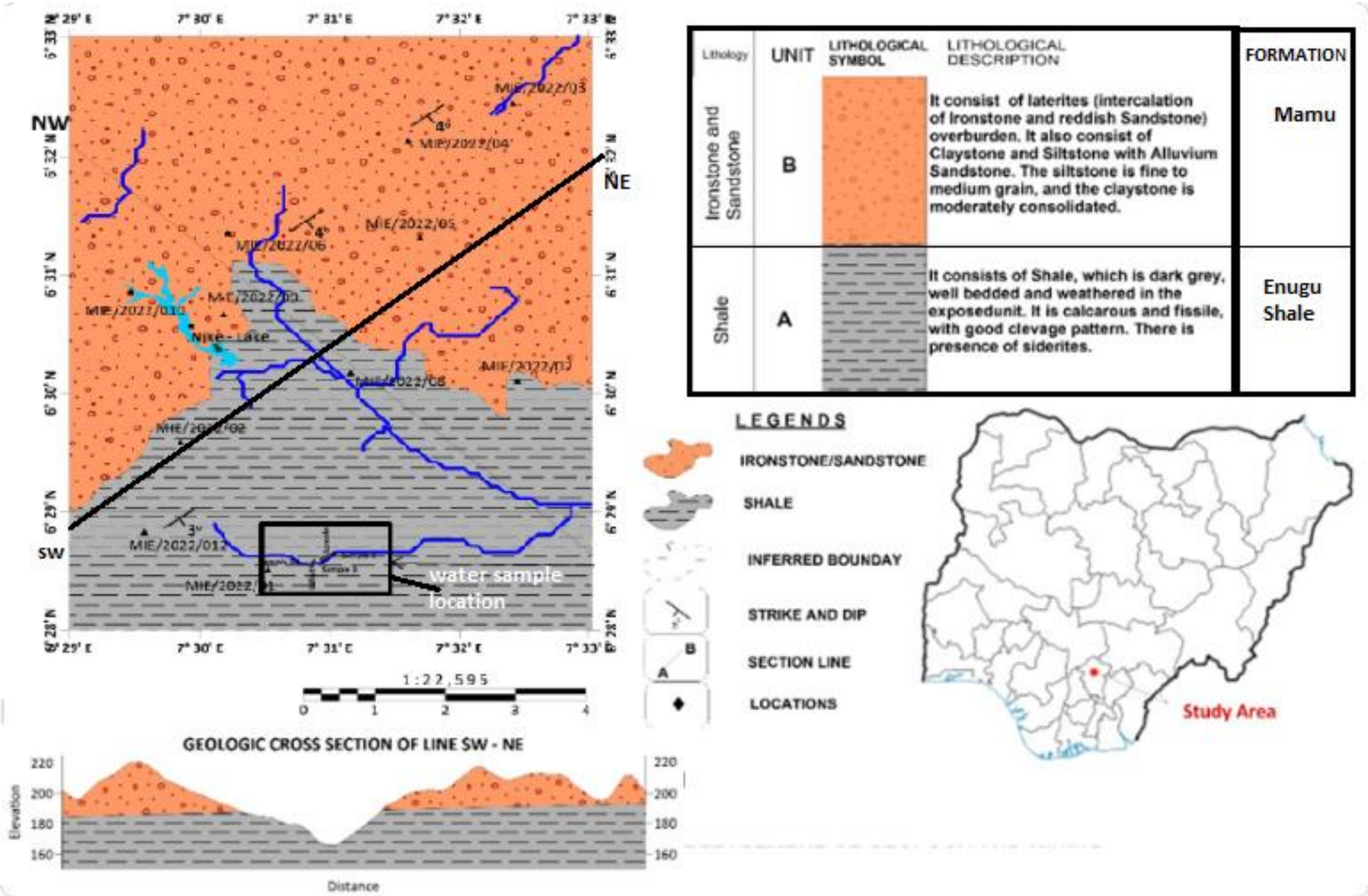

Figure 1**:** Geologic Map of Abakpa-Nike and Environs showing Ekulu River and water sample location.

MATERIALS AND METHODS

HYDROGEOCHEMICAL ANALYSIS

Five water samples at 100m intervals (in order to accommodate possible small changes in water chemistry) were collected along Ekulu river. Before sample collection, the pre-washed polyethylene containers were rinsed several times with the sample water before representative samples were obtained. The representative samples were labelled correctly and transported to a laboratory and later transferred to a refrigerator calibrated to 4 °C. These samples were analyzed within 24 hours. Parameter such as pH, Temperature, Turbidity, Electrical Conductivity, Total Dissolve Solute, Dissolved Oxygen, Biochemical Oxygen Demand, Chemical Oxygen Demand were measured using parameter specific probes e.g., Hanna pH/DO/EC meters. Anions and cations such as Chloride, Sulphate Nitrate, Phosphate, Chromium, Zinc, Cobalt, Lead, Cadmium, Alkalinity, Fluoride, Iron, Manganese, Potassium, Magnesium, Sodium, Silicon (iv) Oxide and Trioxocarbonate were analysed with atomic absorption spectrophotometer (AAS) using standard procedures laid out by the American Public Health Association (APHA, 2005). The samples were also analysed for bacterial content.

GEOCHEMICAL MODELLING

The inverse modelling of the the phisoco-chemical data of the five (5) water samples from the Ekulu river were performed using PHREEQC for windows version 1.5.08 (Parkhurst and Appelo, 1999) in order to determine the mineral phases that led to the evolution of the chemical composition. It involves determining different moles of mineral phases that accounts for changes in composition between initial and final water chemistry (Parkhurst and Appelo, 1999). To achieve this, the code calculates mass balance equations that can predict the final water composition starting with initial water composition. The input data are composition of rain water with ambient temperature, pH of 5.7, major ions that are obtained from chemical composition of the final solution and the software's solution keywords. Predicated mineral phases based on the geology of the area as well as the results of water analyses were added. The minerals selected were halite, siderite, quartz, gypsum, pyrite, goethite, sylvite, galena, sphalerite, kaolinite, pyrolusite, dolomite and goethite.

PIPER DIAGRAM

The results of water samples were plotted in a Piper diagram. The diagram consists of apexes of cation (Ca, Mg, Na + K) and anion (SO_4, Cl. CO_3 + HCO_3) in a separate ternary plot (Piper, 1994). This diagram is good for comparing the ionic composition of water samples by grouping them in hydrochemical facies. Two triangles are used to represent cations and anions while a single diamond summarizes the triangles (Piper, 1994).

RESULTS AND DISCUSSION

The chemical and bacteriological compositions of the Ekulu river are shown in Table 1 and Table 2, respectively. The results were compared with the World Health Organization (WHO) and Nigerian-Standard-for-Drinking-Water-Quality (NSDWQ) standards for drinking water. The major cations and anions are within the specified standards for drinking water by WHO (2022) and NSDWQ (2015). However, the water is contaminated with lead, cadmium and chromium. This is consistent with the studies of Chinedu et al., (2021), Ken-Onukuba (2021), and Ugochukwu et. al., 2019. Some of these contaminants are man induced and others are natural. Therefore, the water is not suitable for human consumption without treatment.

The results of the bacterial content of the samples reveal higher bacterial concentration per 100ml (Tables 2), which is above the WHO standard limit of zero. Total coliform bacteria count is 20 cfc/ml in all the water samples. These colonies of bacteria include both gram-negative aerobic and anaerobic, non-spore-forming bacilli that occur in both sewage and natural waters. Their absence is an indication of cleanliness and distribution system (WHO, 2022). Both Escherichia coli (E.coli) and coliform bacteria amount range from 10 -18 cfc/ml in the water samples. Such high amount of *E.coli* is an indication of recent faecal contamination (WHO, 2022). Aniebone (2014) also found that Ekulu river is highly contaminated with bacterial such as *E.coli* and coliform. This bacterial contaminant might be as a result of faecal matter being dumped into the surface water.

Table 1: The result of chemical analysis from water sample from Ekulu River

Parameters	Unit	sample code						
		A	B	C	D	E	WHO Standard (2022)	NSDWQ (2015)
pH	**(at 27^0C)**	6.7	6.9	7.0	7.1	7.2	6.5-8.5	6.5-8.5
Temperature	^{o}C	25	25	26	27	29	Ambient	Ambient
Turbidity	**(NTU)**	5.5	10.1	10.3	9.9	10.3	5	5
Electrical conductivity	**(us/cm)**	40	130	120	120	150		
Chloride	mg/L	7.2	7.1	7.5	7.4	7.2	250	250
Total Dissolve Solute	mg/L	100	70	80	120	110	500	500
Dissolved Oxygen	mg/L	12	17	18	15	16		
Biochemical Oxygen Demand	mg/L	8	9	10	9	8		
Chemical Oxygen Demand	mg/L	22	20	18	23	24		
Sulphate	mg/L	40	80	70	90	60	100	100
Nitrate	mg/L	14	17	17	20	19	50	50
Phosphate	mg/L	30	34	35	40	18	1.3EU	
Chromium	mg/L	0.5	0.45	0.6	0.54	0.78	0.01	0.05
Zinc	mg/L	1.4	2.2	1.6	1.4	1.2	3	3
Cobalt	mg/L	0.3	0.1	0.2	0.32	0.41		
Lead	mg/L	0.2	0.3	0.1	0.22	0.11	0.01	0.01
Cadmium	mg/L	0.04	0.05	0.06	0.03	0.02	0.003	0.003
Floride	mg/L	0.78	0.98	0.81	0.54	0.63	1.5	
Iron	mg/L	1.3	1.6	1.32	1.7	1.21	0.3	
Manganese	mg/L	0.30	0.21	0.37	0.18	0.21	0.3	0.2
Calcium	mg/L	34	33	36	32	30	100	
Potassium	mg/L	6.1	4.5	6.8	4.4	3.5	20	
Magnesium	mg/L	8	9.5	8.7	7.8	9.0	50	
Sodium	mg/L	12	11	10	15	11	200	
Silicon (IV) Oxide	mg/L	0.34	0.41	0.43	0.38	0.35		
Hydrogen Trioxocarbonate	mg/L	0.01	0.05	0.03	0.04	0.02	350	350

Table 2: The result of microbiological analysis of water sample from Ekulu River

Sample code	Total plate count (cfc/ml)	E.coil (cfu/ml)	Coliform (cfc/ml)	100 (cfu/ml)
A	20	10	10	10
B	20	15	15	15
C	20	12	12	12
D	20	18	18	18
E	20	10	10	10
Comparing the above results with different standards				
WHO (2022)	Free from Bacteria	Free from Bacteria	Free from Bacteria	cfc Not exceed 4/100ml
NSDWQ (2015)	10	0	0	0

The results of the inverse modelling of water from Ekulu river (Table 3) reveal that these waters are supersaturated with ccerussite, goethite, magnetite, hydrozincite and otavite. More than 40 models were found in some of the simulations; however, two representative models were selected for this study. In most of the models both goethite and pyrite precipitated, whereas siderite, pyrolusite, sphalerite, galena, quartz, gypsum dissolved. These minerals dissolve in water to release their different elements such as Pb, Zn, Cd, Mn and Fe into surface, groundwater and soil. This is in agreement with the findings of Adigun and Kayode, 2019 for water samples from Okaba Coal mine. Environmental contamination of heavy metal around the Onyeama and environs revealed that mine spoils and sediments (coal and shale) are highly enriched with Fe, As, Cd, Mn, Ni, Pb and Zn (Ugochukwu et al., 2019). Similarly, sediments and mine dumps samples from Okpara coal mine in Enugu are enriched with high loading of Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn, and serves as a pool capable of releasing these metals into surface and groundwater (Sikakwe et al, 2015). Therefore, secondary mineral as well as dissolved minerals from near by Okpara coal mine contributed to the evolution of the Ekulu river.

This indicates that there may be presence of sphalerite and galena in coals mined at Okpara coal mine. High amounts of lead, iron, chromium, chloride, manganese and zinc have been found in Okaba coal deposit in Nigeria, and these coals contain trace amounts of galena, sphalerite, chalcopyrite, pyrite and clay(Adigun and Kayode, 2019). High lead content has been found in pyrite found in coal (Wang et al. 2005; Wu et. al., 2004). Micron -sized particles of galena exist in coal fractures, organic material, pyrite and clauthalite(PbSe) (Finkelman, 1995). Galena and sphalerite were found in Chinese coal and have contributed to enrichment of Pb and Zn in the coal(Dai et al, 2012).

Table 3: Results of inverse modelling of water from Ekulu River in mmol/kg water

Sample	Models number	Siderite ($FeCo_3$)	Quartz (SiO_2)	Gypsum $CaSO_4$:$2H_2o$)	Pyrite (FeS_2)	Galena (PbS)	Sphalerite (ZnS)	Pyrolusite (MnO_2)	Goethite (FeOOH)
A	1	5.291E-04	7.299E-03	8.158E-05	-1.236E-0	1.656E-04	-	-	-2.333E-05
	2	5.291E-04	7.299E-03	8.158E-05	-1.236E-04	-	1.656E-04	-	-2.333E-0
B	1	3.590E-04	7.299E-03	6.040E-05	-1.243E-04	1.881E-04		1.933E-04	1.447E-04
		3.590E-04	7.299E-03		-2.761E-05		5.523E-05		4.809E-05
C	1	3.204E-04	7.685E-03	4.681E-05	-5.404E-05	6.127E-05	-	-	4.542E-05
	2	-	7.685E-03	-	-4.323E-05	-	8.646E-05	2.162E-05	3.550E-04
D	1	4.928E-04	6.769E-03	7.088E-05	-7.418E-05	7.749E-05	-		-1.377E-05
	2	4.928E-04	6.769E-03	7.088E-05	-7.418E-05	-	7.749E-05	-	-1.377E-05
E	1	1.843E-04	6.187E-03	2.481E-05	-1.420E-05	3.584E-06	-	-	1.212E-04
	2	1.843E-04	6.187E-03	2.986E-05	-5.460E-05	-	7.934E-05	-	-

NB: Positive mole transfers = dissolution; negative mole transfers = precipitation.

The Piper diagram graph revealed that the water samples are Calcium-Chloride type of water (Figure 2). This is as a result of higher concentration of Ca^{2+} + Mg^{+} and Cl^{-} + SO_4^{2-}. Additionally, all the analysed samples ~~all~~ fall within the Ca- SO_4 water, which is typical of water originated from gypsum dissolution and mine drainage. Piper diagram divides water into four basic types according to their placement near the 4 corners of the diamond. From the diagram all the water samples plotted at the top of the diamond, which is an area high in Ca^{2+} and Cl^{-} + SO_4^{2-} , indicating water of permanent hardness.

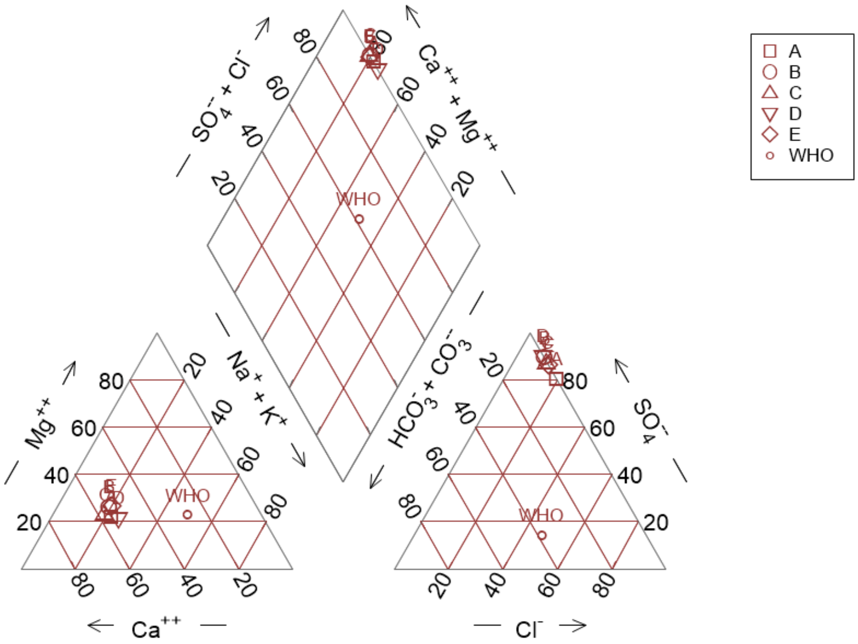

Figure 2: Piper diagram of water samples obtained anions and cations in mg/L.

RECOMMENDATION:

The water samples tested are too contaminated for human consumption. It requires thorough filtration and decontamination before it can be used for domestic purposes. Also, water managers need to put in place a task force to determine the origin of man- induced contamination (such as faecal matter, electronic gadget and waste disposal). This can help reduce the contamination introduced to the river. Sensitization of urban dwellers on the importance of reducing the dumping of waste and faecal matter into the river is also required.

CONCLUSION

This paper has evaluated the water quality and microbiological content of Ekulu River. The results revealed that the water within the study area should not be recommended for drinking because of high *E.coli* and coliform contents, as well as high concentrations of lead, cadmium and chromium. Inverse modelling with PHREEQC reveals that water chemistry evolved from precipitation of goethite and pyrite and dissolution of siderite, pyrolusite, sphalerite, galena, quartz, gypsum. Therefore, secondary mineral as well as dissolved minerals from mine contributed to the evolution of Ekulu river. The piper diagram plot indicates that the water samples are the Calcium-Chloride type, due to their high Ca^{2+} + Mg^{+} and Cl^{-} + SO_4^{2-} contents. In addition, the samples fall within the Ca- SO_4 water, which is typical of water originated from gypsum dissolution and mine drainage. We recommend that government should put in place adequate legal measures to prevent the disposal of faecal matter that may increase the bacterial content.

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