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Heavy metal pollution indexing and multivariate statistical evaluation of hydrogeochemistry of River PovPov in Itakpe Iron-Ore mining area, Kogi State, Nigeria

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ABSTRACT

A total of thirteen (13) surface water samples collected during dry and onset of rain seasons were analysed for some variables. Data collected in both seasons were subjected to heavy metal pollution indexing (HPI) and metal index (MI) approaches in conjunction with multivariate statistical technique. Significant variations were observed between the seasons. The HPI calculated for both seasons are 1408.33 and 299.32 respectively. These are far above the critical index value of 100, indicating pollution with respect to heavy metals. MI index based on total trend evaluation of the river status was 403 and 87.12 respectively, clearly indicating low-quality water. MI > 1 is a threshold of warning. Five factors chosen for interpretation accounts for 95.20% of total variance in the data set. The first factor is an association of pH, Tds, Ec, alkalinity and K while the second factor is characterized by temperature, K, SO_4, Fe and Ni. The third and fourth factors are made up of Cl, NO_3, Pb and temperature, Cd respectively. The fifth factor is characterized by Cu only. R-mode cluster produces four and Q-mode cluster three major groupings respectively with the highest similarity existing among cluster one in each mode. This shows that hydrogeochemical constituents of the water are mainly controlled by Tds, Ec, K, SO_4, NO_3 and Cl. This study reveals the need for heavy metal indexing and statistical approaches in hydrogeochemistry.

Key words: Anthropogenic, Heavy metal pollution index, Itakpe, Multivariate technique.

INTRODUCTION

Iron-Ore mining either by surface or underground methods have irreparable consequences on the environment. Surface mining involves tearing up large tracts of earth surface; removing materials and throwing the removed soil back into the cut [1]. Soils

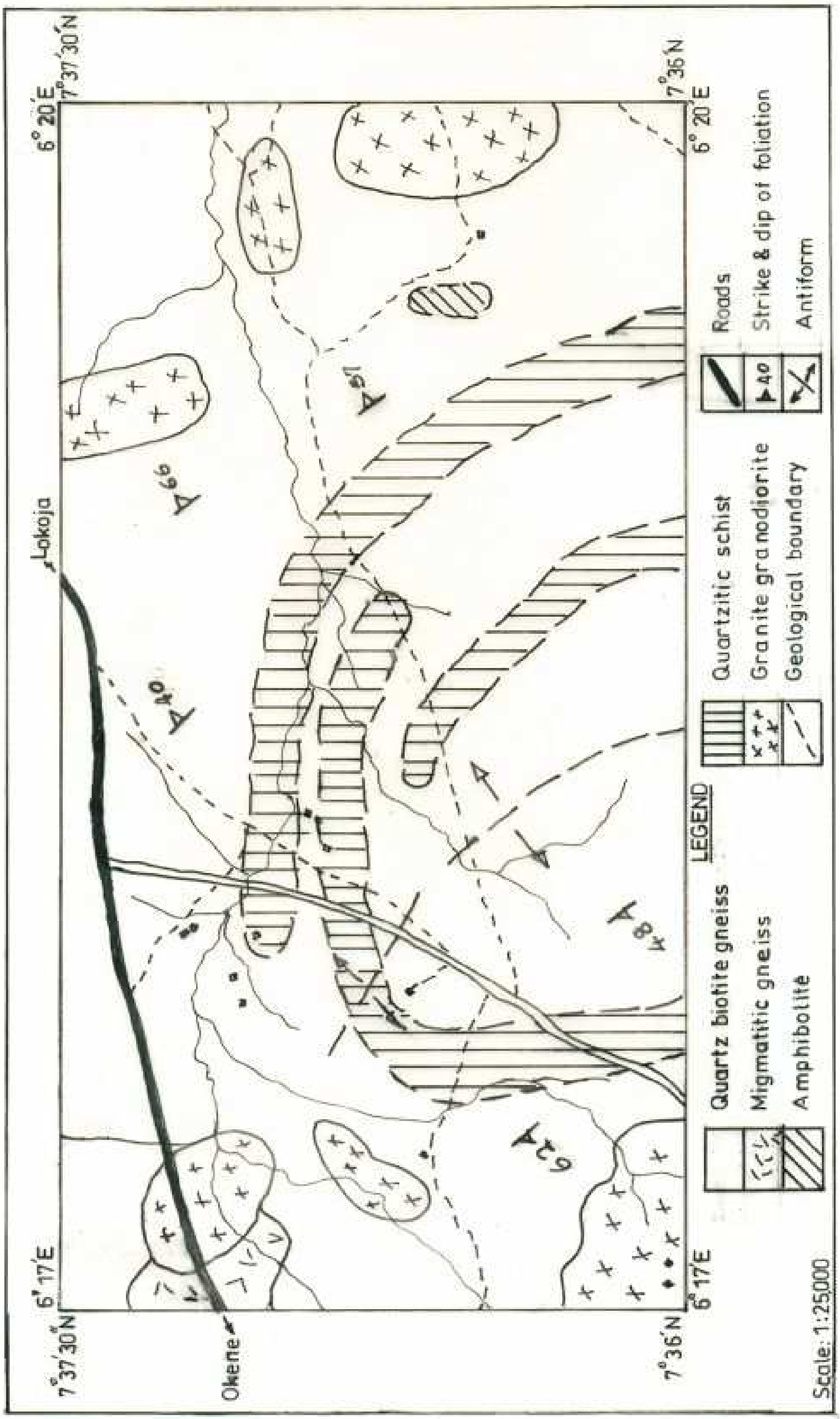


Fig.1: Geological map of Itakpe [5]

on exposure to the surface are subjected to new weathering and compaction, vegetation is removed entirely, surface and groundwater are also impacted due to mining[1]. Mining ruins the land, water, forests and air. It can barren the land, pollute water, denude forests, defile the air and degrade the quality of people that work and live in the area[2]. Mining causes physical, chemical alterations of soil/sediment, alteration of drainage patterns, erosion and siltation of streams. Associated also with mining is heavy metal pollution of soil/sediment and water bodies [3]. River PovPov is a seasonal water body that runs adjacent through the mining, processing and tail points.

This study is to ascertain the level of Iron-Ore mining impact on River PovPov using heavy metal pollution and metal indices and multivariate statistical methods.

Geology:
The study area lies within the Benin-Nigeria shield, situated in the Pan African mobile zone extending between the ancient Basements of West African and Congo Cratons in the region of Late Precambrian to Early Palaeozoic orogenies [4-6]. The Basement Complex rocks of Nigeria are composed predominantly of migmatite gneiss complex; slightly migmatised to unmigmatised paraschists and metaigneous rocks; charnockitic; older granite suites and unmetamorphosed dolerite dykes [4].

Itakpe Iron- Ore mine sites are located within the Nigerian Basement Complex rocks (fig.1). Associated rocks in the area are migmatitic gneisses, schists and igneous intrusions [4,7&5]. The gneisses and schists include quartz-biotite-hornblende-pyroxene gneiss, quartz-biotite garnet gneiss, amphibolite schist, quartzitic schist and muscovite schist. These gneisses and schists are intruded by igneous bodies such as monzodiorites, granodiorites, granites and pegmatites [5&7].

MATERIALS AND METHODS

Water sampling was carried out in the month of February (dry season) and May (onset of rain) 2009. A total of thirteen (13) water samples were collected in all (fig.2). Seven water samples were collected during the dry season and six at the on set of rain. Sampling was done randomly but evenly distributed from upstream to downstream sections of the river. Samples were collected from mid-point and a foot below surface water. Samples were collected in duplicates-one for heavy metal and the other for anion analyses. Samples were filtered as soon as they were collected using cellulose nitrate filter with pores of 0.45 micron diameter. Polyethylene plastic bottles were used as sample containers. New bottles were cleaned with strong- metal free acid. The containers were rinsed with sample water prior to collection. Sufficient air space was allowed and sample stored upright. Teflon lined caps were screwed on tightly to prevent leakage. Water samples for cations and heavy metal analyses were acidified with metal free HNO_3 to a pH of 1- 2. The samples were stored between 1^0C and 4^0C on cool ice packs from the field to the Lab. for analyses.

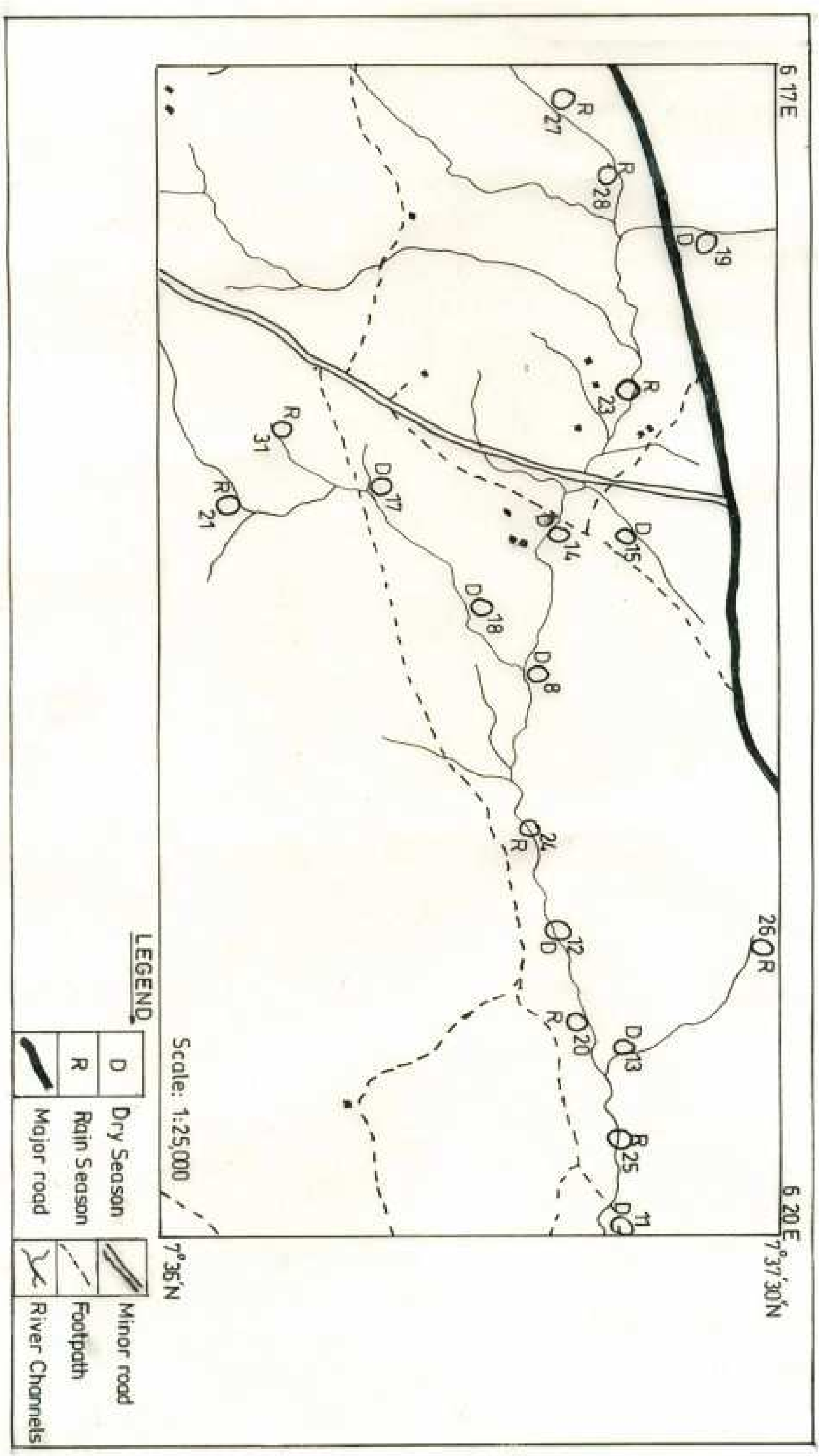


Fig 2: Sample location map of Itakpe

Analytical methods:
Insitu measurements of temperature, pH, Tds and Ec were determined intrusively with their appropriate probes. Spectrophotometer (Model Genesys 20) was used to determine the concentrations of K, Na, Ca, NO_3, and SO4 while AAS (Model 210 VGP) was used to determine the concentrations of Mg, Pb, Zn, Ni, Cu, Cd, and Fe. Titration method was used for the determination of the concentrations of Cl, and alkalinity. All analyses were performed according to [8] in the Dept. of Soil Science Lab, Faculty of Agriculture, Kogi State University, Anyigba.

Data Evaluations:
Heavy metal pollution index and metal index approaches were used for this study. HPI is a method that rates the aggregate influence of individual heavy metal on the overall quality of water. It is defined as Wi taken as inversely proportional to the recommended standard (Si) for each parameter. HPI model is given as

$$HPI=\sum W_iQ_i/\sum W_i \ldots\ldots.. (1).$$

Where Qi = subindex of the ith parameter. Wi is the unit weightage of ith parameter and n is the number of parameters considered. The subindex (Qi) of the parameter is calculated by $Q_i =\sum (M_i (-) I_i)/ (S_i-I_i)$…….. (2). Where Mi is the monitored value of heavy metal of the ith parameter, Ii is the ideal/baseline value of ith parameter, Si is the standard value of ith parameter. The sign (-) indicates the numerical difference of the two values, ignoring the algebraic sign [9].The critical pollution index value is 100 [10.]

Another index used is the general metal index (MI) for drinking water [11] which takes into account possible additive effect of heavy metals on the human health that help to quickly evaluate the overall quality of drinking waters. $MI = \sum [C_i/ (MAC)_i]$ proposed by [12]. Where MAC is maximum allowable concentration and Ci is concentration of each metal. The higher the concentration of a metal compared to its respective MAC value the worse the quality of water. MI value > 1 is a threshold of warning [11].

Univariate and multivariate statistical methods of analysis were also used in the study. The software SPSS 11.0 was used for statistical analysis. The correlation matrix which is based on the Pearson’s correlation coefficient was utilized for displaying relationships between variables. The obtained matrix of hydrogeochemical data was subjected to multivariate analytical technique. Factor analysis which aims to explain an observed relationship between numerous variables in terms of simple relations was applied. Cluster analysis was also used for investigating the similarities between variables found in River PovPov water samples. Evaluations of similarity were based on the average linkage between groups [13].

RESULTS AND DISCUSSION

	Min	Max	Mean	Std. Deviation
TEMP.^{o}C	25.30	26.50	25.8857	.43753
PH	7.40	8.90	8.1143	.55806
TDS	62.00	250.00	109.7143	64.01228
EC	0.08	0.33	.1443	.08541
ALK	0.10	2.75	1.9714	1.73057
K	3.40	7.80	4.9657	1.89827
NA	2.20	11.28	8.8586	3.12959
CA	2.50	3.75	3.3314	.42675
MG	3.93	.345	4.8200	.58447
CL	0.03	0.04	.0343	.00535
NO_3	2.78	4.94	3.5143	.72782
SO_4	0.06	7.40	1.7086	2.62606
FE	0.49	2.05	1.0486	.52793
CU	0.03	0.13	.0629	.03546
ZN	0.48	1.08	.7429	.22669
PB	0.44	0.92	.6214	.16160
NI	1.37	7.05	4.5129	1.96614
CD	0.09	0.81	.4786	.27157

Table 1: Summary statistics of River PovPov dry season water samples.

	TEMP	PH	TDS	EC	ALK	K	NA	CA	MG	CL	NO_3	SO_4	FE	CU	ZN	PB	NI	CD
TEMP	1.000																	
PH	-.490	1.000																
TDS	-.413	.603	1.000															
EC	-.413	.596	.999	1.000														
ALK	-.443	.773	.793	.790	1.000													
K	.214	.330	.593	.577	.589	1.000												
NA	.382	-.502	-.840	-.827	-.877	-.714	1.000											
CA	.275	-.397	-.814	-.816	-.876	-.633	.914	1.000										
MG	.115	-.443	-.541	-.516	-.709	-.878	.835	.657	1.000									
CL	.244	-.750	-.308	-.302	-.687	-.515	.410	.377	.614	1.000								
NO_3	-.215	-.519	-.080	-.083	-.021	-.172	-.256	-.283	-.067	.436	1.000							
SO_4	.543	-.102	-.032	-.053	.139	.774	-.309	-.208	-.717	-.338	.004	1.000						
FE	.397	-.214	-.154	-.168	-.240	.532	.067	.201	-.387	-.234	-.264	.721	1.000					
CU	-.008	.284	.130	.155	.390	-.202	-.049	-.349	.244	-.163	-.043	-.369	-.739	1.000				
ZN	-.028	-.301	-.630	-.639	-.485	-.724	.461	.565	.468	.511	.345	-.323	-.450	.020	1.000			
PB	-.021	-.475	.348	.354	-.146	.209	-.219	-.252	-.032	.474	.380	.018	.273	-.431	-.408	1.000		
NI	.477	-.201	.084	.053	-.045	.565	-.311	-.086	-.519	.211	.144	.709	.426	-.512	.048	.215	1.000	
CD	.547	-.185	.214	.228	-.253	.231	.193	.067	.246	.292	-.485	.019	.270	-.045	-.487	.462	.157	1.000

Table 2: Correlation coefficient of dry season water parameters along River PovPov.

Heavy metals (mg/l)	Mean value (Mi)	Standard value (Si) FEPA, 2007	Baseline value (Ii)	Unit weightage (Wi)	Subindex (Qi)	Wi x Qi
Fe	0.89	0.3	0.64	3.33	73.53	244.85
Cu	0.07	1.0	0.04	1.0	3.13	3.13
Zn	0.72	3.0	0.03	0.33	23.23	7.67
Pb	0.55	0.01	0.17	100	2.38	238
Ni	4.43	0.02	0.48	50	8.59	429.35
Cd	0.37	0.003	0.02	333.33	2059	686326.47

$\sum Wi = 487.99$ $\sum WiQi = 687249.47$ HPI = 1408.33 and MI = 403

Table 3: Dry season HPI and MI values.

Univariate statistical analysis: the data from River PovPov in two sampling seasons were statistically described as average, minimum, maximum and standard deviations in tables1 and 4. The results indicate that there is a significant difference between dry and onset of rain season's parameters.

Multivariate statistical analysis: Variables in dry season samples shows very strong correlation between Tds-Ec, Na-Ca and Mg-Na and strong relationship between alkalinity-pH, Tds-Ec, SO_4-K, Fe-Ni (table 2). These very positive, strong correlations (suggesting same source/environment) exist also in onset of rain water samples between Tds-NO_3; SO_4-Fe, Cu-Zn; NO_3 and Fe, Cu, Zn and SO_4; SO_4-Fe, Cu-Zn; Alk and NO_3, SO_4, Fe, Cu and Zn; and between K and Ca, Mg (table 5).

Factor analysis: Five factors were extracted which reflect the major effective agents controlling the chemistry of dry season water samples (table 7). Variance percentages mean shows that these five factors are enough for clarifying the approximate 95% of the total variance observed in the data. Factor one explain 35.3% of variances in dry season. High positive loadings present in factor one are: Tds, Ec, alkalinity, K and pH. Factor two shows highest positive loadings for SO_4, Ni, temperature, K and Fe. This factor accounts for 19% of total variance. Factor three can also explain 16.5% of total variance. Highest, positive loading for Cl and Pb and moderate loading for NO_3. Factor four shows highest positive loading matrix for Cd and low for temperature. This factor account for 13% of variance while factor five has variance of 11.4% and positive loading for Cu. It is obvious that these patterns have harmony with correlation matrix results (table 2).

Variable	Min	Max	Mean	Std. Deviation
TEMP	26.70	29.00	27.33	.31885
PH	6.70	7.50	7.12	.02317
TDS	141.00	247.00	214.50	.83106
EC	0.39	0.45	0.42	38.99615
ALK	3.40	96.00	19.05	4.76616
K	2.13	2.69	2.36	2.02558
NA	1.76	13.80	4.09	.25467
CA	1.75	7.23	4.28	.28698
MG	3.52	4.19	3.98	.46366
CL	0.02	0.04	0.03	.16108
NO_3	0.05	3.52	2.61	.40874
SO_4	0.05	3.80	2.59	.04764
FE	0.07	1.51	0.73	.09439
CU	0.00	0.41	0.09	.88841
ZN	0.01	2.20	0.39	37.69826
PB	0.02	0.26	0.08	.00579
NI	0.00	1.01	0.18	1.29113
CD	0.01	0.14	0.05	1.32135

Table 4: Summary statistics of River PovPov onset of rain water samples.

	PH	EC	TEMP	TDS	NA	CA	K	MG	ALK	CL	NO_3	SO_4	FE	CU	ZN	PB	NI	CD
PH	1.000																	
EC	-.505	1.000																
TEMP	-.815	.514	1.000															
TDS	-.574	.507	.925	1.000														
NA	.667	-.394	-.306	.014	1.000													
CA	.677	-.441	-.701	-.537	.542	1.000												
K	.336	.253	-.252	-.157	-.018	-.029	1.000											
MG	-.827	.455	.862	.704	-.465	-.695	-.242	1.000										
ALK	-.675	.386	.918	.936	-.134	-.496	-.291	.745	1.000									
CL	-.795	.296	.631	.410	-.500	-.589	-.313	.478	.483	1.000								
NO3	-.949	.414	.841	.576	-.680	-.753	-.317	.878	.659	.776	1.000							
SO4	-.928	.505	.806	.548	-.699	-.743	-.214	.911	.606	.694	.975	1.000						
FE	.269	.307	-.290	-.277	-.029	.256	.710	-.201	-.447	-.262	-.233	-.090	1.000					
CU	-.274	.350	.219	.226	-.139	-.215	.131	.173	.161	.267	.117	.172	.080	1.000				
ZN	.949	-.460	-.830	-.589	.646	.628	.235	-.844	-.680	-.775	-.960	-.959	.099	-.197	1.000			
PB	.821	-.301	-.456	-.117	.809	.621	.149	-.644	-.226	-.687	-.832	-.867	.015	-.172	.830	1.000		
NI	.855	-.122	-.626	-.315	.746	.641	.415	-.706	-.499	-.767	-.902	-.860	.377	-.110	.866	.874	1.000	
CD	.841	-.638	-.795	-.707	.366	.469	.099	-.717	-.756	-.592	-.731	-.720	.105	-.191	.798	.506	.495	1.000

Table 5: Correlation coefficient of onset of rain water sample parameters along River PovPov.

Heavy metals (mg/l)	Mean value(Mi)	Standard value (Si) FEPA, 2007	Baseline value (Ii)	Unit weightage(Wi)	Subindex (Qi)	Wi x Qi
Fe	1.70	0.3	0.64	3.33	3.12	10.39
Cu	0.06	1.0	0.04	1.0	2.08	02.08
Zn	1.17	3.0	0.03	0.33	38.38	12.68
Pb	0.14	0.01	0.17	100	18.75	1875
Ni	0.54	0.02	0.48	50	13.04	652
Cd	0.12	0.003	0.02	333.33	588.23	196074.71

$\sum Wi = 663.6$ $\sum WiQi = 198626.85$ HPI = 299.32 and MI = 87.32

Table 6: Onset of rain HPI and MI values.

Tables 3 & 5 are detailed calculations of heavy metal pollution index HPI and metal index values for both seasons. HPI and MI are useful to study and compare variations in overall pollution levels that include many parameters together. HPI has been determined for both seasons by taking the average values of the heavy metals equations (1) and (2). Suitability of water quality for drinking can be rated using the quality indices [10-11].

Onset of rain factor analysis shows the highest loading for alkalinity, Cu, Zn, NO_3, SO_4, Tds and Fe. Factor one account for 65.8% of total variance. Factor two accounts for 12.9% of total variance with moderate loading for K. Factor three accounts for 10.9% of variance with highest loading for Cl and pH while factor four has weak loading for all the measured variables and have variance of 8.3%. The high loading for SO4, Na and NO_3; Na and Cl in dry season is also repeated in the onset of rain data indicating little changes between these major ions. High loadings of SO_4 and NO_3 can be related to surface water susceptibility versus natural processes or anthropogenic input from agriculture and domestic wastes. The heavy metals on the other hand show changes between dry and onset of rain. High loadings for Cd, Cu, Ni, Pb and Fe were observed during dry season while high loading for Fe, Cu and Zn observed at onset of rain maybe associated with precipitation, ion-exchange, evaporation rate and ion concentration. The high loading for Cd, Ni and Zn may also suggest anthropogenic sources.

Variable	Factor					Communalities
	1	2	3	4	5	
TEMP.°C	-.439	**.691**	.142	**.511**	.220	.999
PH	**.525**	-.208	-.760	-4.207E-02	9.747E-02	.908
TDS	**.958**	-.105	-3.761E-02	.181	-9.414E-03	.962
EC	**.956**	-.126	-3.194E-02	.199	6.512E-03	.971
ALK	**.862**	5.445E-02	-.409	-.186	.226	.999
K	**.641**	**.670**	-.216	.218	-.215	1.000
NA	-.934	-.239	3.821E-02	.251	5.700E-03	.994
CA	-.930	-.169	-2.924E-02	8.987E-02	-.241	.960
MG	-.658	-.587	.296	.259	.258	.999
CL	-.367	-.134	**.878**	7.945E-02	8.002E-02	.936
NO_3	.129	7.581E-02	**.691**	-.652	7.484E-02	.930
SO_4	8.968E-02	**.948**	-.144	-6.366E-03	-.238	.984
FE	-.130	**.542**	-.142	.283	-.745	.965
CU	.145	-.230	-.186	6.625E-02	**.915**	.950
ZN	-.631	-.135	.215	-.568	.265	.855
PB	.362	-3.312E-02	**.747**	.292	-.446	.974
NI	9.128E-02	**.798**	.280	-3.336E-02	-.195	.763
CD	3.438E-02	6.867E-02	.239	**.960**	-2.890E-02	.986
Eigenvalue	6.360	3.358	2.967	2.401	2.048	
% Variance	35.335	18.657	16.485	13.339	11.379	
% Cummulative	35.335	53.992	70.477	83.816	95.196	

Table 7: Varimax rotated factor analysis results of dry season water samples.

Cluster analysis: By using average linkage, variables were interrelated to each other according to their maximum similarities. At first stage, interrelations occur between variables which have the most similarity. Results are presented as dendrograms (figs. 3&4; 5&6). During dry season Tds and Ec shows the maximum similarities. This is followed by that similarity between Na and Ca. Weaker similarities in this order was observed; Tds and alkalinity; K and SO_4; Na and Mg. The similarity between Ec and pH; K and Ni are weaker (fig.3). Q mode cluster shows highest similarities between locations

ITK03 and ITK04. Relatively weak similarities occur between locations ITK03 and ITK05; ITK04 and ITK02; ITK05 and ITK06; and ITK01 and ITK07 (fig.4). From onset of rain dendrograms (fig.6), the highest similarities exist between Cu, Zn, NO_3, alkalinity, Tds, SO_4 and Fe; and that between Ni and Cd. After this first degree of similarities come Ec and Ca. This is followed by Na, Pb and K and Mg. Finally, we have pH and Cl. The Q mode cluster show that ITK10 and ITK12 have maximum similarity, followed by ITK11 and ITK13 and lastly ITK09 and ITK08 in that order (fig.6).

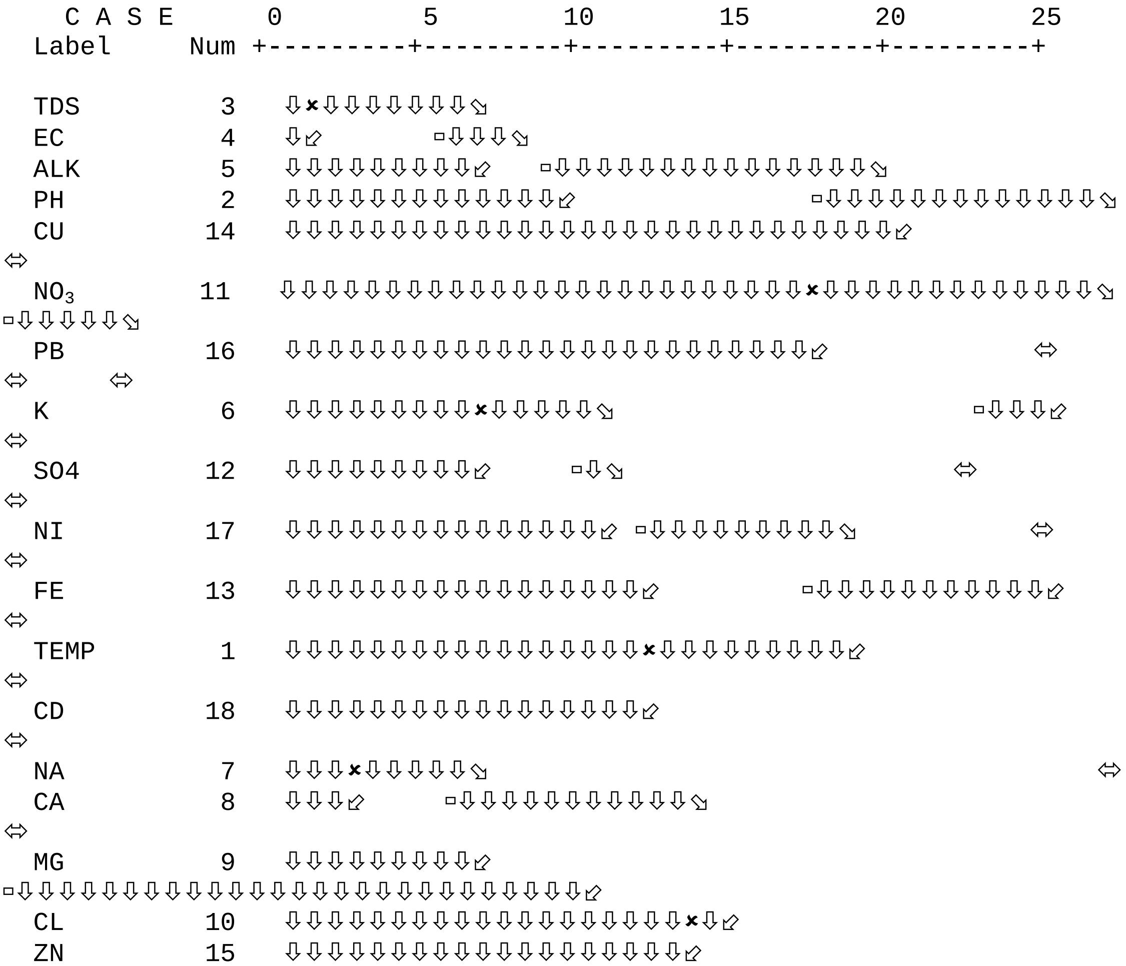
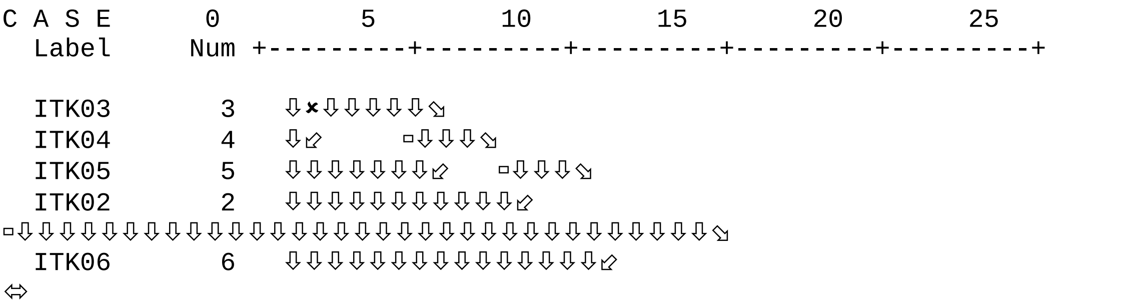


Fig 3: R-mode cluster analysis dendrogram of dry season water samples along River PovPov.



```
  ITK01        1
⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩×⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⬃
  ITK07        7    ⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⬃
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Fig 4: Q-mode cluster analysis dendrogram of dry season water samples along River PovPov.

Variable	Factor 1	2	3	4	Communalities
TEMP	-.409	.260	9.495E-02	-.866	.994
PH	-.240	.305	**.873**	.274	.987
TDS	**.938**	.163	-.187	.239	.999
EC	-.945	-.123	.248	.173	1.000
ALK	**.978**	.146	-2.619E-02	.143	1.000
K	-.751	**.601**	.201	.155	.989
NA	-.161	-.940	-.176	.191	.978
CA	-.838	.113	.378	4.359E-02	.860
MG	-.802	.309	-1.106E-03	.364	.872
CL	8.183E-02	-9.553E-02	**.918**	-.365	.992
NO_3	**.965**	.200	-3.106E-02	.167	.999
SO_4	**.945**	.201	3.132E-02	.216	.980
FE	**.933**	-1.785E-02	-8.643E-03	.317	.972
CU	**.976**	.158	-3.644E-02	.137	.998
ZN	**.974**	.167	-2.747E-02	.145	.998
PB	-.633	-.749	.166	4.169E-02	.991
NI	-.992	-8.836E-02	-1.854E-02	3.460E-02	.993
CD	-.980	.176	3.215E-02	-8.181E-02	1.000
Eigenvalues	11.838	2.320	1.958	1.486	
% Variance	65.768	12.888	10.880	8.253	
% Cumulative	65.768	78.656	89.536	97.789	

Table 8: Varimax rotated factor loading matrix of onset of rain water analysis results.

```
    C A S E      0         5        10        15        20        25
  Label      Num +---------+---------+---------+---------+---------+

  CU          14   ⇩⬂
  ZN          15   ⇩▫
  NO3         11   ⇩▫
  ALK          5   ⇩▫
  TDS          3   ⇩▫
  SO4         12
⇩⇧⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⬂
  FE          13   ⇩⬃                                                ⬄
  NA           7   ⇩⇩⇩⇩⇩⇩⇩×⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⬂
⬄
  PB          16   ⇩⇩⇩⇩⇩⇩⇩⬃                         ⬄
⬄
  PH           2   ⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩×⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⬂
▫⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⬃
  CL          10   ⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⬃                    ⬄  ⬄
  NI          17   ⇩×⇩⬂                         ⬄  ⬄
  CD          18   ⇩⬃  ▫⇩⬂                       ▫⇩⬃
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  EC          4    ⇩⇩⇩⬃ ▫⇩⬂                    ⬄
  CA          8    ⇩⇩⇩⇩⇩⬃ ▫⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⬂   ⬄
  K           6    ⇩⇩⇩⇩⇩⇩⇩▫          ▫⇩⇩⇩⬃
  MG          9    ⇩⇩⇩⇩⇩⇩⇩⬃               ⬄
  TEMP        1    ⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⬃
```

Fig 5: R-mode cluster analysis dendrogram of onset of rain water samples along River PovPov.

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C A S E       0         5         10        15        20        25
  Label      Num +---------+---------+---------+---------+---------+

  ITK10       3
⇩×⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⬂
  ITK12       5    ⇩⬃                                              ⬄
  ITK11       4    ⇩⇩⇩⇩⇩⇩⇩⇩⇩×⇩⇩⇩⇩⇩⬂
⬄
  ITK13       6    ⇩⇩⇩⇩⇩⇩⇩⇩⇩⬃    ▫⇩⇩⇩⇩⇩⇩⇩⇩⇩⬂
⬄
  ITK09       2    ⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⬃
▫⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⬃
  ITK08       1    ⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⬃
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Fig 6: Q-mode cluster analysis dendrogram of onset of rain water samples along River PovPov.

DISCUSSION

In dry season samples, strong positive correlations exist between Tds and Ec. This is not so with the onset of rain water samples. Strong correlations exist also between the physiochemical in both seasons. In wet season the physiochemical correlates with few of the heavy metals which are not evident in dry season samples (tables 2 and 5). In both seasons major ions correlates with the heavy elements while in wet season the heavy metals have strong correlations among themselves. This correlation does not exist in dry season samples. These variations can be attributed to dilution effects of runoff during onset of rain [14].

The heavy metal pollution index calculated with mean values of all six heavy metals for both seasons are (1408.33 and 299.32 respectively) far above the critical index value of 100. This indicates that the water is contaminated with respect to the heavy metals [10]. The MI for the same river in both season revealed “low-quality water” with MI values of 403 and 87.12 respectively [15 &11.] MI value >1 is a threshold of warning [15].

In dry season five factors were extracted and four at onset of rain with all factors explaining 95.2% and 97.8% respectively of total variance. Factor one in dry season shows high loadings for Tds, Ec, alkalinity, K and pH. High Tds and consequently Ec are due to K presence which also explains the high alkalinity [13]. Factor two which consists of SO_4, Ni, K, temperature, and Fe in dry season may be due to natural processes/ anthropogenic input [15]. Factor three include Cl, Pb and NO_3 and maybe due to contamination from mining activities, organic and domestic sewage [16]. Factors four and five can also be attributed to heavy metal pollution arising from mining activities. At onset of rain, factor one consists of Tds, alkalinity, NO_3, SO_4, Fe, Cu and Zn. The SO_4

and NO_3 are associated with agricultural/ domestic wastes while Fe, Cu and Zn are attributed to mining in the area [17]. Factor two is made up of K which is abundant and mobile and so may be a natural process. Same natural process is likely of factor four which are both associated with mafic rocks hence similar geochemistry. Factor three is associated with domestic waste and the pH due to the Cl. These factor associations interestingly are correlated suggesting same source. Between rain season and dry season samples there are differences between the factor variables suggesting changes due to dilution effect of run off during rain season which in turn affects evaporation/precipitation, ionic concentration, and ionic exchange [15].

Four clusters were extracted each during dry season and at onset of rain. At onset of rain, cluster one consist of Cu, Zn, NO_3, alkalinity, Tds, SO_4 and Fe. This cluster is a mixture of natural processes/ anthropogenic sources [17]. Cluster two consists of Na and Pb while cluster three is made up of Cl and pH. These clusters are attributed to anthropogenic sources. Cluster four contains Ni, Cd, Ec, Ca, K, Mg and temperature which may suggest natural processes. Cluster one in dry season consists of Tds, Ec, alkalinity, pH and Cu. Cluster two consists of NO_3 and Pb. Cluster three include K, SO_4, Ni, Fe, temperature and Cd. Cluster four consists of Na, Ca, Mg, Cl and Zn. Clusters two and three may suggests anthropogenic sources [13].

CONCLUSION

The major cations and heavy metals have lower concentration values at onset of rain when compared to dry season values, the exception are Ca, SO_4 and Cu. This observation is in contrast with the physiochemical were all having concentrations higher in onset of rain than dry season. HPI and MI are useful in overall pollution level of surface water in terms of heavy metal presence. The calculated HPI in both seasons are far above the critical level of 100 which reveals that the water is polluted with respect to heavy metals due mainly to mining in the area. The MI value is also far above the threshold of warning with respect to heavy metals in the river. FA analysis carried out in both seasons indicates that factors one in each season are the dominant water parameters. The R-mode cluster analysis in both seasons also alludes to the dominant parameters which are clustered in cluster one in both seasons. The study also shows the latent processes/factors shaping the water quality to include, natural processes, agricultural/ domestic wastes and heavy metal pollutants from mining activities. This study illustrates the utility of HPI and MI and multivariate statistical analysis in hydrogeochemistry.

REFERENCES

[1] Priester, M and Hentschel, T. (**1993**): *National resources Journal Tubingen*, Germany.vol.37.pp.66-81.
[2] Koval, P.V. and Belogolova, G.A. (**1995**): *Journal of geochemical exploration*. Elsevier science, vol.55:pp.193-201.
[3] Sutherland, R.A. (**2000**): *Environmental Geology* 39: 611-37.
[4] Rahaman, M.A. (**1976**): Review of the basement geology of southwestern Nigeria. In geology of Nigeria (C.A. Kogbe, Ed). Elizabethan publishing Co., Lagos.

[5] Odigi, M.I (**2002**): *Journal of mining and geology* vol. 38 (2), pp.81-89.
[6] Ekwueme, B.N. (**2003**): The Precambrian geology and evolution of the southeastern Nigerian basement complex. University of Calabar press.
[7] Ezepue, M.C. and M.I. Odigi (**1994**): *Journal of mining and geology* vol. 30, no. 1, pp. 1-9.
[8] APHA (**2002**): Standard Methods for the Examination of water and Waste water. APHA, Washington, D.C. 200005.
[9] Bably Prasad (**2008**). Evaluation of heavy metal pollution index for surface and spring water near limestone mining area of lower Himalayas. Scientist central mining research institute Dhanbad 826-001, India.
[10] Reza, R and Singh, G (**2010**): *Int. J. Environ. Sci. Tech*., 7 (4), 785-792.
[11] Bakan, G., Hulya, B. O., Sevtap, T. and Huseyin, C. (**2010**): *Turkish journal of Fisheries and Aquatic Sciences* 10: 453- 462.
[12] Caeiro, S., Costa, M.H., Ramos, T.B., Fernandes, F., Silveira, N., Coimbra, A., Medeiros, G., and Painho, M (**2005**): Assessing heavy metal contamination in Sado Estuary sediment: An index analysis approach. Ecological Indicators 5 pp 151- 169.
[13] Reghunath Rajesh; T.R. Sreedhara Murthy; B.R. Raghavan (**2002**): *Water Research* 36 (2002) 2437-2442.
[14] Elueze, A.A., Anyanwu, A.J. and Bolarinwa, A.T. (**2001**): *Journal of mining and geology* vol.37 (1), pp. 91-100.
[15] Pathak, J.K; Mohd Alam and Shikha Sharma (**2008**): *E-journal of Chemistry*. Vol.5, nos.3, pp.607-619.
[16] Yang, Li; Linyu, Xu; Shun, Li (**2009**): *Journal of water resources and protection* (JWARP).
[17] Praveena, S.M; Ahmed, A; Radojevic, M; Abdullah, M.H and Aris, A.Z (**2007**): The *Malalysian Journal of analytical Sciences*. Vol.11, no.2, pp.421-430.