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Hydrogeochemical processes in groundwater resources located around abandoned Okpara coal, Enugu SE. Nigeria

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Abstract

A detail understanding of the hydrogeochemical characteristics and groundwater quality is indispensable for the sustainable utilization of the groundwater sources. This is in line with sustainable development goal of United Nation. The following parameters were analyzed using APHA, 2012 standard: pH, Ec, total dissolved solid (TDS,) total hardness (TH), magnesium (Mg^{2+}), sulphate (SO_4^{2-}), chloride (Cl^-), bicarbonate (HCO_3^-), carbonate (CO_3^{2-}), nitrate (NO_3^-), potassium (K^+), sodium (Na^{2+})and calcium (Ca^{2+}). Findings revealed that pH value reveals that groundwater is acidic. Bivariate plots showed that groundwater quality is influenced by number of factors. Hydrogeochemical assessment of groundwater samples was based on the following model:End-member, Parson's and Diamond field plots. Results from these plots revealed that silicate and carbonate weathering are the major factors that control groundwater quality and that groundwater samples were of different water type namely, Ca–Mg–SO4, Ca–Mg–Cl, Na–SO4 water type and high Ca+Mg & SO4+Cl respectively. It was observed that 99 % of groundwater within the study area fell within fresh water category and groundwater is influenced by various factors.

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Introduction

The history of coal industry in Nigeria was dated back to 1909, when coal was first discovered at the streams along Udi escarpment in Enugu State, Southeastern Nigeria (Buchanan, 1999). Enugu has been known for coal mining activities in time past, these mine were located at Udi, Onyeama, Okpara, Iva Valley and Ribadu respectively. Obiadi *et al*. (2016) stated that the mining of coal was a major source of economic for people around the study area decades ago, the discovery of crude oil in south-south part of Nigeria has lead to low demand of coal. Increased demand for alternative energy sources and the country quest for improved power supply have lead to attention be directed towards the exploitation of the crude oil as an alternative source of energythereby neglectingcoal deposit mineral within the study area. Coal mining, during that timegave rise to lots of mine waste which were dumped in landfills and surface dumps. Globally, mine waste are derived from active or abandoned mines, which is a serious problem due to its negative effects on the environment and water quality for domestic, industrial and irrigation use. As at that time, the sitting of these wastes dump sites were chosen for convenience and proximity to waste source rather than for environmental, geological, engineering consideration resulting in environmental degradation and potential groundwater contamination (Ezeigbo and Ezeanyim 1993; Heikkinen, *et al*., 2009; Eyankware *et al*., 2020; Moses and Ruth, 2015; Allen *et al*., 1996). In addition, mine waste left near abandoned and active mines are major source of contamination to surface and groundwater quality.

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Water resource isthreatens by mining activities across the world (Allen *et al*., 1996; Choubey, 1991; Khan *et al*., 2005; Singh *et al*., 2008; Singh, 1998). Generally the quality of groundwater is primarily influenced by the recharge pathways, anthropogenic activities and aquifer rock mineral (Eyankware *et al*., 2018). Obiadi *et al*. (2016) is of the opinion that groundwater flows through its recharge pathways from recharge to discharge points, several other types of hydrogeochemical processes take place that alter physicochemical attribute of groundwater.Emphasis on the study is to evaluate the effect of abandoned coal mine over the years on geochemical quality of groundwater.

Location, Geology and Hydrogeology

The study area is located in Enugu Sate, Southeastern Nigeria. It lies between latitude $6^{0}20'$N-$6^{0}30'$N and longitude $7^{0}30'$E -$7^{0}35'$E (Fig. 1). The coal deposit in Enugu area is mainly of sub-bituminous grade, black to brownish black in colour and is estimated atover 80 million tonnes. The outcrops of the coal was noticed along the road cut, Enugu escarpment, gullies and mine sites. The Enugu coal deposits as with most other coal deposits are associated with pyrite and marcasite which is stable below water table environment but is oxidized if exposed or the water table is lowered (Obiadi *et al*., 2016). The mining processes remove the overburden materials and exposes mine spoils to oxidation. The Mamu Formation and the Nsukka Formation are the coal bearing formation of the Anambra Basin formally referred to as the lower coal measures and upper coal measures respectively. The coal seam varies with thickness from a few centimeters to about 2m. Obaje (2009) stated that the Mamu Formation (MF) marks the regressive phase of the Upper Campano–Maastrichtian transgressive cycle, the lithology of the Nsukka Formation is very similar to that of the MF and consists of an alternating succession of sandstone, dark shale and sandy shale, with few relatively thin coal seams at various positions in the lower horizons. Thin limestone occurs at the top of the sequence. Heikkinen *et al*. (2009); Offodile (2002) were of the opinion that the MF contributes nearly all the groundwater entering the Enugu coal mines. The source of recharge is by precipitation.

Materials and methods

For the purpose of the study, fifteen(15) groundwater samples were collected and analyzed (Fig.1). Samples were collected in pre-cleaned, sterile polythene bottles and analyzed for major ions as per the standard methods of APHA, 2012. The result of physicochemical parameters

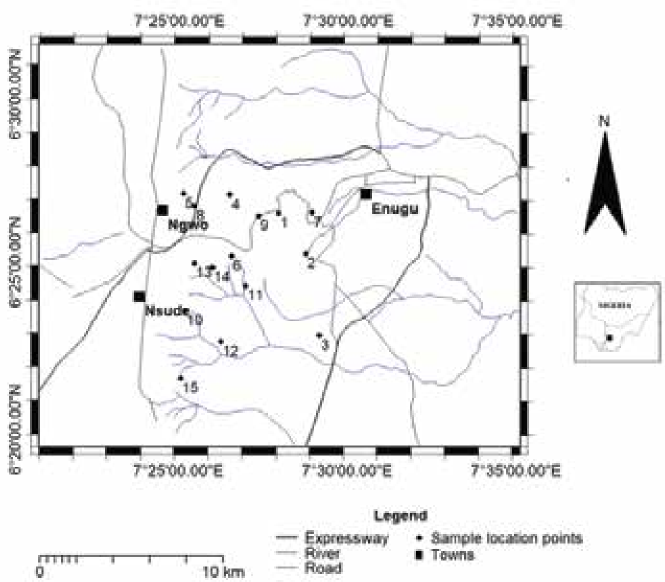

Fig. 1. Accessibility and topographic map of the study Area

are presented in Table II. To check of accuracy of results ion balance equation was used to confirm the accuracy of samples as shown in Eq. (1).

Eqn (1)

Most of the sample has a % CBE within ± 10%

Results and discussion

pH

pH refers to the degree of acidity or alkalinity of a solution or water. It is a crucial indicator that can be used for assessing water quality and degree of contamination in water bodies. pH is considered as an important factor that influences water quality. Findings of Ezeigbo and Ezeanyim (1993) revealed that low pH values in waters is associated with the Okpara coal mine. The pH values within the study area varies from 4.2 to 6.8 are an indicative that the groundwater is acidic (Table II). The low pH values showed evidence of oxidation of pyrite causing acid mine drainage (Cathles, 1982)

Total dissolved solid (TDS)

TDS signifies the various types of minerals present in water in dissolved form. TDS compose of carbonates, bicarbonates, silica, calcium, magnesium, chlorides, sulfates, phosphates, sodium and potassium (Gnanachandrasamy *et al*., 2015; Adimalla, *et al*., 2018). The value of TDS ranges from 9.5 to

Table I. Process/methods used to analyze physicochemical parameters

Sl.No.	Parameters	Analytical method	Reference
1	pH	pH meter Hach sensION + PH1 portable pH meter and Hach sensION + 5050 T Portable Combination pH Electrode	(Gnanachandrasamy *et al*., 2018)
2	Electrical Conductivity (EC)	HACH Conductivity	Gnanachandrasamy *et al* ., 2018
3	Total dissolved solids (TDS)	TDS meters (model HQ14D53000000, USA).	Gnanachandrasamy *et al* ., 2018
4	Magnesium (Mg^{2+})	EDTA titrimetric method	Gnanachandrasamy *et al* ., 2018
5	Calcium (Ca^{2+})	Titrimetric method	Gnanachandrasamy *et al* ., 2018
6	Chloride (Cl^{-})	Titrimetric method	Gnanachandrasamy *et al* ., 2018
7	Nitrate (NO_3^-)	Ion-selective electrode (Orion 4 star)	Gnanachandrasamy *et al* ., 2018
8	Sulphate (SO_4^{2-})	Turbidimetric method using a UV-Vis spectrometer	Gnanachandrasamy *et al* ., 2018
9	Potassium (K^+)	Jenway clinical flame photometer (PFP7 model)	Gnanachandrasamy *et al* ., 2018
10	Sodium (Na^+)	Jenway clinical flame photometer (PFP7 model)	Gnanachandrasamy *et al* ., 2018
11	Bicarbonate (HCO_3^-)	Titrimetric method	Gnanachandrasamy *et al* ., 2018

Most of the sample has a % CBE within ± 10%

Table II. Results of groundwater samples

Sample Code	pH	TDS (mg/l)	TH	EC (μS/cm)	CO_3^{2-} (meq/l)	SO_4^{2-} (meq/l)	Cl^- (meq/l)	NO_3^- (meq/l)	Ca^{2+} (meq/l)	Mg^{2+} (meq/l)	Na^+ (meq/l)	K^+ (meq/l)	HCO_3^- (meq/l)
OK/01	4.6	9.75	42.7	1038.14	0.18	0.29	0.10	0.02	3.05	0.14	0.27	0.06	0.16
OK/02	5.8	11.34	21.66	679.35	0.19	0.53	0.05	0.05	0.57	0.38	0.06	0.04	0.03
OK/03	4.9	56.45	81.00	76.04	0.26	0.77	0.07	0.09	0.05	0.76	0.11	0.03	0.18
OK/04	6.2	47.91	36.33	311.95	0.14	1.93	0.05	0.19	1.73	0.21	0.16	0.01	0.26
OK/05	6.8	16.71	116.00	96.84	0.22	2.26	0.03	0.26	0.50	0.66	0.05	0.04	0.14
OK/06	5.8	361.28	242.00	147.55	0.13	0.23	0.08	0.02	0.24	2.18	0.18	0.03	0.06
OK/07	4.7	14.61	139.00	396.84	0.04	0.15	0.05	0.06	0.42	0.97	0.12	0.44	0.11
OK/08	4.6	57.11	87.00	287.16	0.16	0.09	0.06	0.45	0.28	0.60	0.43	0.06	0.17
OK/09	5.2	181.23	97.00	47.00	0.16	0.29	0.05	0.76	0.17	0.80	0.71	0.01	0.12
OK/10	6.5	46.30	58	173.96	0.12	0.14	0.03	0.04	0.41	0.17	0.35	0.21	0.13
OK/11	6.2	62.06	98	208.64	0.05	0.21	0.05	0.02	0.35	0.63	0.21	0.01	0.16
OK/12	5.7	25.81	100	95.07	0.07	0.15	0.04	0.01	0.16	0.84	0.14	0.01	0.25
OK/13	4.2	57.05	168	274.87	0.01	0.46	0.06	0.07	0.25	1.43	0.22	0.05	0.46
OK/14	5.2	102.26	102	853.96	0.13	0.63	0.05	0.03	0.06	0.96	0.36	0.03	0.11
OK/15	4.5	27.12	133	551.14	0.24	0.16	0.01	0.02	0.03	1.30	0.15	0.02	0.15
Min	4.2	9.75	21.66	47	0.01	0.09	0.01	0.01	0.03	0.14	0.05	0.01	0.03
Max	6.8	361.28	242	1038.14	0.26	2.26	0.1	0.76	3.05	2.18	0.71	0.44	0.46
Mean	5.40	85.17	105.02	371.97	0.13	0.62	0.05	0.16	0.66	0.84	0.25	0.08	0.17

Table III. TDS classification of groundwater, modified after Freeze and Cherry, 1979

TDS (mg/l)	Classification	Number of samples
<1000	Fresh water	OK/02-15
1000-10000	Brackish	OK/01
10000-10000	Saline Water	
100000	Brine	

361.28 mg/l (Table III). The plot of TDS against TH revealed that groundwater fell within fresh water category (Fig. 2).

Geochemical mechanism of groundwater

The plot of X-Y co-ordinate can be used to understand the geochemical variations in the ionic concentrations in the groundwater (Eyankware *et al*., 2018). Results obtained from the chemical analyses were used to identify the geochemical processes and mechanisms in the groundwater system. The data obtained from analysed groundwater samples result were plotted in (HCO_3 +SO_4) vs. (Ca+Mg) shows that majority of the samples fell below the equiline indicating that the silicate weathering is the considered to be dominant process that

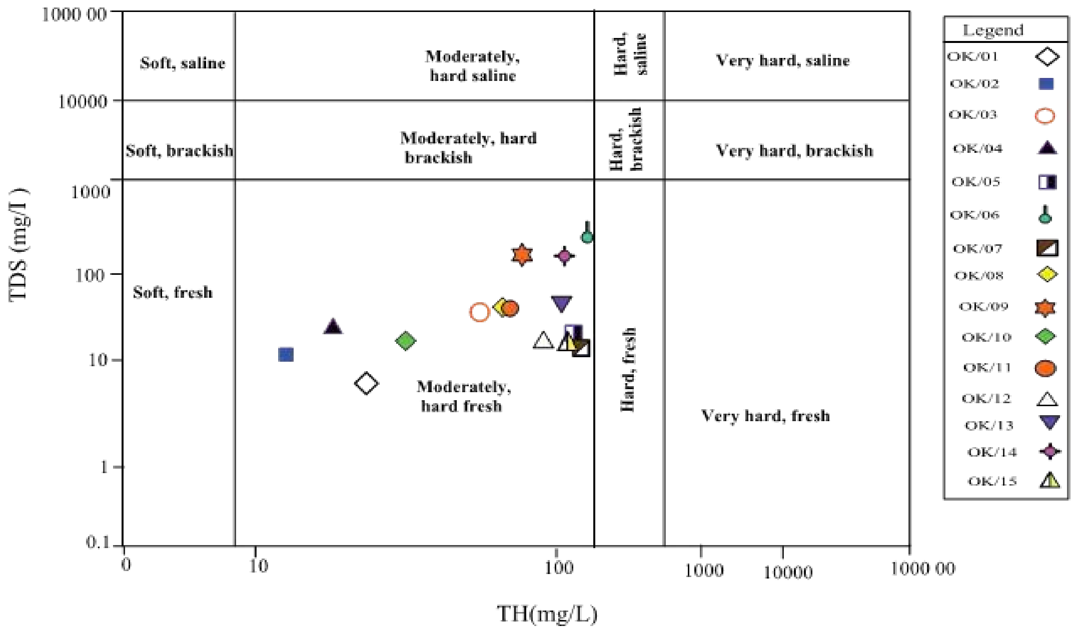

Fig. 2. Plot of TDS vs. TH

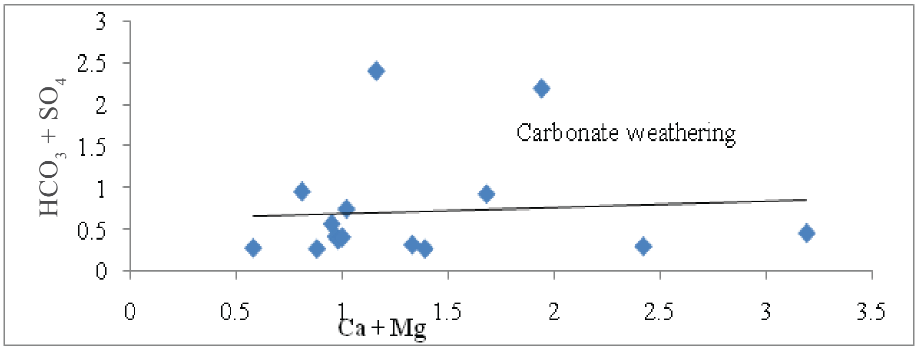

Fig. 3a. Scatter diagram of carbonate and silicate weathering Ca + Mg vs. HCO_3+ SO_4(meq/l)

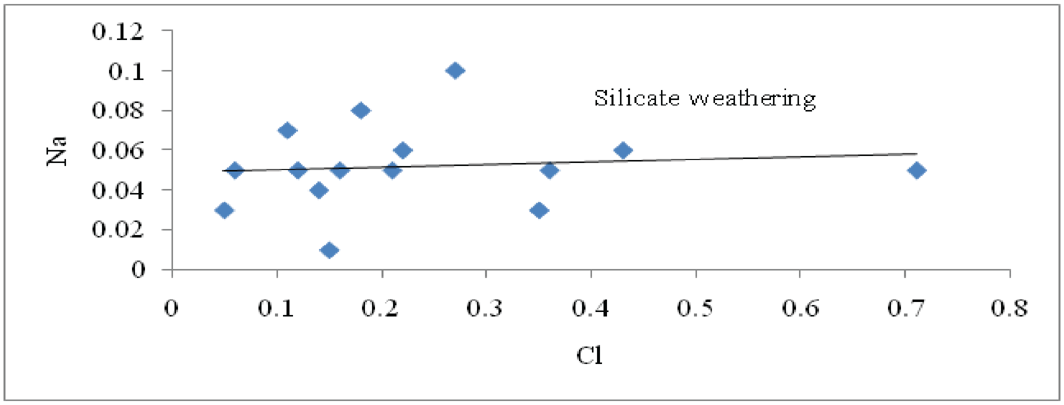

Fig. 3b. Scatter diagram of Na^+ vs. Cl^- (meq/l)

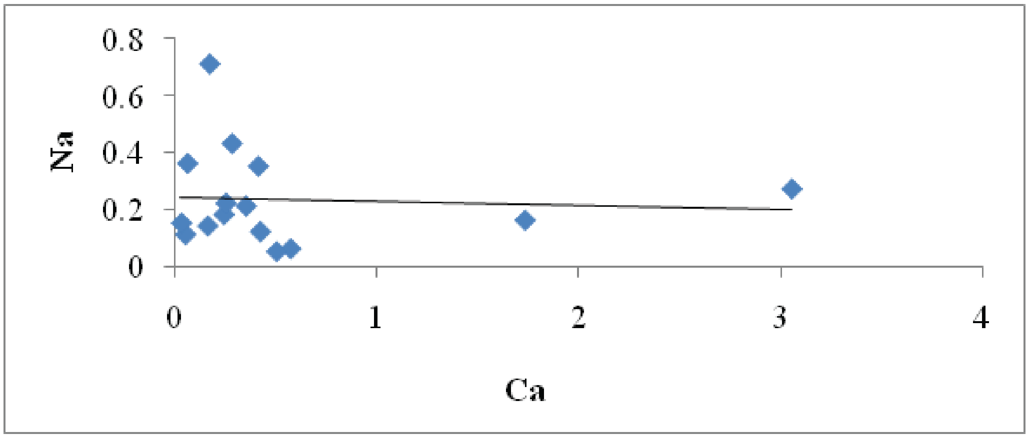

Fig. 3c. Scatter diagram of Na^+ vs. Ca^{2+} (meq/l)

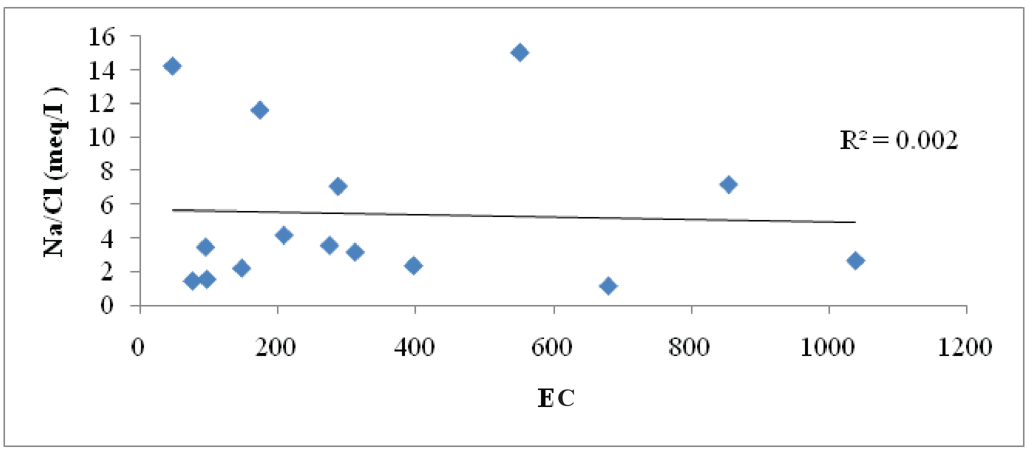

Fig. 3d. Scatter diagram of Na/Cl vs. EC plot

influence groundwater quality (Fig. 3a). Whenever halite dissolution process is responsible for the Na^+ concentration in the groundwater, Na vs. Cl ratio should be approximately 1, whereas the Na vs. Cl ratio > 1 typically indicates that the sodium was released from silicate weathering (Fig. 3b). Fig. 3c showed that the ion exchange reactions, were Na is plotted against Ca in which Ca levels are ranges from 0.03 to 3.05 (meq/l), Na^+ levels are ranges from 0.05 to 0.71 (meq/l). The plot of EC against Na/Cl reveals that the trend line is inclined with the increasing EC, indicating that the evaporation is not the dominant process (Fig. 3d)

Groundwater results sample was modeled after End-member plot (Gaillardet *et al*., 1999). Fig. 4 reveals that groundwater is influenced mostly by silicate weathering.From Parson plot groundwater within the study area are of different origin samples OK/01, 02, 03, 04, 05, 06, 07, 08, 09 and 11 are of Ca–Mg–SO_4 water type, samples OK/10 is of Ca–Mg–Cl water type. Samples OK/13, 15, 14, and 15 are of Na-SO_4 water type (Fig. 5). The water classification of hydrogeochemical facies of Piper diagram was reconstructed by Lawrence and Balasubramanian (1994) in the new reconstructed diamond field (Fig. 6). It classified water in the various zones on the basis of various reactions occurring in the groundwater aquifer system. The reconstructed diamond field shows that groundwater sample lies within High Ca+Mg+SO_4+Cl hydrogeochemical facies as shown in Fig. 6. This implies that, Ca and Mg, are the primary courses of hardness in water. Any water with high Ca + Mg is said to be hard.

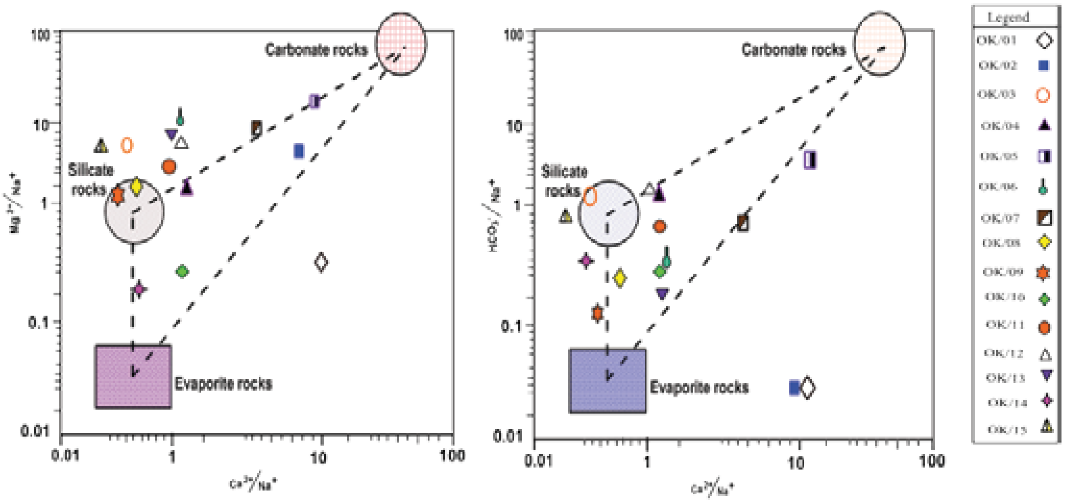

Fig. 4. End-member plot for groundwater samples

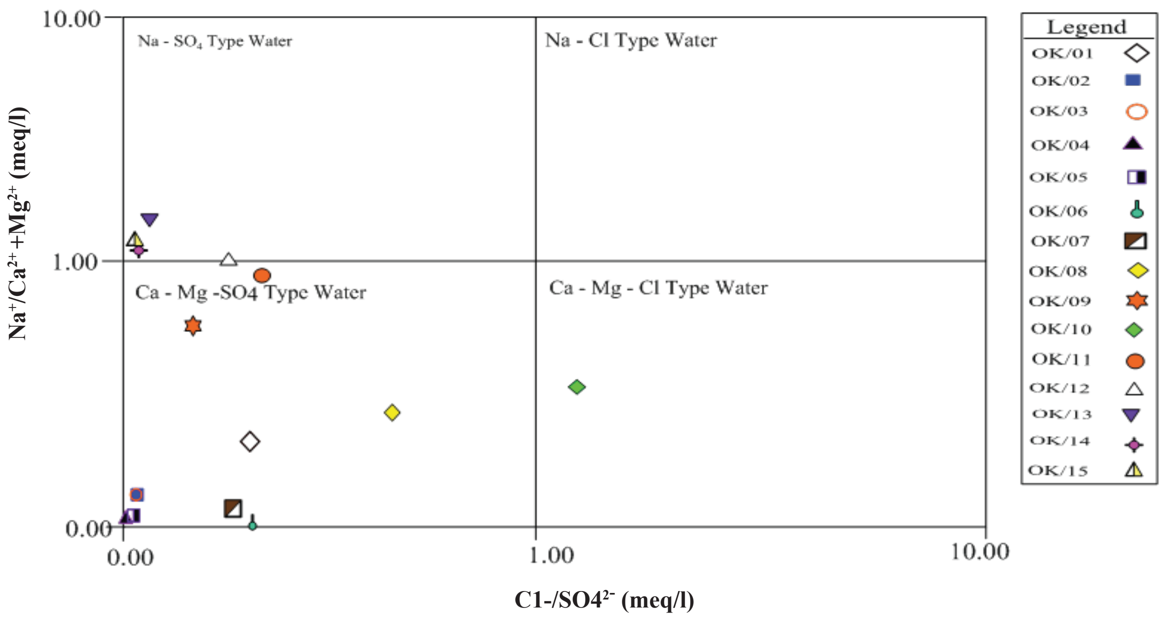

Fig. 5. Groundwater origin on a Parson's plot

Conclusion

The prime objective of this study is to evaluate the influence of abandoned Okpara coal mine on groundwater quality using bivariate plot and hydrogeochemical approach. Result from findings revealed that pH value within the study area is said to be acidic, values obtained fromTDS showed that groundwater fell within fresh water category. Bivariate plots revealed that groundwater is influencd by various factors. Parson's and Diamond field plots showed that groundwater within the study area were characterized to be of different water type Ca-Mg-SO_4, Ca-Mg-Cl and Na-SO_4 water type and groundwater samples fell within high Ca + Mg and SO_4 + Cl respectively. In conclusion groundwater within the study area is influenced by various factors.

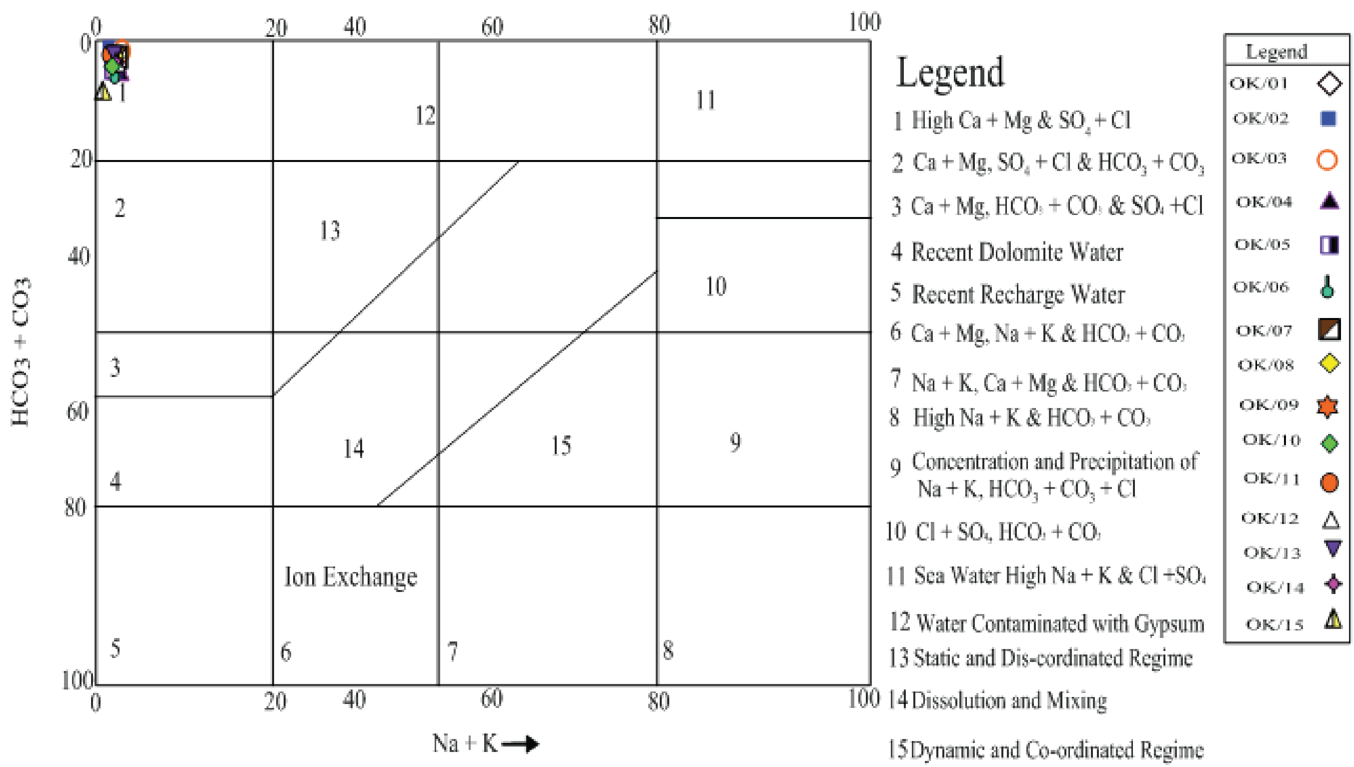

Fig. 6. Classification of Hydrogeochemical Facies (Reconstructed Diamond field of Piper by Lawerence and Bal-Subramanian, 1994)

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