

Interpretation of Hydro-geochemical Characteristics of Deep Aquifers in parts of Port Harcourt, Eastern Niger Delta

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Abstract

This study aims at assessing the hydro-geochemical characteristics of deep boreholes in Port Harcourt, Nigeria. Hydro-geochemical investigations were carried out both in the field and the laboratory. Groundwater samples from boreholes in the area were analyzed for various physico-chemical parameters using standard methods. StatistiXL 1.5 which is an add-in to Microsoft Excel, was used for performing the hierarchical cluster analysis (HCA). The HCA was used to explore and reveal natural groupings or clusters within the physico-chemical variables that would otherwise not be apparent. The determination of spatial variance equality/homogeneity in means of the physico-chemical parameters was made with the single factor/one-way analysis of variance and further plots of group means was made with means plots. The physico-chemical parameters for the deep boreholes show the following range: Temp. °C (27.02 – 29.03), pH (4.28 – 7.72), EC (350.60 – 618.20µS/cm), TDS (122.70 – 381.31mg/l), TSS (BDL – 35.00mg/l), Hardness (2.50 – 36.00mg/l), Cl⁻ (115.00 – 410.00mg/l), Eh (123.22 – 196.00mV), SO₄²⁻ (48.00 – 90.10mg/l), Fe (0.020 – 0.820mg/l), Salinity (12.00 – 355.00mg/l), NO₃⁻ (0.201 – 6.300mg/l), HCO₃⁻ (6.701 – 54.011mg/l), Ca²⁺ (3.000 – 7.633mg/l), Na⁺ (0.834 – 3.400mg/l), Mg²⁺ (0.445 – 5.677mg/l), K⁺ (0.220 – 0.555mg/l), PO₄²⁻ (0.030 – 0.732mg/l), Mn²⁺ (0.011 – 0.727mg/l), F⁻ (0.411 – 2.310mg/l), SiO₂ (0.55 – 4.94mg/l), Zn²⁺ (0.14 – 0.60mg/l), Cu²⁺ (0.01 – 0.06mg/l), Pb (0.01 – 0.06mg/l) and Br⁻ (12.50 – 79.70mg/l). Generally, for the deep boreholes the water is soft on account of the hardness values recorded (2.50 – 36.00mg/l). The study also reveals saltwater contamination in the area as EC, TDS, salinity as well as chloride contents in some boreholes are high. This shows saltwater encroachment at those locations. This is probably due to the closeness of these locations to the sea. Therefore, saltwater-freshwater interface should be delineated in the area. The test of homogeneity in mean variance of the physico-chemical properties of groundwater samples across the sampling locations for the boreholes revealed significant heterogeneity $\{F_{(32, 51)} > F_{Crit (3.87)}\}$ at $P > 0.05$. A further post-hoc structure detection of group means using means plots revealed that salinity (82.00), Eh (143.00), TDS (22.30), Cl (300.00) and EC (513.00) were most responsible for the observed heterogeneity in all sampling locations. The hydro-geochemical interpretation presented here strongly illustrates that rational plans for long-term and sustainable management of the aquifer systems cannot be based simply on regulatory water quality targets, which are focused on current anthropogenic causes of water quality degradation (e.g. in relation to saline intrusion or industrial contaminants). Although recent management effort may have an influence on the quality of the aquifer (e.g. in relation to the dynamic movement of freshwater), palaeo-hydrogeological events, perhaps resulted in the presence of relict saline components in the aquifer isolated from their original sea water source.

Key Words: Groundwater quality, borehole, hydro-geochemistry, saltwater intrusion, contamination.

INTRODUCTION

Water in adequate supply and quality is a necessity for everyday life and the largest available source of freshwater lies underground. The water underground is referred to as groundwater and it is the water held in the subsurface within the zone of saturation under hydrostatic pressure below the water table. The quantity, chemical and biological characteristics of the water determine its usefulness for industry, agriculture or domestic purposes. The chemical composition of groundwater and the water types found in an environment are determined greatly by the composition of water of precipitation, local geology, types of minerals found in the environment through which recharge and groundwater flows, anthropogenic activities such as mining and waste disposal as well as climate and topography (Akpah and Ezeigbo, 2010). Other factors affecting groundwater chemistry includes the chemistry of the infiltrating water at the recharge source, the chemistry of the porous media including the interstitial cement or matrix of the aquifer, the rate of groundwater flow in the aquiferous medium and the permeability of the aquifer (Offodile, 2002).

Within aquifers, groundwater is hosted by minerals which influence its hydro-geochemistry and ultimate quality (Etu-Efeotor, 1998). The quality of water is determined by its chemical composition and therefore its ultimate usability and its assessment and the parameters examined depend on the envisaged usage. In some cases, water quality is far more important than its availability. On account of the wide variety of water hydro-geochemical characteristics and the consequent different standards of portability, it is impossible to set rigid standards of chemical quality.

The evolution of groundwater is explained by the order of encounter as stated by Freeze and Cherry (1979). This theory states succinctly that the order in which groundwater encounter strata of different mineralogical composition can exert an important control on the final water chemistry. As groundwater flows through the strata of different mineralogical composition, the water composition undergoes adjustments caused by imposition of new mineralogically controlled thermodynamic constraints (Edet, 1993).

A lot of studies have been carried out on the interaction of groundwater with the host rock in parts of the Niger Delta (Amadi et al., 1989; Olobaniyi and Owoyemi, 2006; Edet and Ekpo, 2008, Nganje *et al.*, 2010 and Amadi *et al* 2010). None of the studies have been able to evaluate the hydro-geochemistry of groundwater in the area, especially of the deep aquifer systems. This paper therefore, aims at interpreting the hydro-geochemical processes in the area that takes into account the degree to which various waters currently encountered in the aquifer already are complex mixtures between modern recharge waters. The knowledge of hydro-geochemical processes that control groundwater chemical evolution could lead to improved understanding of hydro-geochemical characteristics of an aquifer. This would contribute to effective management and use of groundwater resources in the area.

Description of the Study Area

Port Harcourt is located within latitudes $6^{\circ} 58'$ to $7^{\circ} 6'N$ and longitudes $4^{\circ} 40'$ to $4^{\circ} 55'E$ (Figure1). It falls almost entirely within the lowland swamp forest ecological zone and is flanked in the east, west and southern limits by mangrove swamp forest (Braide *et al.*, 2004; Chindah; 2004). The area experiences heavy rainfall averaging 25000mm/annum. It rains for about eight months (March to October) during the year and even the months considered as dry months are not free from occasional rainfall (Gobo, 1990). The area has an almost flat topography and is underlain by superficial soil that consists of silty clays mixed with silty sands. The water table is less than 10m below ground surface.

Port Harcourt is located within the Quaternary alluvium tidal wetlands of the Niger Delta, with strong reversing tidal currents. The geology of the Niger Delta has been extensively documented by various research including Reyment (1965), Allen (1965), Short and Stauble (1967). The Niger Delta has an area of about 75000km² and the overall sedimentary sequence is dominantly composed of sand, shale and clay. The pro delta developed on the northern part of the basin during the Campanian transgression and terminated with the upper Maastrichian regression (Reyment, 1965). The formation of the modern Niger Delta is made up of marshy land masses criss-crossed by numerous rivers and creeks whose banks are made up of levees with back swamps. The formation of the land mass has been explained to be a result of sediment deposition generally associated with the River Niger and its tributaries.

METHODS OF STUDY

Hydro-geochemical data were interpreted by descriptive statistics and multivariate statistical analyses were performed using Statistica 6.0 software, SPSS Version 17.0 and MS Excell 2007, respectively. Hydro-geochemical investigations were carried out both in the field and the laboratory. Groundwater samples from boreholes in the area were analyzed for various physico-chemical parameters using standard methods. StatistiXL 1.5 (StatistiXL (2007), which is an add-in to Microsoft Excel, was used for performing the hierarchical cluster analysis (HCA). The HCA was used to explore and reveal natural groupings or clusters within the physico-chemical variables that would otherwise not be apparent. The determination of spatial variance equality/homogeneity in means of the physico-chemical parameters was made with the single factor/one-way analysis of variance (ANOVA). Further plots of group means was made with means plots.

Ward's method was used to combine the clusters. This method is commonly applied in water chemistry investigations, e.g., by Farnham *et al.* (2000), Kuells *et al.* (2000), Alberto *et al.* (2001), Guler and Thyne (2004), and Thyne *et al.* (1995). Ward's method uses an analysis of variance approach to evaluate the distances between cluster, attempting to minimize the sum of squares of any two (hypothetical) clusters that can be formed at each step (Swan and Sandilands 1995). The result is displayed as a dendrogram (tree diagram) providing a visual summary of the clustering process. The great benefits of cluster analysis is that it provides a relatively simple and direct way to classify samples, and it presents results as a dendrogram, which is easy to interpret (Davis, 2002). The methodology allows consideration of all variables, and a coherent group of samples well not be split up (potentially arbitrarily) among different categories. Furthermore, using a semi-objective technique such as cluster analysis, provides an element of objectivity to the classification of samples. This is an advantage compared to a more subjective approach in an area like the Niger Delta where data quality on geology and hydrogeology is relatively weak.

RESULTS AND DISCUSSION

The following physico-chemical properties of groundwater for deep boreholes were analysed: Temp, pH, EC, TDS, TSS, Hardness, Cl^- , Eh, SO_4^{2-} , Fe, Salinity, NO_3^- , HCO_3^- , Sr^{2+} , Na^+ , Mg^{2+} , K^+ , PO_4^{2-} , Mn^{2+} , F^- , SiO_2 , Zn^{2+} , Cu^{2+} , Pb and Br^- (Tables 1). The physico-chemical parameters for the deep boreholes (Table 1) show the following range, Temp. $^{\circ}\text{C}$ (27.02 – 29.03), pH (4.28 – 7.72), EC (350.60 – 618.20 $\mu\text{S}/\text{cm}$), TDS (122.70 – 381.31mg/l), TSS (BDL – 35.00mg/l), Hardness (2.50 – 36.00mg/l), Cl^- (115.00 – 410.00mg/l), Eh (123.22 – 196.00mV), SO_4^{2-} 48.00 – 90.10mg/l), Fe (0.020 – 0.820mg/l), Salinity (12.00 – 355.00mg/l), NO_3^- (0.201 – 6.300mg/l), HCO_3^- (6.701 – 54.011mg/l), Ca^{2+} (3.000 – 7.633mg/l), Na^+ (0.834 – 3.400mg/l), Mg^{2+} (0.445 – 5.677mg/l), K^+ (0.220 – 0.555mg/l), PO_4^{2-} (0.030 – 0.732mg/l), Mn^{2+} (0.011 – 0.727mg/l), F^- (0.411 – 2.310mg/l), SiO_2 (0.55 – 4.94mg/l), Zn^{2+} (0.14 – 0.60mg/l), Cu^{2+} (0.01 – 0.06mg/l) and Br^- (12.50 – 79.70mg/l).

Generally, results of the study show the boreholes have higher pH 4.28 – 7.72 (Table 1). This shows slightly acidic water in the area. Results also reveal that, because the water table is very close and near the surface for the shallow boreholes, it exposes the groundwater to anthropogenic and meteorological influences. This is attributed to the heterogeneity of the rock units resulting from the underlying geology in the study area, hence, impacting heterogeneity on the chemistry of the water (Conti *et al.*, 2000).

The nitrate levels recorded in the boreholes are low [NO_3^- (0.201 – 6.300mg/l)] and show that the groundwater is free from pollution, safe for consumption by human and livestock with respect to this parameter. Nitrate in groundwater owes its origin from activities such as application of fertilizers in farms, plant decomposition, human sewage, soak ways, industrial and domestic effluents, and emissions from combustion engines (Lenntech Water Treatment and Air Purification, 2008).

Table1. Groundwater quality for deep boreholes (>100m)

BH No.	Location	Temp (°C)	pH	EC (µS/cm)	TDS (mg/l)	TSS (mg/l)	Hardness (mg/l)	Cl ⁻ (mg/l)	Eh (mV)	SO ₄ ²⁻ (mg/l)	Fe (mg/l)	Salinity (mg/l)	NO ₃ ⁻ (mg/l)	HCO ₃ ⁻ (mg/l)
1	Moscow Rd 1 (Pumping Station)	27.02	4.50	522.00	230.60	10.0	14.50	330.00	170.00	ND	ND	355.00	0.201	6.701
2	Moscow Rd 2(Post Office)	28.33	7.40	513.00	221.30	12.00	20.40	300.00	143.00	75.00	0.400	82.00	0.831	10.321
3	Borokiri (Comprehensive Sch.)	29.03	7.72	618.20	297.20	BDL	36.00	410.00	191.00	90.10	ND	163.40	ND	54.011
4	Borokiri Sandfill	27.92	6.23	429.30	241.00	35.00	13.5	250.00	196.00	48.00	0.020	113.21	6.300	23.171
5	Rumuolumeni	27.51	5.90	350.60	122.70	3.00	2.50	115.00	193.00	72.96	0.820	210.32	0.600	30.000
6	Onne	28.13	4.28	519.40	381.31	2.00	25.22	215.00	123.20	80.00	0.361	12.00	0.378	12.000

Table1. Continuation

Sr ²⁺ (mg/l)	Ca ²⁺ (mg/l)	Na ⁺ (mg/l)	Mg ²⁺ (mg/l)	K ⁺ (mg/l)	PO ₄ ³⁻ (mg/l)	Mn (mg/l)	F ⁻ (mg/l)	SiO ₂ (mg/l)	Zn ²⁺ (mg/l)	Cu ²⁺ (mg/l)	Pb (mg/l)	Br ⁻ (mg/l)
3.80	7.633	1.022	0.826	0.505	0.030	0.033	2.310	0.94	0.60	0.05	0.01	18.30
4.50	4.111	0.834	4.500	0.300	0.732	0.780	0.800	0.60	0.33	0.03	0.02	29.11
2.00	6.123	3.400	0.445	0.431	0.233	0.011	0.411	4.94	0.48	0.01	0.02	12.50
3.99	4.223	2.321	1.789	0.424	0.232	0.230	2.000	0.80	0.15	0.02	0.01	79.70
4.00	3.000	1.443	5.677	0.555	0.221	0.727	1.520	4.55	0.14	0.03	0.04	31.72
3.78	8.000	1.376	2.341	0.220	0.220	0.030	0.734	0.55	0.24	0.30	0.06	19.78

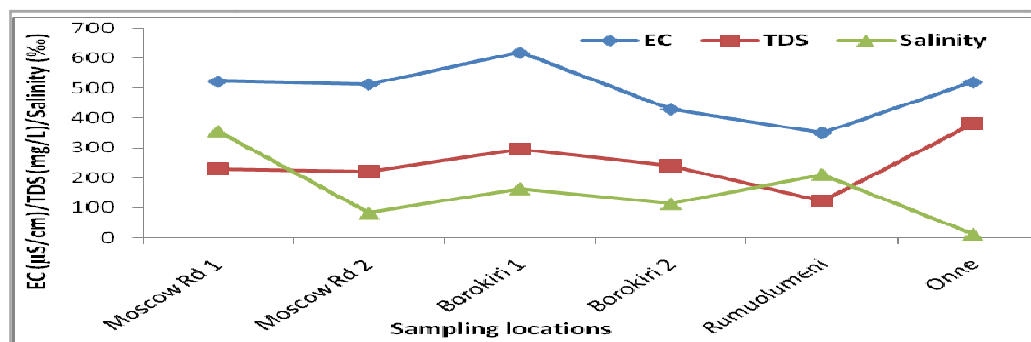


Figure2. Variation plots of EC, TDS and Salinity

Hydrochemical Indices

Ionic relationships studied to check the salinity and origin of the groundwater in the study area includes: Mg/Ca, Cl/HCO₃, and the Cationic Exchange Value (CEV = [Cl - (Na + K)]/Cl). Mg/Ca values were all less than 2.0 (Table 2) ranging from 0.029 – 1.892. According to the interpretation of this index, the groundwater in the study area appears to be slightly of inland origin, because waters under marine influence would have values of about 5 (Morell *et al.*, 1986) except where other processes such as cationic exchange intervene. If this happens, the values could be 4 or less.

The HCO₃/Cl values range from 0.0173 – 0.2609. Values of this hydrogeochemical index given for inland waters are between 0.1 and 5 and for seawater between 20 and 50 (Custodio, 1987). In general, the CEV for seawater ranges from +1.2 to +1.3 (Custodio, 1983), where low-salt inland waters give values close to zero, either positive or negative. The CEV values for groundwater of Port Harcourt area are generally below 1.0 (Table 2), ranging from 0.98 – 0.99, indicating that the groundwater is inland in some locations with respect to provenance. This result agrees with the findings of Bolaji (2009).

Table 2. Hydrogeochemical Indices, Ionic Ratios and CEV of Groundwater in the Area

BH No.	HCO ₃ /Cl	Na/Ca	Na/Cl	Ca/Cl	Mg/Cl	K/Cl	SO ₄ /Cl	Mg/Ca	Ca/SO ₄	Ca/HCO ₃	CEV
1.	0.0173	0.1339	0.0031	0.0231	0.0025	0.0015	0.0000	0.1080	0.0000	1.3389	0.99
2.	0.0344	0.2029	0.0028	0.0137	0.0150	0.0010	0.2500	1.0951	0.0548	0.3983	0.99
3.	0.1317	0.5553	0.0083	0.0057	0.0011	0.0011	0.2198	0.0730	0.0679	0.1134	0.98
4.	0.0927	0.5496	0.0093	0.3213	0.0072	0.0017	0.1920	0.4240	0.0879	0.1823	0.98
5.	0.2609	0.4767	0.0125	0.0169	0.0494	0.0048	0.6344	1.8920	0.4011	0.1000	0.98
6.	0.0558	0.3249	0.0491	0.1512	0.0109	0.0088	0.3721	0.2933	0.1000	0.6667	0.99

Implications for Saltwater Intrusion

Hydro-geochemical studies have been aimed at determining and differentiating the potential sources of salinization. The hydro-geochemical evidence as shown in this study suggests further that the saline water bodies themselves are sourced from mixing both recent and past seawater intrusion of the aquifers of the area. This means that the hydro-geochemistry of the aquifer is the result of interplay between various natural and anthropogenic processes. And especially useful indicator of groundwater ages for the saline components is provided by the dissolved SO₄/Cl ratios, increased values reflecting longer residence time and thus greater rock-water interaction.

The physico-chemical characteristics of the groundwater in the study area generally reflect a situation of salinization that is associated principally with marine intrusion. This can be appreciated from the high Cl, TDS, and EC. Groundwater contamination by chloride can also result from other means than by seawater intrusion. Hem (1985) suggested that seawater intrusion into coastal aquifers may also be indicated by sulphate ionic proportions similar to that in seawater, and by low Ca and Mg concentrations. Industrial activities and urbanization can alter groundwater chemistry as reported by Knuth *et al.* (1989) which present an integrated approach involving hydro-geological, geochemical, and geophysical methods to determine the source of salinity contaminating a groundwater supply in the area.

Structure of Group Means Plots

In the means plots for the deep boreholes, Moscow Road is the predictor variable (independent variable). In the means plot between Moscow Road 2 and Moscow Road 1, the following contributed majorly to the observed heterogeneity in the locations: Salinity (82.000), Eh (143.000), TDS (221.300), Cl (300.000) and EC (513.000). For Borokiri 1 and Moscow Road 2: TDS (82.000), Eh (143.000), Salinity (221.300), Cl (300.000) and EC (513.000), respectively. In the case of Borokiri 2 and Moscow Road 2, Cl (513.000), TDS (300.000), Eh (143.000), Salinity (82.000). Moreso, the means plots between Rumuolumeni and Moscow Road 2 shows that the following contributed immensely {Cl (300.000), TDS (221.000), Eh (143.000), Salinity (82.000), and EC (513.000)}. For Onne and Moscow Road 2: Eh (143.000), Cl (300.000), TDS (221.000), and EC (513.000) (Figure2 - 6).

Homogeneity in Spatial Mean Variance

The test of homogeneity in mean variance of the physico-chemical properties of groundwater samples across the sampling locations for the deep boreholes revealed significant heterogeneity { $F_{(32, 51)} > F_{Crit(3,87)}$ } at $P > 0.05$.

A further post-hoc structure detection of group means using means plots revealed that salinity (82.00), Eh (143.00), TDS (22.30), Cl (300.00) and EC (513.00) were most responsible for the observed heterogeneity in all sampling locations (Figures.2 - 6).

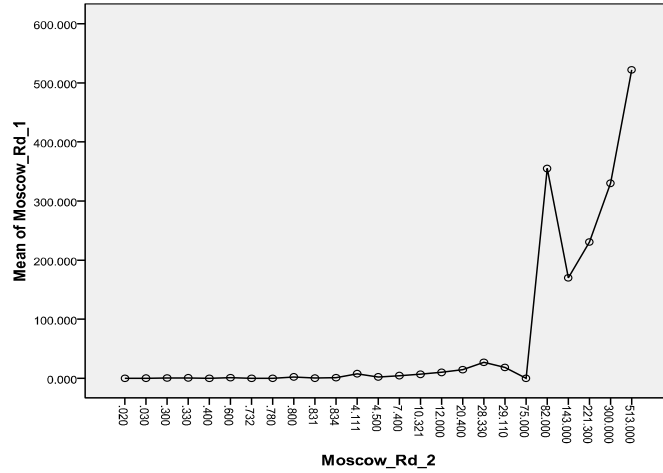


Figure2. Means plot between Moscow Road 2 and Moscow Road 1

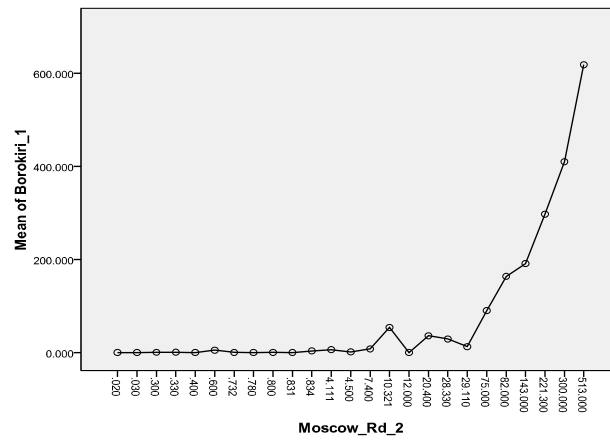


Figure3. Means plot between Borokiri 1 and Moscow Road 2

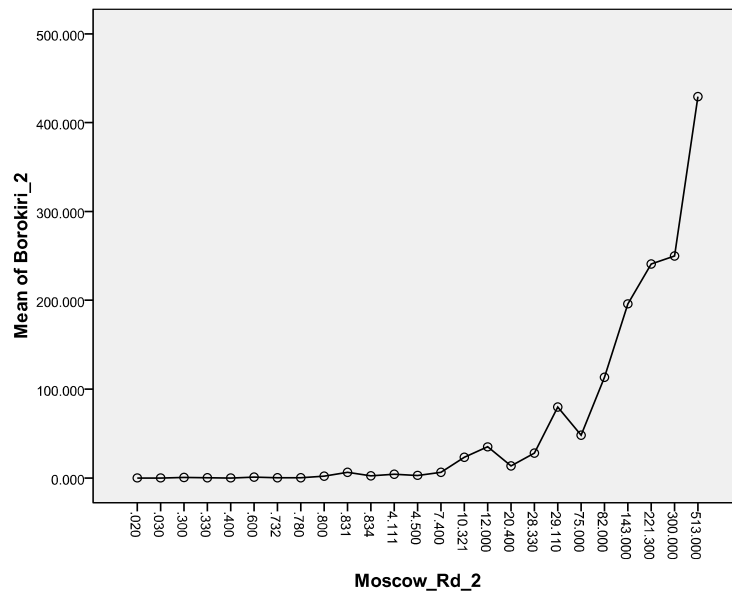


Figure4. Means plot between Borokiri 2 and Moscow Road 2

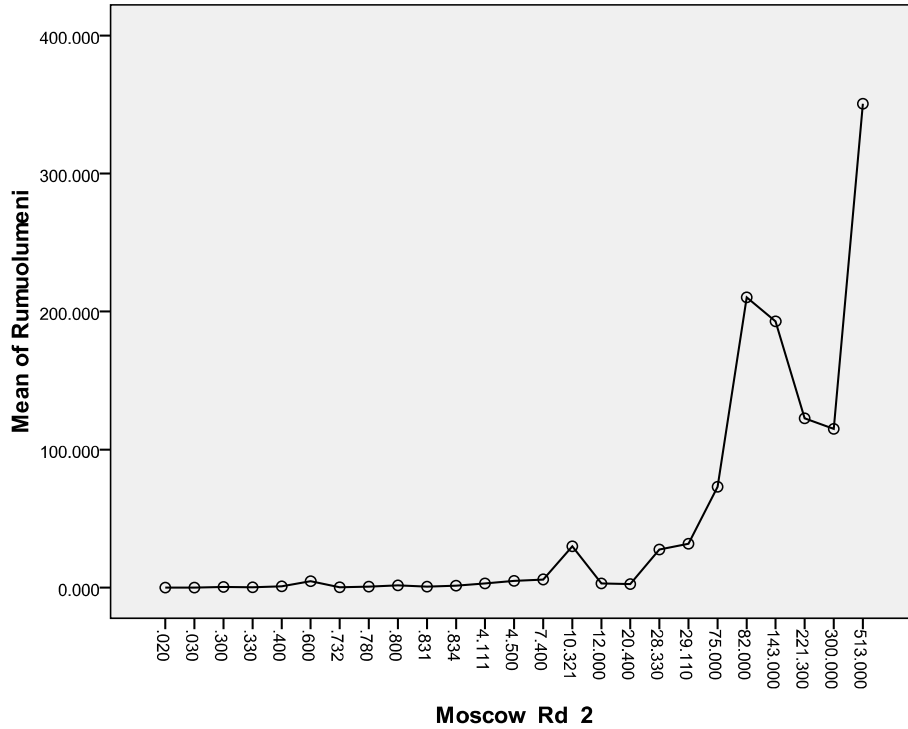


Figure 5. Means plot between Rumuolumeni and Moscow Road 2

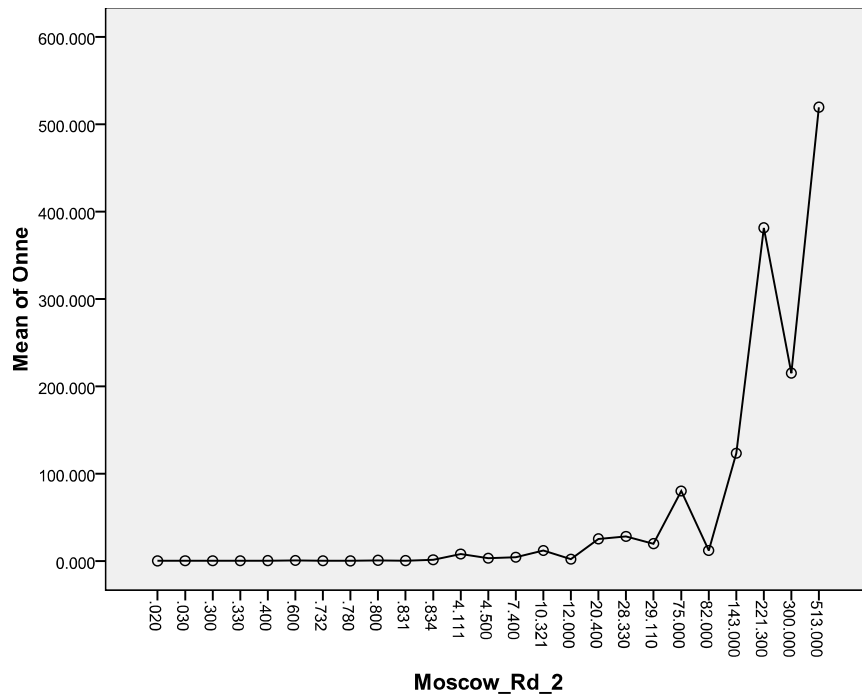


Figure 6. Means plot between Onne and Moscow Road 2

Agglomeration Schedule

The agglomeration schedule is a numerical summary of the cluster solution. With the complete linkage solution, 2 clusters were formed. At the first stage, cases 2 and 6 are combined with farthest distance, and the cluster created by

their joining next appears in stage 4. In stage 4, the clusters created in stages 0 and 1 are joined and the resulting cluster next appears in stage 5. However, the coefficient column reveals a large gap between stages 2 and 3 (Figure7). Dendrogram using Complete Linkage Rescaled Distance Cluster Combine.

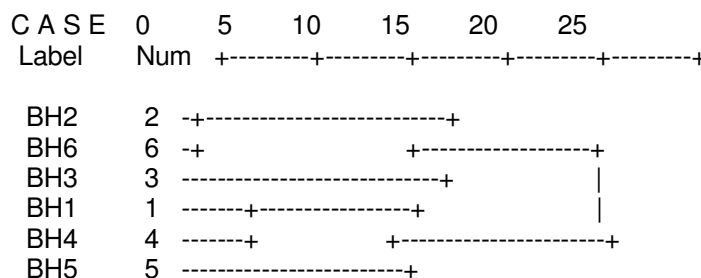


Figure7. HCA Dendrogram generated from hydrochemical data showing relations between variables

CONCLUSION

This study reveals that the water is soft on account of the hardness values recorded (2.50 – 36.00mg/l). According to Todd (1980); Sawyer and McCarty (1967) classification, 0 – 75mg/l is the range for soft water. The study also reveals saltwater contamination in the area as chloride contents in some boreholes are up to 40mg/l. This shows saltwater encroachment at those locations. This is probably due to the closeness of these locations to the sea. Therefore, saltwater-freshwater interface should be delineated in the area.

The hydrochemical interpretation presented here strongly illustrates that rational plans for long-term and sustainable management of the aquifer systems cannot be based simply on regulatory water quality targets, which are focused on current anthropogenic causes of water quality degradation (e.g. in relation to saline intrusion or industrial contaminants). Although recent management effort may have an influence on the quality of the aquifer (e.g. in relation to the dynamic movement of freshwater), palaeo-hydrogeological events have resulted in the presence of relict saline components in the aquifer isolated from their original sea water source.

Following the above scenario, such isolated (and potentially dynamic) sources must be taken into account when assessing boundary conditions for water quality modeling. To determine whether the groundwater salinity in the area is derived from anthropogenic origin such as excessive groundwater use or it is a natural phenomenon, consecutive groundwater monitoring of water level, Electrical Conductivity (EC) and groundwater chemistry is required for many years. Hydro-geochemical studies in the area should be carried out regularly to detect any future degradation of the water.

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