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ARTICLE A Comparative Study of Groundwater between Geological Groups of Southern Benue Trough, Nigeria Using Modelling Approach

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ABSTRACT

Groundwater studies were carried out between two geological groups to evaluate factors that influences groundwater geochemistry. To achieve this, 30 groundwater samples were collected. Parameters such as pH, Electrical Conductivity (Ec), Total Dissolved Solids (TDS), Total Hardness (TH), and hydrochemical characteristics (Na²⁺, K⁺, Ca²⁺, Mg²⁺, HCO₃⁻, NO_3^- , Cl^- , CO_2^{3-} , and SO_4^{2-}) of groundwater were determined. Findings revealed that the pH value for Asu River Group ranges from 5.3 to 7.5, and that of Eze Aku Group ranges from 4.1 to 7.9. It was observed that areas around the mines had low pH values. Analyzed results that were obtained were interpreted using various hydrogeochemical models. Parson plots reflected that groundwater within the two geological groups fell within Ca-Mg-SO4 and Ca-Mg-Cl. Results from End-member plots showed that 96% of groundwater samples analyzed were categorized under carbonate weathering, 4% fell silicate weathering. Gibbs plots revealed that interactions between groundwater and surrounding host rocks are mostly the main processes responsible for chemical characteristics of groundwater, Diamond field plots suggested that groundwater within the study were categorized to be high in Ca + Mg & SO₄ + Cl, the plot of Ca²⁺/(HCO₃⁻ + SO₄²⁻) against Na+/Cl⁻ revealed that groundwater was considered to be within the natural state for the two group. The plot of TDS against TH showed that groundwater is classified as soft freshwater. The study revealed there was no significant difference between factors that influence groundwater within the two geological.

1. Introduction

Groundwater is preferred to surface water based on the fact that it is readily free from surface contamination, and considered to be less prone to contamination when compared to surface. In most scenarios groundwater is contaminated by infiltration from surface pollution such as leakage from septic tanks, mining activities, indiscriminate waste disposal close to surface water sources, and others. Several factors are for the alteration of the groundwater resource. Groundwater resource is considered to be a major source of water for various users across the world. In the same vein ^[1] reported that groundwater resources are recognized as an important aspect of freshwater resources and that is required for sustaining ecosystems, natural and human development. Therefore is considered necessary to constantly evaluate its quality and suitability for various uses. Various scholars within the southern Benue Trough

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of Nigeria have assessment water resources for various uses ranging from irrigation, industrial and domestic use ^[2-4]. Their findings suggested that groundwater quality and geochemistry are altered by geogenic and anthropogenic activities such as rock-water interaction, weathering, and mining, among others.^[5] thought that the geochemistry of groundwater within the Asu River Group of the southern Benue Trough is highly influenced by geogenic activities such as carbonate and silicate weathering and that the movement of groundwater is influenced by factors such as thickness, lithofacies, and the formation process of rock. On the same note ^[6-8] acknowledge that hydrochemistry of groundwater resources depends on the following; the quality of recharge water, level of chemical weathering of diverse rock types, local or regional of an area, and lastly, human activities. According to [2-5], awareness of hydrogeochemistry is of paramount importance as it plays a major in determining the origin, chemical composition, and characterization of groundwater concerning a particular region or locality. The importance of hydrogeochemistry cannot be underestimated as it has led to several detailed studies on groundwater quality deterioration and geochemical evolution of groundwater in many parts of the globe [9-11]. A detailed study on hydrochemical processes of aquifer system help gives information about the interaction between aquifer system and its surrounding environment and the effect of anthropogenic and geogenic activities on groundwater chemistry. Several factors such as evaporation, precipitation, oxidation-reduction, weathering, sorption, and ion exchange reactions tend to may play a major role in altering the chemical composition of groundwater^{[12], [5]} pointed out that the reaction between groundwater and aquifer minerals has a major role to play in groundwater quality which is useful to predicate the source of groundwater. It is essential to evaluate the relationships among the chemical parameters and also factors that influence the chemical composition of groundwater. Additionally, recent studies conducted on groundwater quality revealed that groundwater within the Asu River Group fell with two categories temporary and permanent hardness Ca²⁺- Mg²⁺- HCO₃⁻ and Ca²⁺- Mg²⁺- Cl⁻ they attributed groundwater hardness to the presence of calcium and magnesium in water ^[13]. Lately, studies have been carried out of the hydrogeochemical assessment of groundwater quality within different geological groups of southern Benue Trough, especially around the mines within the southern Benue Trough of the sedimentary basin, but detailed study has not been carried to evaluate factors that influence groundwater within the Asu River Group (ARG) and the Eze Aku Group (EAG) of southern Benue Trough of Nigeria. Two mines exist within the study area; these are the lead-zinc mine at Envigba and Ameka. The leakage of chemicals from these mines sites. geogenic and anthropogenic activities have influenced the chemical composition of groundwater within the area ^[2,14]. Hence, a detailed study is necessary to get a piece of baseline information that will in-turn be needed to establish long-term groundwater monitoring programs for sustainable development of groundwater within the study area. This study is aimed at (i) evaluating the geochemical characteristics of groundwater and (ii) investigating factors that influence the groundwater chemistry within the ARG and EAG of southern Benue Trough of Nigeria. It is believed that findings from this study will help monitor factors that influence the hydrochemistry of groundwater and also help in enhancing the groundwater quality.

Geographical, geological, and hydrogeological overview

The study area lies between 6°03' and 6°15'N and longitudes 8°03' and 8°15'E as shown in Figure 1. It is located in Ebonyi state, southeastern Nigeria. The study area is accessible via a network of roads. Geologically, the study area lies within the southern part of Benue Trough, which is regarded as a sedimentary succession of pre-Santonian periods that is of the Albian and Turonian times (Table 1). The two major groups that cut across the study area are the Asu River Group (ASG) and Eze Aku Group (EAG), according to ^[15] the ASG is Albian in age. The Abakaliki and Ebonyi Formation underlie the ASG^[16].^[17,18] report that the rock unit that exists within the study area are alternating shales and siltstones with occurrences of fine-grained micaceous and feldspathic sandstone, limestone, and mudstone. [19] reported that the EAG is Turonian in age and it uncomfortably overlies the ARG and that the EAG entails lithostratigraphic sections deposited from the late Cenomanian to Turonian in age. Previous reports according to [20-22] revealed that several factors such as integration of tectonism with magmatism coupled with diagenesis have altered the mineralogical and geochemical constituents of subsurface rock, which trigger there baking making them suitable for construction. Various authors reported the occurrence of lead-zinc (Pb-Zn)^[23]; ^[24] stated that the presence of Pb-Zn minerals within the study area exists in veins as open space-fillers within en echelon, tensional, and steeply dipping fracture systems in the darkgray to black shales of the Asu River Group also encouraged their rampant excavation. Groundwater (aquifer) within the study area was classified into two aquifers (i). The shallow unconfined (ii). The deep confined aquifer system ^[25]. Although ^[26] believed that the shallow unconfined aquifer is



Figure 1. Geology Map of the Study Area Showing Groundwater Sampling Points

said to occur in fractured, weathered, jointed shale and some patched sandstone in the study area. Groundwater movement and storage within the study area are primarily influenced by thickness, lithology, and structure of rock formation.

2. Materials and Methods

For this study, 30 groundwater samples were randomly collected within the study area as shown in Figure 1. Groundwater samples were determined using appropriate titrimetric method as described by ^[27]. Groundwater samples were collected and filtered and further stored in plastic containers in an icebox with temperatures ranging from 3°C to 5° C and preserved in a refrigerator (<5°C) after acidification by nitric acid (5 mL of 6 N HNO₃). Certain parameters such as pH, temperature (T), Electric Conductivity (Ec), and Total Dissolved Solids (TDS) were determined in-situ using the HACH conductivity meter. While chemical parameters such as; calcium (Ca²⁺), magnesium (Mg²⁺)[•] bicarbonates (HCO₃⁻), and chlorides (Cl⁻) ions were analyzed by volumetric titrations. Sulfate (SO₄^{2⁻}) ions were analyzed using a Jenway clinical

fame photometer (PFP7 model. Sodium (Na⁺), and Potassium (K⁺) ions were analyzed by atomic absorption spectrometer Jenway clinical fame photometer PFP7 model in the laboratory.

The cation-anion balance was also assessed using electrical neutrality equation, expressed in meq/L.

$$\% \ difference \ \left(\frac{meq}{L}\right) = \left(\frac{\sum cations - \sum anions}{\sum cations + \sum anions}\right) \times 100\% \ (1)$$

Total hardness

Total hardness of the groundwater was calculated using the formula given by ^[28,29].

$$TH = (Ca^{2+} + Mg^{2+}) \times 100 \tag{2}$$

3. Results and Discussion

Based on the results of the physicochemical analysis for the two geology group with the minimum, maximum, and mean values in meq/L and the statistical parameters are determined, as shown in Table 1.

Sampling Code	Latitude and Longitude	EC (μS/ cm)	pН	TDS	TH (mg/L)	Ca ²⁺ (meq/ L)	Mg ²⁺ (meq/ L)	Na ⁺ (meq/L)	K ⁺ (meq/ L)	Cl ⁻ (meq/L)	NO ₃ ⁻ (meq/L)	SO ₄ ²⁻ (meq/ L)	HCO ₃ ⁻ (meq/ L)	CO_2^{3-} (meq/L)
MS/01	6°14/32//- 8°14/53//	736	7.3	482	81	0.33	0.48	0.10	0.37	3.19	0.03	3.22	0.03	0.87
MS/02	6°12/56//- 8°09/57//	48	6.8	165	91	0.16	0.75	0.03	0.12	2.40	0.00	1.54	0.01	0.75
MS/03	6°11⁄09⁄⁄- 8°10⁄41⁄⁄	191	5.7	592	105	0.47	0.58	0.06	0.29	1.21	0.00	5.07	0.44	1.38
MS/04	6°10/11//- 8°10/13//	585	5.5	502	106	0.12	0.94	0.30	0.02	3.03	0.01	4.69	0.13	1.42
MS/05	6°08/55//- 8°09/55//	384	6.9	644	124	0.43	0.81	0.05	0.13	2.49	0.01	2.53	0.40	1.84
MS/06	6°08/32//- 8°11/43//	294	7.5	843	71	0.32	0.40	0.30	0.28	4.17	0.02	6.46	0.42	0.43
MS/07	6°08/20//- 8°13/43//	1084	6.4	211	28	0.25	0.03	0.05	0.39	6.38	0.01	4.67	0.03	0.64
MS/08	6°06⁄32⁄/- 8°10⁄28⁄/	492	6.6	482	17	0.11	0.06	0.01	0.24	1.30	0.00	1.46	0.23	1.33
MS/09	6°05/22//- 8°13/08//	550	6.1	707	98	0.23	0.75	0.03	0.14	2.47	0.00	7.46	0.23	1.88
MS/10	6°04⁄08//- 8°13⁄43//	495	5.6	229	17	0.14	0.03	0.04	0.58	3.03	0.05	3.66	0.48	0.35
MS/11	6°05/11//- 8°09/53//	707	6.4	494	7	0.32	0.38	0.03	0.13	6.28	0.01	2.53	0.23	0.17
MS/12	6°04/36//- 8°09/48//	694	5.3	585	7	0.13	0.57	0.01	0.45	5.11	0.02	5.64	0.10	1.56
MS/13	6°03/32//- 8°11/27//	94.4	7.4	647	31	0.24	0.07	0.01	0.27	6.35	0.00	7.03	0.30	1.84
MS/14	6°07/18//- 8°13/27//	308	6.1	192	65	0.33	0.32	0.04	0.11	7.44	0.00	8.43	0.00	1.66
MS/15	6°06/47//- 8°13/36//	411	5.6	854	75	0.17	0.58	0.03	0.32	4.03	0.00	3.08	0.23	1.36
MA/16	6 [°] 14⁄55⁄⁄- 8 [°] 04⁄28⁄⁄	996	6.5	290	4	0.20	0.20	0.02	0.48	3.04	0.03	4.74	0.20	0.58
MA/17	6°13/44//- 8°05/45//	495	7.3	308	104	0.46	0.58	0.04	0.12	5.69	0.00	6.30	0.17	1.75
MA/18	6°11/53//- 8°04/51//	184	6.5	404	96	0.92	0.04	0.01	0.26	7.31	0.00	6.05	0.04	1.05
MA/19	6°11⁄57//- 8°06⁄15//	794	6.0	553	92	0.72	0.20	0.02	0.49	4.60	0.01	2.53	0.30	1.13
MA/20	6°11/15//- 8°07/30//	839	4.1	347	112	0.61	0.51	0.07	0.07	2.91	0.02	1.60	0.43	1.49

Table 1. Result of hydrochemical Parameters

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Sampling Code	Latitude and Longitude	EC (μS/ cm)	pН	TDS	TH (mg/L)	Ca ²⁺ (meq/ L)	Mg ²⁺ (meq/ L)	Na ⁺ (meq/L)	K ⁺ (meq/ L)	Cl ⁻ (meq/L)	NO ₃ ⁻ (meq/L)	SO ₄ ²⁻ (meq/ L)	HCO ₃ ⁻ (meq/ L)	CO ₂ ³⁻ (meq/L)
MA/21	6°10⁄51⁄/- 8°07⁄09⁄/	1173	4.4	575	125	0.82	0.43	0.09	0.21	5.32	0.00	2.33	0.15	1.07
MA/22	6°09/25//- 8°04/03//	1083	4.1	854	111	0.94	0.17	0.04	0.20	6.00	0.05	4.65	0.27	1.39
MA/23	6°10/12//- 8°06/44//	861	4.9	543	64	0.31	0.33	0.03	0.38	2.39	0.02	6.30	0.82	1.04
MA/24	6°08/39//- 8°04/23//	619	4.4	354	115	0.54	0.61	0.08	0.12	4.24	0.01	9.02	0.53	1.33
MA/25	6°07/02//- 8°07/21//	599	7.3	544	85	0.48	0.37	0.01	0.22	1.04	0.01	1.53	0.08	1.50
MA/26	6°05/44//- 8°06/53//	408	7.0	967	97	0.92	0.05	0.01	0.11	4.47	0.00	4.57	0.01	1.42
MA/27	6°05/54//- 8°04/13//	814	7.9	588	74	0.72	0.02	0.11	0.42	0.26	0.00	2.35	0.05	0.53
MA/28	6°04/47//- 8°04/38//	69.3	5.7	865	76	0.52	0.24	0.20	0.11	2.74	0.00	1.43	0.04	0.99
MS/29	6°04/31//- 8°06/35//	50.1	7.5	678	104	0.93	0.11	0.03	0.39	5.57	0.00	2.45	0.03	1.53
MS/30	6°03/36//- 8°03/58//	274	6.0	575	142	0.99	0.43	0.05	0.32	6.33	0.03	5.75	0.02	1.51
Minimum	N/V	48	4.4	165	4	0.11	0.02	0.01	0.02	0.26	0.00	1.43	0.00	0.17
Maximum	N/V	1173	7.9	967	142	0.99	0.94	0.3	0.58	7.44	0.05	9.02	0.82	1.88
Average	N/V	548.5	6.40	537.6	77.18	0.46	0.37	0.06	0.26	4.01	0.01	4.36	0.22	1.18

Where= MS is sampling code for groundwater from ARG, MS is sampling code for groundwater from EAG, N/V= No value

Hydrochemistry Evaluation of Groundwater

pН

Electrical Conductivity (Ec)

According to ^[30], Ec is considered one of the major parameters that are used to determine the suitability of groundwater for use. For this study, the value of Ec ranges from 48 to 1173 μ S/cm, with an average value of 548.52 μ S/cm. The highest value of Ec was at sample location MS/21 within the EAG axis of the study area as shown in Table 2. This can be attributed to the presence of dissolved ions. Based on Ec obtained, groundwater is considered to be fresh except for sample locations MS/07, MA/21, and MA/22 that were slightly above 1000 μ S/cm which were considered saline in nature. Based on the EC, the groundwater of the study area is fresh (< 1000 μ S/cm) and only three samples are slightly saline (> 1000 μ S/cm). On a general note, pH determines the acidity or alkalinity of a solution ^[31]. The result from Table Irevealed that measured pH within the ARG ranges from 5.3 to 7.5 with a mean value of 6.34, hence it's classified to be slightly acidic to basic. 99% of groundwater within the ARG was classified to be acidic except for sample location MS/01, 06, and 13 which was classified to be basic as shown in Figure 2a. while the pH of sampled groundwater within the EAC ranges from 4.4 to 7.9 with the mean value of 6.46, hence groundwater was said to be classified to be slightly acidic to basic as shown in Figure 2b. From Figure 2a and 2b, it was observed that the value of pH around the mine site tends to low when compared to other parts of the study area. That implies that groundwater within the mine is considered to

highly acidic, this was observed around the Enyigba and Ameka mine as shown in Figure 2b. The acidic nature of groundwater around the mine sites can be attributed to the active chemical reactions ongoing around the mine sites, this results in mine water from the active mine site flowing into adjoining streams and river channels while the other water infiltrates into the ground thereby polluting groundwater and making it unsafe for various use ^[32].



Figure 2a. Spatial Distribution of pH in groundwater within ARG axis of the study area.



Figure 2b. Spatial Distribution of pH in groundwater within EAG axis of the study area.

Hydrochemical facies

Report according to ^[5] revealed that hydrochemical facies helps define groundwater in aquifer system and their diverse chemical composition. Further studies conducted by ^[33] revealed that facies is the function of lithology solution kinetics and flow pathway of their aquifer. They further pointed out that it is complex to interpret a huge table of analytical data as regards water quality. For a better interpretation of water resources, data models and graphs are mostly used for its interpretation and better understanding. Most study models are more preferable and are easily used to characterize water resources. Models used for this study include Parson, End-Member, Gibbs plots, reconstructed Diamond field, the plot of TDS against TH among others.

Parson Plot

The water classification of hydrogeochemical facies of Piper diagram was reconstructed by Lawrence and Balasubramanian, in the new reconstructed diamond field. A Parson plot classified that groundwater samples were classified in two categories Ca-Mg-SO₄ and Ca-Mg-Cl water type see Figure 3a and 3b. From Figure 3a Groundwater samples it was observed that samples MS/01, 03, 04, 05, 06, 08, 09, 10, 12,13, and 14 fell within Ca-Mg-SO₄ water type, while MS/02, 11, 07, and 15 fell within Ca-Mg-Cl water type such water type is classified to permanently hard water. Similar study conducted by ^[14] within the southern Benue trough, Nigeria reported that groundwater within the Asu River Group is permanently hard, this may be due to the fact that host rock weather and eventually residence over time in groundwater thereby altering the geochemistry of groundwater. From Figure 3b, it was observed sample location MA/16, 17, 24, 25, 26, and 27 was classified to be of Ca-Mg-Cl water type, and samples MA/18, 19, 20, 21, 22, 23, 28, 29, and 30, Similar studies done in Enyigba and Umuoghara mining of Ebonyi state, Nigeria ^[5,14] revealed groundwater within that terrain is classified to be hard due to rock water interaction.

End-Member Plot

The End-member plot is used to analyze the hydrogeochemistry of groundwater and rock weathering that influence groundwater. ^[35] first proposed an Endmember plot using the ratio of Ca^{2+}/Na^+ versus Mg^{2+}/Na^+ and HCO_3^-/Na^+ . For this present study, the ratios of Ca^{2+}/Na^+ , Mg^{2+}/Na^+ , and HCO_3^-/Na^+ ranges from 0.4 to 92, 0.18 to 57, and 0.00 to 27.33, respectively. Findings revealed that 96% of groundwater is majorly influenced by carbonate weathering, suggesting that the weathering of carbonate is a major hydrogeochemical process controlling groundwater hydrochemistry, 4% is influenced by silicate (Figure 4a and 4b).



Figure 3a. Parson's Plot Modified after, ^[34] of the study area showing ground water origin within ARG axis of the study area.



Figure 3b. Parson's Plot Modified after, ^[34] of the study area showing ground water origin within EAG axis of the study area.



Figure 4a. End-member plot for groundwater samples within ARG axis of the study area.



Figure 4b. End-member plot for groundwater samples within EAG axis of the study area.

Gibbs Plot

Gibbs plot is a plot of log (TDS) against ratios of Na⁺/ (Na⁺ + Ca²⁺) and Cl⁻/(Cl⁻ + HCO₃⁻), are widely used to assess the distinction between waters controlled by water-rock interaction (i.e. weathering, leaching, and dissolution), evaporation and precipitation ^[36]. The plot is used to interpret the main factor(s) that influence groundwater geochemistry. From Figure 5a and Figure 5b, it was observed that the major factor that influences groundwater is the rock weathering process. The result obtained is in line with previous research conducted by ^[5] which stated that groundwater within the study is

influenced by rock water interaction.

The reconstructed Diamond field plot was used to classify groundwater within the study area (Figure 6a and 6b). Its classification is based on reaction within the aquifer system. Results obtained from the model revealed that groundwater collected from ARG and EAG fell within high $Ca + Mg + SO_4 + Cl$ hydrogeochemical facies as shown in Figure 6a and 6b. The previous study within the study area revealed that groundwater was classified as moderately hard ^[2], the presence of Ca and Mg ions, is the primary cause of hardness in groundwater within the study area. On general note water with high Ca+Mg is said to be hard.



Figure 5a. Gibbs Plot of groundwater collected from ARG axis of the study area.



Figure 5b. Gibbs Plot of groundwater collected from EAG axis of the study area.



Figure 6a. Classification of Hydrogeochemical Facies reconstructed Diamond field of Piper by ^[37] of groundwater from ARG axis of the study area.



Figure 6b. Classification of Hydrogeochemical Facies reconstructed Diamond field of Piper by ^[37] of groundwater from EAG Axis of the study area

For a better understanding of the exchange of ions $Ca^{2+}/(HCO_3^- + SO_4^{2-})$ was plotted against Na⁺/Cl⁻. Figures 7a and 7b showed that sampling points were categorized under natural state, results from Figure 7a and 7b revealed that natural salt dissolution such as carbonates rock, and silicate is the main processes controlling groundwater chemistry within the study area, this is in line with previous studies by ^[2].

^[1] pointed out that TDS and TH are two major important parameters reflecting the quality of groundwater In this study. The value of TH within the Asu River Group ranges from 7 to 124 mg/L with a mean value of 62 mg/L. The results obtained indicate that groundwater was categorized as soft fresh category, this could be attributed to low concentration of Ca and Mg ions found in groundwater samples as shown in Table 1 and Figure 8a. This is in line with previous research carried out by ^[2]. The value of groundwater within the EAG of the study area ranges from 4 to 142 mg/L with a mean value of 91 mg/L, findings revealed that groundwater fell within soft freshwater category as shown in Figure 8b.



Na⁺/Cl⁻ (meq/L)

Figure 7a. Showing the effect of cation exchange, reverse cation exchange, natural state, carbonate rock dissolution and silicate hydrolysis on groundwater composition within ARG



Figure 7b. Showing the effect of cation exchange, reverse cation exchange, natural state, carbonate rock dissolution and silicate Hydrolysis on groundwater composition within EAG.



Figure 8a. Plot of TDS versus TH for groundwater samples collected from the ARG that is Albian in age.



Figure 8b. Plot of TDS versus TH for groundwater samples collected from the EAG that is of Turonian in age.

4. Conclusions

The present study was to evaluate the possible difference between factors that influences the hydrochemistry of groundwater between the ARG and EAG of the sedimentary basin of Nigeria. Hydrochemical data of groundwater samples were collected from the aquifer within the study area. From studies carried, it was observed that sampling points close to mine (MA/20, 21, 22, 23, and 24) had low pH values indicating that groundwater around those mines area was considered acidic. Results from model use in evaluating groundwater revealed that End-member plots suggested that 96% of groundwater is influenced by carbonate weathering, 4% fell within silicate weathering. The diamond field plot suggested that groundwater was categorized to be high Ca+ Mg +SO₄+Cl hydrogeochemical facies. Gibbs's plots revealed that the major ion composition of the groundwater of the study area is influenced by the composition of the contiguous lithology and reflects rock dominance in its composition. Plots of TDS against TH reveals that groundwater within the study area is considered fresh. The aquifer material/mineralogy together with anthropogenic activities with geogenic factors played a major role in controlling groundwater quality within the two geological groups. Conclusively, it was observed that there were no major differences between factors that influence groundwater within the two geological groups, This could be attributed to the fact that the ARG and EAG of the study area lie within the same sedimentary basin of the southern Benue Trough, but different in age formation.

Conflict of Interest

The authors dare no conflicting interests.

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