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# Comparative analysis of lithium enrichment mechanisms in aquifers in the Benue Trough

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## Abstract

This study investigates the extractability of lithium for energy use from groundwater sources in the Awe part of the Middle Benue Trough. Field measurements of electrical conductivity (EC), total dissolved solids (TDS), temperature, and pH were conducted using a portable meter. Lithium concentrations in 53 groundwater sources, including 17 well samples, 31 borehole samples, and 5 springs were sampled and analysed using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Oxygen isotopes ($\delta^{18}O$) were analysed using$CO_2$ equilibration, and hydrogen isotopes ($\delta^{2}H$) were analysed by thermochemical reduction to characterize the aquifers.The results indicate that three well water samples (A18, A19, and A38a) have lithium concentrations within seawater values (100-200 µg/L). Similarly, three borehole samples (A6, A15, and A38b) fall within this range, while three other borehole samples A17(794.6µg/L), A35a(1,826µg/L), and A37b(330.2µg/L) exhibit significantly higher concentrations respectively. Among the spring water samples, three samples have lithium concentrations below seawater values, while the remaining two samples A13(1,810µg/L) and A35b(1,968µg/L) show elevated levels.Isotopic analysis of $\delta^{2}H$ and $\delta^{18}O$ identified three distinct types of aquifers in the study area. Water from the deeper aquifer contains high concentrations of lithium, TDS, EC, and elevated temperatures. The lithium concentrations in the deeper saline aquifers A13(1810µg/L) and A35b(1968µg/L)suggest significant potential for extraction and use as an energy source.

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## 1. Introduction

Lithium is one of Earth's naturally occurring metals, and it is found throughout the environment [1]. Oil and gas resources which serve as the major source of income for many countries have gradually declined, with new energy sources, such as Li and hydrate sources, gradually replacing them [2]. Lithium occurs naturally in some ground and surface water used for drinking [3]. It is very important to study the development and utilization of new energy sources, such as Li [2, 4]. Groundwater at great depth has both thermal energy and valuable elements, such as lithium, which is an indispensable strategic key metal that has been widely used in many new industrial fields, such as new energy, new materials, electronic information, and aerospace [5]. Due to the vigorous development of electric vehicles in recent years, the demand for lithium has also increased

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rapidly. The desire to shift from traditional energy sources and electric cars will increase the production of lithium dramatically up to 2 Mtons lithium equivalent carbonate per year by 2030 [6]. However, conventional hard-rock and Solar mining are facing environmental and social concerns. Therefore, alternative lithium resources may help meet the global demand for the next decades [7].

Lithium is widely used for energy storage (Li-ion rechargeable batteries, around 70% of global lithium consumption) in ceramics, glass and lubricating grease [8]. The lithium demand had increased from 37 ktons of lithium in 2016 to 52 ktons of lithium in 2018. Therefore, it is forecasted to exceed 0.38 Mtons of lithium by 2028 due to the increased need for rechargeable Li-ion batteries for electromobility [9]. Seeking more lithium mineral resources is an urgent goal for many countries around the world and Africa is not left out in this race. In addition to lithium resources of the rock, Salt Lake, and ground brine types, lithium resources in groundwater have received extensive attention in recent years [10, 11]. The lithium concentration in some groundwater can reach industrial grade and has good production prospects, such as that in some groundwater in Tibet (China) and Europe [2].

Groundwater in sedimentary basins has been widely recognized for carrying appreciable amounts of metals (hundreds to thousands of mg/L) in their dissolved load [12]. The potential "ore-forming solutions "may also be considered "liquid ores" [13]. From the perspective of increasing lithium demand, groundwater has recently attracted considerable attention for extracting lithium as a by-product of geothermal energy. Deep saline groundwater in sedimentary basins could also be of interest but has not been studied in detail. Yet, sedimentary formation waters are usually produced in large volumes in oil and gas fields, low-enthalpy geothermal fields and CCUS (carbon capture, utilization and storage) operations in saline reservoirs [14, 15]. Lithium concentrations in these waters have been widely documented. However, a global analysis of the potential resources of lithium is still lacking [7].

Mahmudiono *et al.* [16] concluded that the highest water Li content was attributed to Mexico (2,209.05 μg/L), Bolivia (1,444.05 μg/L), Iraq (1,350 μg/L), and Argentina (516.39 μg/L). At the same time, the lowest water Li content was associated with Morocco (1.20 μg/L), Spain (0.46 μg/L), and India (0.13 μg/L). Production of Li from deep brines in continental sedimentary basins is the most common and cost-effective source of Li. Southern Manitoba has a complex groundwater aquifer system, with salinities ranging from brines in the deeper aquifers to freshwater in the shallower and eastern aquifers. Brines are accumulations of saline groundwater that occur in continental sedimentary basins and can be a common source of dissolved trace metals, including Li. Metal extraction from these deep brines through evaporitic methods is currently the most common and economical way of extracting Li, Refs.[17,18]. This study aimed to determine the concentrations of Li and types of aquifers in the groundwater using Oxygen isotopes ($\delta^{18}O$) and hydrogen isotopes ($\delta^{2}H$) in Awe, part of Middle Benue Trough, Nigeria.

### *1.1. Geological setting of the study area*

The study area is a sedimentary environment which is defined by longitudes 9° 0′ 0′′ - 9° 20′ 0′′ E and latitudes 8° 0′ 0′′ - 8° 30′ 0′′ N, part of the Middle Benue Trough (Figure 1). Stratigraphy of the Cretaceous sediment fill of the Middle Benue Trough can be divided into six (6) depositional units. A geological map of the study area (Figure 2) revealed five formations which include the Asu River Group, Awe-Keana, Ezeaku, Agwu Formations and the newer basalt [19]. The mineralization of the Asu River Group is quartz, feldspar, hematite, calcite, and copper [20]. The Awe Formation lithostratigraphically consist of flaggy, whitish, medium to coarse-grained and sometimes calcareous sandstones on average about 30 cm in thickness and interbedded with carbonaceous shales or clays from which brines issue copiously [21]. Lithostratigraphically, the Keana formation is heavily current bedded, fine to very coarse, sometimes conglomeritic, at times indurated, gritty and arkosic [22]. The oldest rock in the study area is the Asu River Group and the basalt is the youngest rock in the study area [23]. The mineral contents of the basaltic rocks are plagioclase, pyroxene, olivine, iron ore and analcite. Saline water in the artesian borehole and the two hot springs found in the study area are associated with the Asu River Group Formation.

## 2. Materials and methods

Fifty-three groundwater samples were collected (17 well samples, 31 borehole samples and 5 spring samples) using 250ml plastic bottles which were previously soaked in acidified water and washed. The sample containers were rinsed at each sampling point with the sampled water before sampling. One sample was collected at every sampling point and acidified with two (2) drops of concentrated hydrochloric acid for homogenization and prevention of absorption/adsorption of Li to the walls of the plastic container. At every sampling point, coordinates were taken using the Geographical Positioning System (GPS), GARMIN model. The water's electrical conductivity (EC $\mu$S/cm), Total Dissolved Solids (TDS mg/l), temperatures and pH were directly measured using a portable meter in the field, The water samples were transferred into 60mls plastic bottles and sent to ACME-Laboratories in Canada where Inductive Coupled Plasma Mass Spectrophotometer (ICPMS) was used for the analysis. Oxygen isotopes ($\delta^{18}O$) in water samples were analyzed via $CO_2$ equilibration, and hydrogen isotopes ($\delta^{2}H$) in water samples were analyzed by thermochemical reduction method.

## 3. Results

The results of temperature, pH, TDS, EC and lithium concentration are presented in Table 1. From Table 1, temperature ranges from 23°C (A22b, A23, and A44) to 46°C (A13). The pH ranges from 5.05 (A34a) to 7.77 (A29). Total dissolve solid values ranges from 10 mg/L (A34a, A34c) to >10000 mg/L (A13, A35a, A35b) while the EC ranges from 1.3 μg/L (A34a) to 20,000 μg/L (A13, A35a, A35b)

Table 1. Concentrations of Li ($\mu$g/L), TDS, EC, pH, and temperatures of groundwater of Awe and environs.

| Sample ID | Locations | Sources | X | Y | Temp | pH | TDS | EC | Li ($\mu$g/L) |
|---|---|---|---|---|---|---|---|---|---|
| A18 | Azara (AngwaWuje) I | Well | 9°14′ 9.5′′ | 8° 21′ 49.6′′ | 29 | 6.97 | 582 | 1164 | 106.1 |
| A19 | Azara (AngwaWuje) II | Well | 9° 14′ 45.6′′ | 8°21′ 45.3′′ | 31 | 6.81 | 553 | 1106 | 173.1 |
| A22a | Arugwagu I | Well | 9°12′27.6′′ | 8°21′ 3.7′′ | 26 | 7.45 | 503 | 1011 | 28.9 |
| A22b | Arugwagu II | Well | 9°12′27.2′′ | 8°21′ 2.8′′ | 23 | 6.69 | 394 | 770 | 28.6 |
| A24 | AgwanEggon I | Well | 9°8′34.3′′ | 8°6′5.0′′ | 32 | 6.96 | 226 | 465 | 6.7 |
| A25 | AgwanEggon II | Well | 9°8′30.4′′ | 8°6′7.5.′′ | 30 | 7.27 | 523 | 1044 | 18.9 |
| A26 | AgwanEggon III | Well | 9°8′38.8′′ | 8°5′3.5′′ | 30 | 7.28 | 360 | 730 | 84.9 |
| A27 | Angwan Mission | Well | 9°8′11.2′′ | 8°6′10.6′′ | 31 | 5.9 | 124 | 249 | 12.1 |
| A29 | Tunga Sabo II | Well | 9°19′25.5′′ | 7°59′55.5′′ | 29 | 7.77 | 1082 | 2211 | 52.3 |
| A30a | Tsohon Tunga I | Well | 9°18′54.5′′ | 8°3′42.9′′ | 30 | 7.72 | 678 | 1332 | 97.1 |
| A31a | Gidin Kade I | Well | 9°16′49.6′′ | 8°6′17.6′′ | 30 | 6.5 | 285 | 567 | 64.5 |
| A32b | Keffi Moyi II | Well | 9°16′0.3′′ | 8°5′20.9′′ | 31 | 7.09 | 265 | 518 | 15.7 |
| A33b | Baure II | Well | 9°12′49.5′′ | 8°7′31.7′′ | 31 | 5.35 | 37 | 76 | 1.3 |
| A34b | Kekura II | Well | 9°10′42.1′′ | 8°6′49.5′′ | 33 | 5.16 | 12 | 24 | 1.3 |
| A36a | Anuku I | Well | 9°5′24.3′′ | 8°15′30′′ | 29 | 6.36 | 92 | 184 | 6 |
| A38a | Kanje I | Well | 9°5′24.8′′ | 8°13′49.5′′ | 32 | 7.1 | 710 | 1414 | 130.8 |
| A46c | Jangwa Town | Well | 9°5′59.9′′ | 8°26′04.0′′ | 26 | 6.15 | 93 | 186 | 4.8 |
| A5 | Shirka (Angwa Zaki) | Borehole | 9°6′22.9′′ | 8°19′27.8′′ | 30 | 6.68 | 237 | 475 | 84 |
| A6 | Shirka (Angwa MB) | Borehole | 9°6′21.7′′ | 8°19′37.8′′ | 30 | 6.32 | 183 | 364 | 100.9 |
| A7 | Shirka (Angwa Teacher) | Borehole | 9°6′21.4′′ | 8°19′42.6′′ | 30 | 6.74 | 222 | 447 | 82.1 |
| A9 | Gidan Adudu I | Borehole | 9°9′15.4′′ | 8°19′15.7′′ | 30 | 6.58 | 365 | 729 | 38.2 |
| A10a | WambaiUkpo I | Borehole | 9°10′44.2′′ | 8°18′24.5′′ | 31 | 6.42 | 355 | 710 | 62.9 |
| A10b | WambaiUkpo II | Borehole | 9°10′46′′ | 8°18′25.9′′ | 30 | 6.76 | 367 | 737 | 62.4 |
| A11 | Ingbien | Borehole | 9°12′00.6′′ | 8°19′18.8′′ | 30 | 7.2 | 302 | 606 | 33.7 |
| A14 | Akiri town | Borehole | 9°19′45.7′′ | 8°23′4.4′′ | 31 | 6.13 | 105 | 223 | 11.5 |
| A15 | Wuse town | Borehole | 9°18′35.4′′ | 8°22′15.2′′ | 31 | 6.82 | 429 | 858 | 168.7 |
| A16a | Azara (Rimi Sabo) I | Borehole | 9°14′ 55.8′′ | 8°21′45.1′′ | 31 | 6.32 | 633 | 1266 | 72.2 |
| A16b | Azara (Rimi Sabo) II | Borehole | 9°14′ 54.4′′ | 8°21′43.6′′ | 30 | 6.47 | 540 | 1077 | 11.2 |
| A17 | Azara (Gidin Rimi) | Borehole | 9°14′ 58.3′′ | 8°21′48.9′′ | 26 | 6.87 | 1723 | 3420 | 794.6 |
| A20 | Azara (Motor Park) | Borehole | 9°14′57.6′′ | 8°21′37.9′′ | 31 | 6.6 | 287 | 573 | 70.5 |
| A23 | Sambegh | Borehole | 9°9′46.9′′ | 8°21′ 41.9′′ | 23 | 7 | 210 | 422 | 6.8 |
| A28 | Tunga Sabo I | Borehole | 9°19′23.4′′ | 8°0′0.1′′ | 29.5 | 7.04 | 829 | 1665 | 35.8 |
| A30b | TsohonTunga II | Borehole | 9°18′54.5′′ | 8°3′42.9′′ | 29.5 | 7.29 | 329 | 670 | 56.8 |
| A31b | GidinKade II | Borehole | 9°16′49.6′′ | 8°6′17.6′′ | 30 | 7.07 | 270 | 542 | 21.9 |
| A32a | KeffiMoyi I | Borehole | 9°16′8.3′′ | 8°5′21.7′′ | 31 | 6.6 | 212 | 426 | 35.7 |
| A33a | Baure I | Borehole | 9°12′21.2′′ | 8°7′27.9′′ | 32.5 | 5.2 | 12 | 24 | 1.8 |
| A34c | Kekura III | Borehole | 9°10′49.7′′ | 8°6′48.6′′ | 34 | 5.7 | 10 | 20 | 1.4 |
| A35a | Tsohongari Awe I | Borehole | 9°7′46.1′′ | 8°6′2.2′′ | 40 | 6.28 | >10000 | >20000 | 1826 |
| A37a | Abuni I | Borehole | 9°2′47.6′′ | 8°11′23.12′′ | 30 | 6.83 | 412 | 826 | 72.1 |
| A37b | Abuni II | Borehole | 9°2′49.1′′ | 8°11′26.1′′ | 30 | 6.7 | 1851 | 3077 | 330.2 |
| A38b | Kanje II | Borehole | 9°5′24.8′′ | 8°13′49.5′′ | 31 | 6.83 | 1053 | 2110 | 194.6 |
| A39 | Undora | Borehole | 9°6′9′′ | 8°11′22.1′′ | 31 | 6.95 | 288 | 581 | 10.7 |
| A40 | Mahanga | Borehole | 9°7′18.8′′ | 8°9′2.7′′ | 30 | 7.06 | 310 | 624 | 24.6 |
| A41 | Awe police station | Borehole | 9°8′33.8′′ | 8°6′49.9′′ | 33 | 7.24 | 510 | 1018 | 75.3 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| A42 | Awe Kufar Ademola | Borehole | 9°8′45.7″ | 8°6′27.3″ | 30 | 7.06 | 310 | 624 | 4 |
| A47 | Human | Borehole | 9°7’39.1″ | 8°15’34.3″ | 30 | 7.5 | 289 | 576 | 51.5 |
| A48 | Iorbo | Borehole | 9°7′46.5″ | 8°15′49.4″ | 29 | 7.56 | 218 | 550 | 35 |
| A49 | Kpegher | Borehole | 9°9′37.6″ | 8°17’35.2″ | 29 | 7.74 | 205 | 412 | 28.7 |
| A13 | Akiri salt farm | Spring | 9°20′7.0″ | 8°22′52.0″ | 46 | 6.24 | >10000 | >20000 | 1810 |
| A34a | Kekura I | Spring | 9°10′30.1″ | 8°6′51.5″ | 33 | 5.05 | 10 | 21 | 3.2 |
| A35b | Tsohongari Awe II | Spring | 9°8′8.3″ | 8°5′3.8″ | 38 | 6.54 | >10000 | >20000 | 1968 |
| A36b | Anuku II | Spring | 9°5′18.7″ | 8°15′21.1″ | 29 | 5.56 | 17 | 36 | 5.4 |
| A44 | Gidan Soja | Spring | 9°14′41.6″ | 8°25′05.4″ | 23 | 6.78 | 19 | 38 | 4.2 |

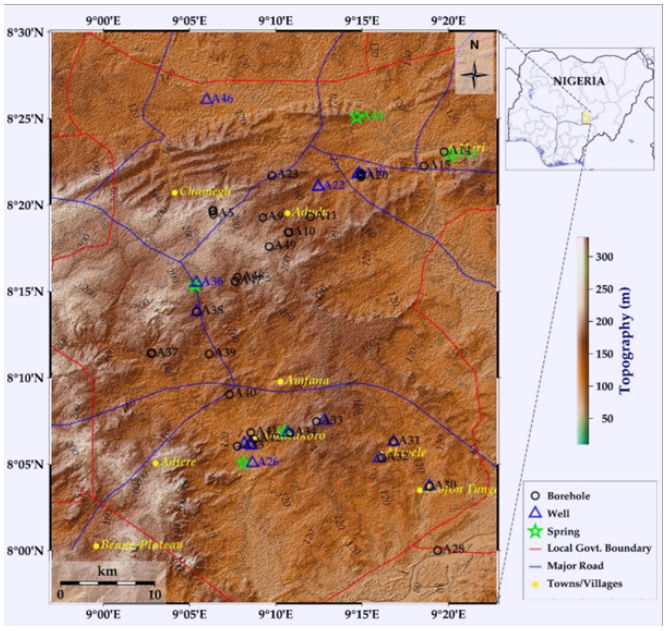


Figure 1. Location Map of Awe and environs.

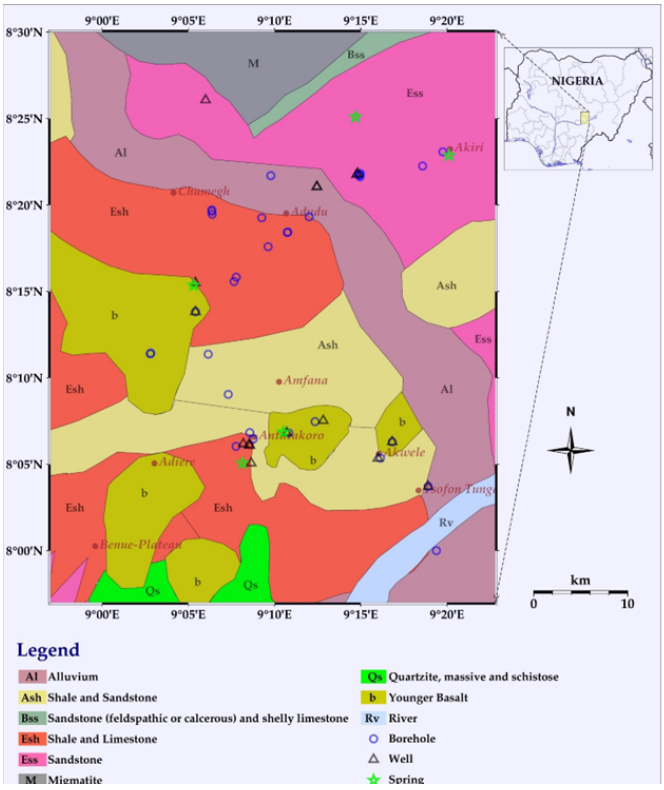


Figure 2. Geological Map of the Awe and environs.

The pH result is plotted on a distribution map and presented in Figure 3. The pH of sedimentary rocks and groundwater can significantly impact lithium concentration. According to Ref. [24] fluid-sediment interaction affects the lithium isotopic compositions in sediments and hydrothermal fluids, with temperature, pressure, and the water-to-rock ratio all being important factors. In a similar vein, Ref. [25] showed that lithium isotopes are susceptible to variations in aquifer conditions, with primary mineral weathering and secondary mineral precipitation rates being important determinants. A low pH can enhance the leaching of host rocks, thereby increasing the concentrations of elements in the waters.

The temperature distribution in Awe and environs is presented in Figure 4. Temperature is an important parameter that affects the thermodynamic properties of elements and their compounds and can promote the dissolution of elements in host rocks, thereby increasing the concentrations of elements in groundwater. Therefore, it could have a significant impact on the lithium concentrations in the study area. Temperature can be divided into geothermal water temperature and reservoir temperature [2].

The t of total dissolved solids (TDS)in Awe and environs is presented in Figure 5. Lyon and Welch Ref. [26] discovered that temperature and salt concentration improve the dissolving of lithium, pointing to a possible connection between total dissolved solids (TDS) and lithium occurrence. Sanjuan and Millot [27] suggested that basalt-seawater reactions—which are impacted by TDS—have a major part in the lithium cycle.

The electrical conductivity EC is presented in Figure 6. Lithium has been recognised as a major prospective resource found in groundwater from sedimentary basins [7]. This is especially important given the rising need for lithium brought on by the development of electric vehicles. The geologic occurrence of lithium ore in sedimentary rocks can be significantly impacted by the electrical conductivity of this groundwater, which is determined by elements including water content and lithium concentration [28]. The ts of Cannon [29], noted differing lithium concentrations in sediments, plants, and natural waterways in hydrologically closed and open basins. However, the examination of lithium in deep basalt groundwaters has also

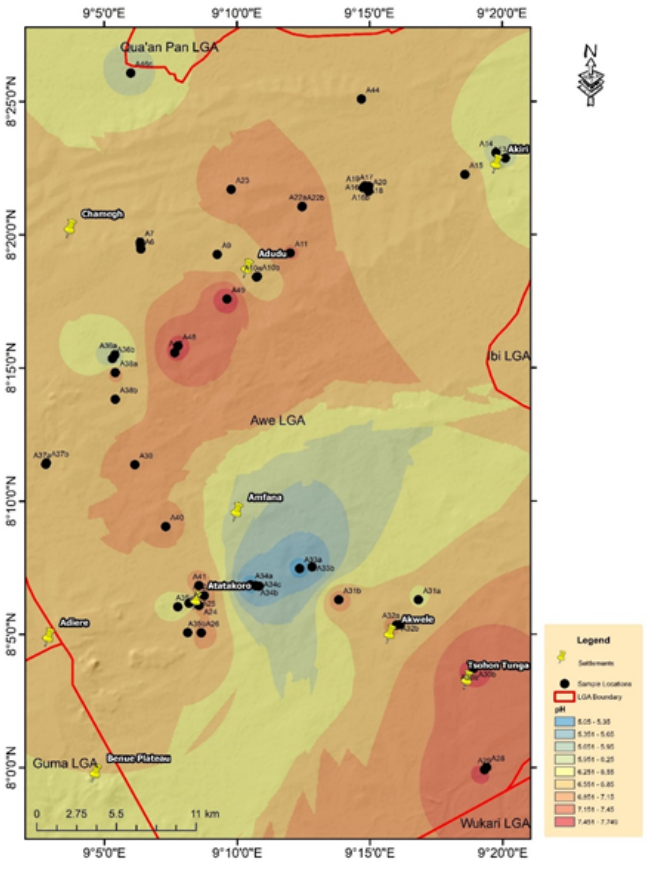


Figure 3. pH distribution map in Awe and environs.

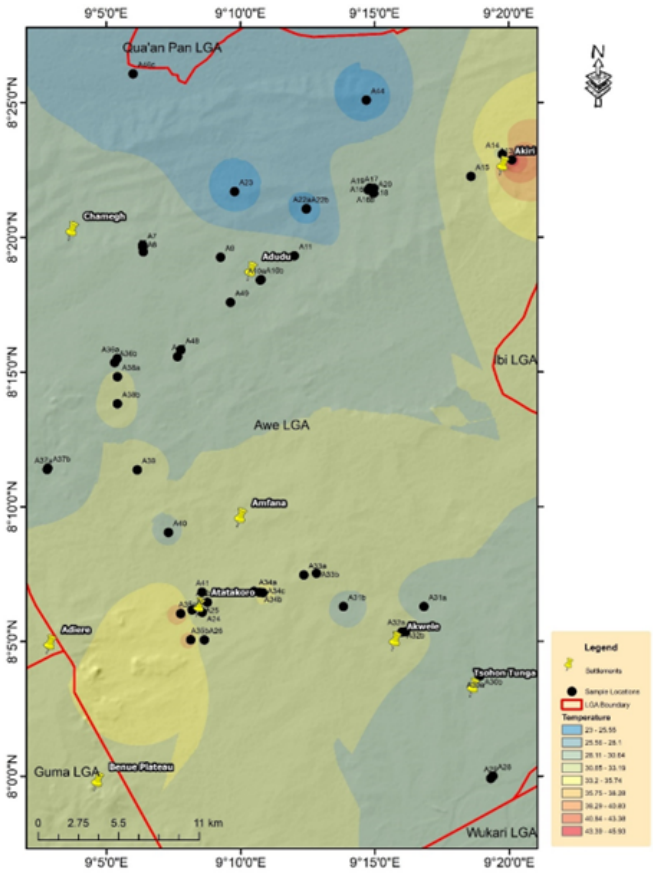


Figure 4. Temperature distribution map over Awe and environs.

brought attention to the necessity of taking silicate interference into account [30].

Lithium concentration map is presented in Figure 7. Lithium occurs in both shallow and deep groundwater and the presence of lithium is dependent on many circumstances. According to Ref. [31], the presence of silicate can have an impact on the concentration of lithium in deep groundwater. This effect can be lessened by using certain modifiers. Qi *et al.* [32] found that intrusion of saltwater affects the presence of lithium in both shallow and deep groundwater, with seawater intrusion affecting the latter. Lithium has the potential to be a substantial resource in groundwater from sedimentary basins, according to Ref. [7].

## 4. Discussion

The analysis of well water samples from the Awe – Keana Formation reveals significant variations in physicochemical parameters. Sample A34b, characterized by the lowest pH (5.13), total dissolved solids (TDS) (12 mg/L), electrical conductivity (EC) (24 $\mu$S/cm), and lithium concentration (1.3 $\mu$g/L), also recorded the highest temperature of 33 °C. These findings align with the observations of Ref. [2], indicating that low pH, TDS, and EC values, coupled with high temperatures.In contrast, sample A19 exhibited the highest lithium concentration (173.1 $\mu$g/L) but did not correlate with the highest pH, TDS, and EC values. Instead, it recorded a pH of 6.81, TDS of 553 mg/L, and EC of 1,106 $\mu$S/cm, with the second-highest temperature at 32 °C. This suggests a complex interplay between these parameters and lithium concentration. Sample A38a, also from the Awe – Keana Formation, shared characteristics with A34b but did not exhibit the same extreme values. Most well water samples analysed were classified as freshwater based on their TDS values, except for sample A29 from the Agwu Formation, which had TDS slightly exceeding 1,000 mg/L. Sample, A29, exhibited the highest values for pH (7.77), TDS (1,082 mg/L), and EC (2,211 $\mu$S/cm), but a relatively low lithium concentration (52.3 $\mu$g/L). The consistent relationship between TDS and EC across the samples indicates that higher TDS corresponds with higher EC values. However, variations in lithium concentration among samples with differing physicochemical parameters suggest that other geochemical processes might influence lithium distribution in these formations.

Lithium concentrations in well water samples reveal that only three samples (A18, A19, and A38a) from the ASU River Group of Azara and the Awe and Keana Formation of Kanje exhibit lithium concentrations (1,06.1, 1,73.1, and 130.8 $\mu$g/L, respectively) that fall within the minimum seawater values (100 $\mu$g/L or 1 ppm). All samples remain below the maximum seawater lithium value of 200 $\mu$g/L (2 ppm), a concentration that has been commercially extracted in some regions. The distri-

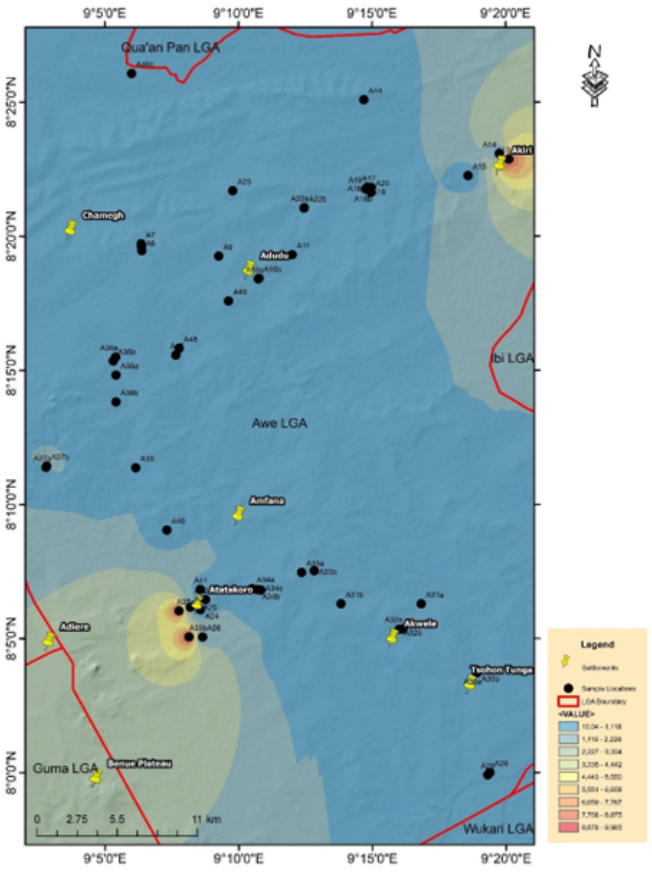


Figure 5. Total dissolved solid over Awe and environment.

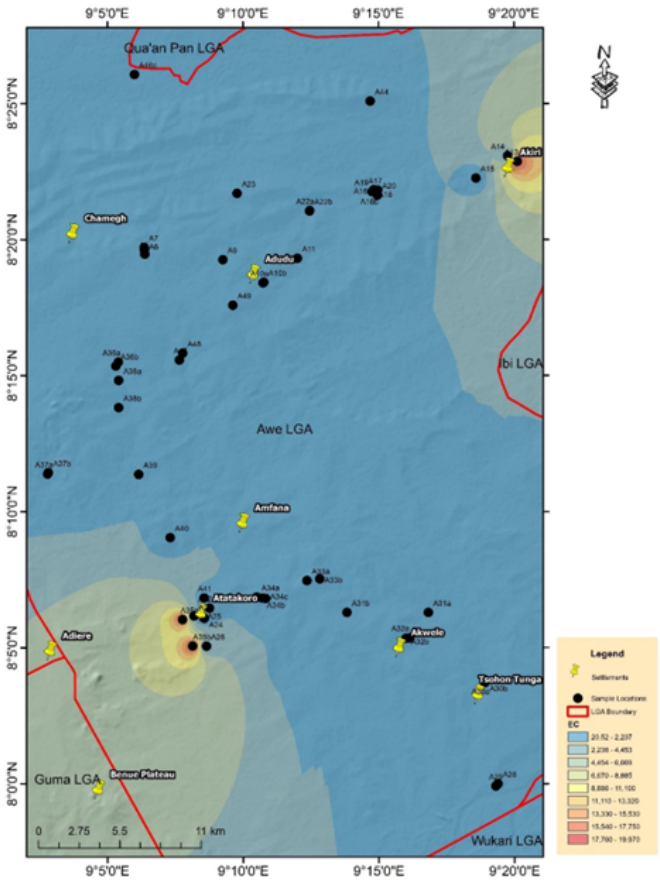


Figure 6. Electrical conductivity of Awe and environs.

butions of TDS, EC, and temperature appear to exert minimal influence on lithium distribution in these well water samples, possibly due to their relatively shallow depths, as suggested by Ref. [2].In borehole water samples, A33a and A34c exhibit high temperatures (32.2°C and 34 °C, respectively) but have the lowest pH (5.2 and 5.7), TDS (12 and 10 mg/L), EC (24 and 20 $\mu$S/cm), and lithium concentrations (1.8 and 1.4 µg/L). Conversely, three borehole water samples (A6, A15, and A38b) have lithium concentrations (100.9, 168.7, and 194.6 $\mu$g/L) that fall within the seawater minimum and maximum concentration range (100-200 $\mu$g/L). These samples also show thermal characteristics, with TDS values indicating that A6 and A15 are freshwater, while A38b slightly exceeds the freshwater threshold of 1,000 mg/L. Notably, three borehole samples, A17(794.6 $\mu$g/L), A35a(1,826 $\mu$g/L) and A37b(330.2 $\mu$g/L) exhibit lithium concentrations surpassing seawater maximum values. Sample A37b is sub-thermal, while samples A17 and A35a are thermal. These observations suggest that temperature, TDS, and EC have limited effects on lithium distribution in these samples.

Spring water samples A34a, A36b, and A44 show very low lithium concentrations (3.2, 5.4, and 4.2 $\mu$g/L), significantly below the minimum seawater values (100 $\mu$g/L). In contrast, the two hot springs A13(1,810 $\mu$g/L) and A35b (1,920 $\mu$g/L) exhibit high lithium concentrations, exceeding those reported in Bolivia, Iraq, and Argentina, Ref. [16]. According to Ref. [2], low pH, high temperature, TDS, and EC play crucial roles in lithium distribution in the hot springs (Akiri salt farm and Tsohongari Awe II), but not in the spring samples A34a, A36b, and A44.

Table 2. Comparison between groundwater with maximum and minimum values with those of other countries.

| Source | Minimum values ($\mu$g/L) | Maximum values($\mu$g/L) |
|---|---|---|
| Well water | 1.3 | 173.1 |
| Borehole water | 1.4 | 1,826.00 |
| Spring water | 3.2 | 1,968.00 |
| Mexico | | 2,209.05 |
| Bolivia | | 1,444.05 |
| Iraq | | 1,350.00 |
| Argentina | | 516.39 |
| Morocco | 1.2 | |
| Spain | 0.46 | |
| India | 0.13 | |

The pH value is a reliable indicator of water hardness, with pure water having a pH of 7. A pH below 7 is acidic, while a pH above 7 is alkaline. Surface water typically ranges from pH 6.5 to 8.5, and groundwater ranges from pH 6 to 8.5 [33]. Over 70% of groundwater in Awe and environs is slightly acidic, with the remaining percentage being slightly alkaline. More than 90% of the groundwater samples have pH values within acceptable

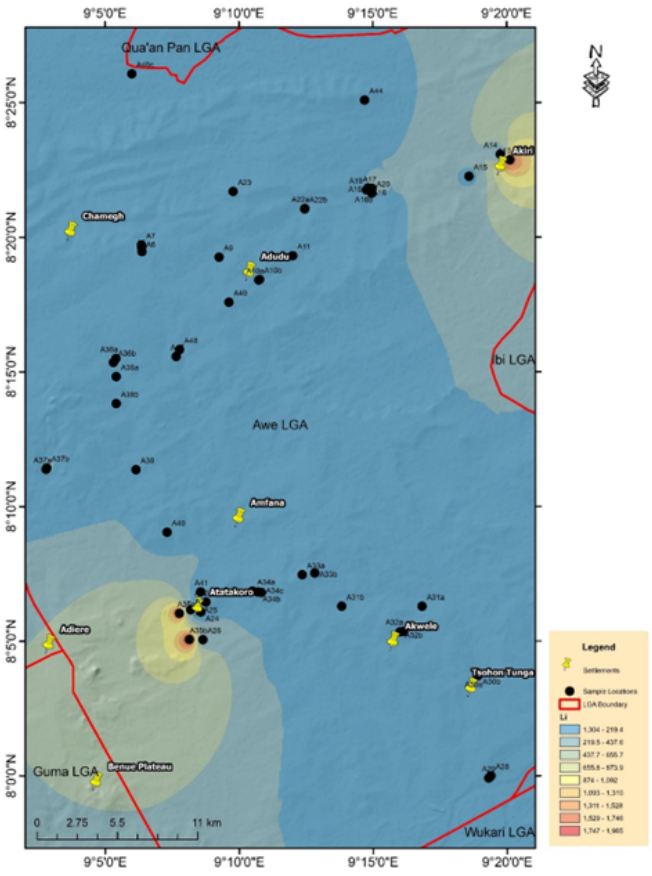


Figure 7. Lithium distribution over Awe and environs.

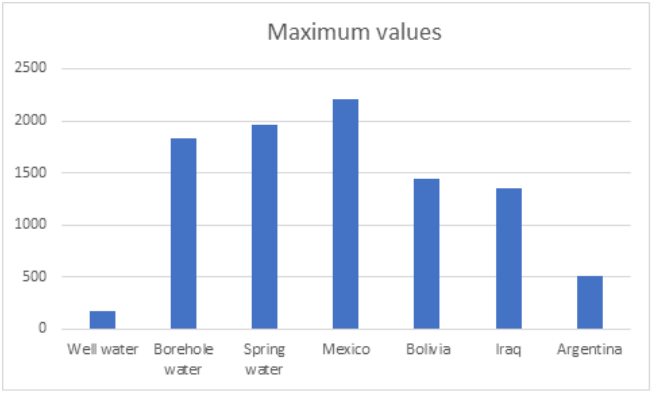


Figure 8. Comparison of maximum concentrations of Li($\mu$g/L) in groundwater of study area with those of other countries.

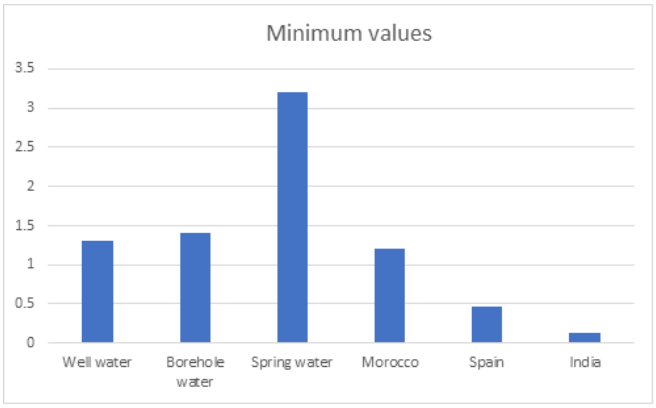


Figure 9. Comparison of minimum concentrations of Li($\mu$g/L) in groundwater of study area with those of other countries.

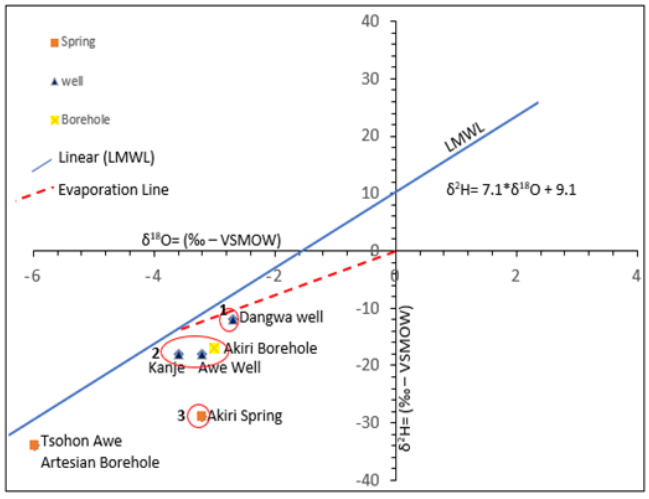


Figure 10. Plot of $\delta^2H$ versus $\delta^{18}O$ (‰).

drinking water limits.The United States Environmental Protection Agency (EPA) recommends treatment when TDS concentrations exceed 500 mg/L. TDS is considered a Secondary Drinking Water Standard, indicating it is not a health hazard [34]. Over 60% of the groundwater samples have TDS values below 500 mg/L, classifying them as fresh and suitable for drinking. Rusydi [35] classifies water with EC values between 500 and 3000 µS/cm as natural water, with only about 10% of the groundwater samples falling outside this range.Based on the classification by, Ref. [36], which defines water temperatures from 25 to 37 °C as warm, 38 to 50 °C as hot or hyperthermic, and above 50 °C as scalding, the groundwater in the study area is categorized as warm to hot. Lithium distribution is influenced by TDS, EC, and temperature, while pH appears to have no significant effect on lithium distribution.

### *4.1. Comparison of lithium in groundwater samples in the study area with those of other parts of the world*

The highest concentrations of lithium (Li) in water from the study area were observed in the artesian borehole in Tsohongarin Awe I (1,826 µg/L), spring water from Tsohongarin Awe II (1,868 µg/L), and the Akiri salt farm (1,920 µg/L). These concentrations exceed those found in water bodies from Bolivia, Iraq, and Argentina, and are second only to concentrations in Mexico (Table 2). The geological characteristics of the study area significantly influence the distribution of Lithium, with higher concentrations associated with the older formations

Table 3. $H^2$ and $O^{18}$ isotopes analyzed values of groundwater [38].

| ID No | Locations | Sources | X | Y | Z | $\delta^{18}O$ (‰)/vs VSMOW | $\delta^{2}H$ (‰)/vs VSMOW |
|---|---|---|---|---|---|---|---|
| I 13 a | Akiri salt farm | Spring | 9°20′7.0" | 8°22′52.0" | 116 | - 3.2 | - 29 |
| I 13b | Akiri town | Borehole | 9°19′45.7" | 8°23′4.4" | 114 | - 3.0 | - 17 |
| I 25 | AgwanEggon II | Well | 9°8'30.4" | 8°6'7.5" | 113 | - 2.7 | - 12 |
| I 35b | Tsohongari Awe II | Spring | 9°8'8.3″ | 8°5'3.8″ | 108 | - 5.98 | - 34 |
| I 38a | Kanje I | Well | 9°5'24.8″ | 8°13'49.5″ | 173 | - 3.2 | - 18 |
| I 46c | Jangwa Town | Well | 9°5'59.9″ | 8°26'04.0″ | 113 | - 3.6 | - 18 |

of the ASU River Group in the Middle Benue Trough.In contrast, the minimum concentration of Li (1.3 µg/L) was found in well water samples from Baure and Kekura. Wells, being shallower than boreholes and springs, generally exhibit lower Li concentrations due to their limited depth. The geology of the region, specifically the Awe – Keana Formations, also plays a role in the lower Li concentrations observed in these shallow wells. Despite these low concentrations, the Li levels in the groundwater of the study area are higher than those in countries with typically low Li concentrations in their water, such as Morocco, Spain, and India (Table 2 and Figures 8 and 9). Research by Ref. [37] indicates that average brine deposits (1.45 Mt Li) are significantly larger than average pegmatite deposits (0.11 Mt Li), with brine deposits, particularly those in the Atacama (Chile) and Uyuni (Bolivia), representing a much larger total lithium resource (21.6 Mt Li). Brine deposits have a greater capacity for large-scale, long-term production compared to pegmatite deposits. Notably, samples A13, A35a, and A35b from the present study contain Li concentrations higher than those typically found in both pegmatite and brine deposits, despite being classified as saline water (Table 1).

## 5. Classification of aquifers in the study area using $H^2$ and $O^{18}$ isotopes.

Isotopic analysis of hydrogen ($H^2$) and oxygen ($O^{18}$) revealed distinct patterns among these aquifers. A well water sample from Jangwa was identified within the shallow aquifer. Two well water samples from Kanje I and AgwanEggon II in Awe and one borehole sample were identified within the intermediate aquifer. This intermediate aquifer is characterized by mixing recharge water from the shallow aquifer and discharge water from the deeper aquifer. Additionally, two water samples, a hot spring from Akiri and an artesian borehole from Tsohongari Awe, were identified within the deeper aquifer [38]. The shallow hand-dug wells (Kanje I and AgwanEggon II in Awe) and the Akiri borehole samples were plotted close to the local meteoric water line (LMWL) on the isotopic plot, indicating recent recharge and minimal evaporation effects. In contrast, the Jangwa well water sample plotted closer to the evaporation line, suggesting significant evaporative enrichment (Table 3). The spring water samples, however, plotted far from both the LMWL and the evaporation line, indicating a different hydrological history.Compared to other groundwater samples, the hot spring samples (I13a and I35b) are relatively enriched in stable isotopes and deviate slightly from the LMWL (Figure 10). These samples are characterized by high levels of total dissolved solids (TDS > 10,000 mg/L) and electrical conductivity (EC > 20,000 $\mu$S/cm), reflecting the influence of deep geological processes. The isotopic data show a trend of increasing depletion with depth, consistent with the deeper aquifer sources [38]. These observations underscore the complexity of the hydrogeological system in the study area, highlighting the influence of aquifer depth and mixing processes on the isotopic composition and physicochemical properties of the groundwater.Three aquifers were identified in the study area: shallow, intermediate, and deeper aquifers.

## 6. Conclusion

The isotopic evidence, combined with the high total dissolved solids (TDS) and electrical conductivity (EC) values observed in the deep aquifer samples, suggests that these waters have undergone significant geochemical evolution. Notably, the deep aquifer samples also exhibit the highest lithium concentrations (1,810 - 1,968 $\mu$g/L), indicating a potential for lithium extraction. The multi-tracer investigation of groundwater chemistry of part of the Middle Benue Trough was carried out using $^2$H and $^{18}$O isotopes. The groundwater of the trough was found to be stored in three different aquifers (shallow, intermediate, and deeper) based on $^2$H and $^{18}$O results. There is a dearth of data on Li content in groundwater sources in Nigeria. The study is noble because the results and the outcome of the research will serve as available data on the concentration and distribution of lithium in groundwater in Nigeria and Africa in general. The isotopic analysis of hydrogen ($\delta^2$H) and oxygen ($\delta^{18}$O) in groundwater samples from the study area reveals distinct characteristics of three types of aquifers: shallow, intermediate, and deep. The shallow aquifer, represented by the Jangwa well sample, shows significant evaporation effects, as indicated by its position close to the evaporation line. In contrast, the intermediate aquifer, consisting of samples from Kanje I and AgwanEggon II wells, and the Akiri borehole, aligns closely with the Local Meteoric Water Line (LMWL), suggesting minimal evaporation and a mixture of recharge and discharge waters. The deep aquifer samples, including the hot spring from Akiri and the artesian borehole from Tsohongari Awe, show the greatest depletion in isotopic composition and are enriched in stable

isotopes compared to other groundwater samples. The study demonstrates that the distribution of lithium in the groundwater of the study area is influenced by both geological formations and aquifer depth. The deeper aquifers, particularly those associated with the ASU River Group, show the highest potential for lithium extraction due to their higher lithium concentrations, TDS, and EC values. Understanding the hydrogeochemical processes influencing lithium distribution is crucial for developing sustainable extraction strategies in Awe and environs.

## Data availability

Data used in this study will be made available based on request.

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