Demystifying Heavy Metals and Physicochemical Characteristics of Groundwater in a Volcano-Tectonic Region of Middle Awash, Ethiopia, for Multipurpose Use

Yosef Abebe 1,2,*, Taye Alemayehu 2,3, Behailu Birhanu 2,4, Tena Alamirew 2,3 and Esayas Alemayehu 1,5

1 Africa Center of Excellence for Water Management, Water Science and Technology, Addis Ababa University, Addis Ababa P.O. Box 1176, Ethiopia
2 Water and Land Resource Center, Addis Ababa University, Addis Ababa P.O. Box 1176, Ethiopia
3 Ethiopian Institute of Water Resources, Addis Ababa University, Addis Ababa P.O. Box 1176, Ethiopia
4 School of Earth Sciences, Addis Ababa University, Addis Ababa P.O. Box 1176, Ethiopia
5 Faculty of Civil and Environmental Engineering, Jimma Institute of Technology, Jimma University, Jimma P.O. Box 378, Ethiopia
* Correspondence: yosef.abebe@aau.edu.et

Abstract: This study investigates the concentrations of physicochemical and heavy metal contaminants in the groundwater of the Middle Awash Basin, Ethiopia, to inform targeted water management strategies. A total of 32 groundwater samples were collected from 16 stations via piezometers and boreholes at the end of both the dry (June 2021) and wet (October 2021) seasons. Utilizing Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Atomic Absorption Spectroscopy (AAS), and in situ metering, 22 physicochemical and 24 heavy metal parameters were analyzed. The data revealed significant levels of contamination; notably, sample GW11 had extraordinarily high concentrations of total dissolved solids (10,826 mg/L), strontium (908 μg/L), molybdenum (802.4 μg/L), zinc (6060 μg/L), and electrical conductivity (15,645 μS/cm), while GW12 exhibited elevated levels of aluminum (2615 μg/L), zinc (4446 μg/L), and arsenic (117.2 μg/L). Contaminants such as arsenic, vanadium, gallium, lithium, rubidium, chromium, manganese, copper, and zinc were found enriched in groundwater near Lake Beseka, majorly influenced by geogenic activities, volcanic ash, and weathering of rocks. The sampled waters might be affected by human activities including agricultural runoff from sugarcane plantations, sugar factories wastewaters, and agro-industry activities (decade’s activities). Over half of the groundwater sources were unsuitable for drinking, posing significant health risks to local communities that rely heavily on these sources due to limited access to clean surface water. The findings emphasize the urgent need for comprehensive groundwater management and remediation plans in the Middle Awash region to ensure safe and sustainable water use, particularly addressing the variation in contamination levels influenced by Lake Beseka. These measures are critical to protect public health and support local development in the face of ongoing environmental and anthropogenic pressures.

Keywords: Awash Basin; groundwater; heavy metals; Lake Beseka; water quality

1. Introduction

Groundwater is the world’s main resource for drinking, irrigation, and industrial uses [1]. It is one of the most valuable natural resources both in developed and developing countries including Ethiopia. In fact, in arid and semiarid areas, groundwater is a vital resource for domestic, industrial, and irrigation uses [2,3]. In Ethiopia, in most cities and towns including Addis Ababa, groundwater serves as the major and/or alternative to surface water supplies [4]. For instance, in the Middle and Lower Awash and in some parts of the Oromia and Afar regions, where there is not enough potable surface water for the population’s daily needs, notably drinking, groundwater (GW) is the main water supply...
source. According to several studies, the previously projected groundwater potential was understated, coming in at nearly 2.6 BMC. However, recent GW researchers estimate/show that it may be greater than the previous numbers and predict roughly 12 to 30 BMC, or even more if we evaluate all of the lowland aquifers [5,6].

The GW chemistry of the study area is essential for providing insight into water types for the groundwater data scarce basins, geochemical processes that might be taking place, and characteristics based on hydro-geochemical benchmarks. Therefore, by combining geochemical and groundwater chemistry, it may be possible to identify trends and environmental challenges in the study, which could improve our understanding of the groundwater resources water quality, suitability, and contamination. The Awash Basin, partly located in the Main Ethiopian Rift (MER), is a densely populated and industrialized area where numerous enterprises rely on groundwater for their operations (WLRC, WA, report, 2023). Therefore, the majority of human development initiatives in the basin will continue to depend heavily on the quantity and quality of groundwater.

In the Middle Awash Basin and the country at large, the water quality of most groundwater sources is inadequately monitored and insufficiently regulated. Consequently, areas within the upstream Awash Basin, particularly around Modjo, Bishoftu, Gelan, and Addis Ababa, are highly susceptible to unregulated abstraction and pollution of groundwater [7]. Groundwater is susceptible to pollution as well. Overuse of pesticides and fertilizers from intensive farming in the basin (both in upstream and downstream of Koka dam) can leak into aquifers, and an industry with negligent regulations can cause a discharge of hazardous untreated chemicals to seep through the soil. Research indicates that these groundwater sources are at risk of contamination from industrial waste, sewage, and solid waste leachates due to the prevalent discharge of poorly treated wastewater by industries [8]. Moreover, factors such as excessive groundwater abstraction, the overuse of agricultural chemicals, mismanagement of human waste, and rapid population growth further exacerbate GW contamination [9].

The Ministry of Water Resources [6] report identifies key groundwater quality issues in Ethiopia as predominantly natural, notably high fluoride concentrations in certain areas and iodine deficiencies in others, alongside general GW salinity. Studies suggest that the sources of some pollutant chemical concentrations in ground water may vary, but research conducted by the MoWR suggests that the analysis of groundwater contamination should concentrate on soil characteristics, hydrology, and geological conditions (confined or unconfined). For example, certain substances, like Fe, K, Cl, and SO₄, are well-known in the concentrations found in the Awassa-Yirgachfie, Butajera-Assela, Afderra & Dallol, and Ogaden basin, respectively [9]. These naturally occurring elements, particularly fluoride and arsenic, when concentrated in drinking water, can detrimentally impact human health, causing widespread suffering globally [10]. However, attributing these GW quality issues solely to natural causes may oversimplify the complexity of the underlying geology and topography, especially in regions like the Rift Valley. Pollution sources such as heavy metals, pesticides, and pharmaceutical wastes can permanently degrade GW, making its purification significantly more difficult. Therefore, preventing GW pollution is essential and should be prioritized to safeguard this vital resource for future generations. Groundwater management requires the utmost attention and proactive measures due to the global challenges posed by rapid population growth, urbanization, climate change, and various human activities [11–14].

The expanding urban-industrial centers in the Awash Basin, including Addis Ababa, Modjo, Bishoftu, and Addama, are taking water from the Awash River and groundwater. Accordingly, the groundwater withdrawals are greatly accelerating and not well governed. Not only this, but also the GW contamination has become a significant issue and cause for concern in recent years [15]. There are many different types of sources that might contaminate groundwater. For example, the main causes of groundwater contamination in developed nations include the use of pesticides and fertilizers, the discharge of hazardous microbes and chemical pollutants in urban areas, and domestic and industrial wastes [16].
The study area is mainly known by sugar farm estate, because the Wonji, Methara, and Kessum sugar factories are situated in this basin. Unregulated sugar mill effluent contains a considerable amount of potentially harmful substances including soluble salts and heavy metals such as Fe, Cu, Zn, Mn, and Pb [17]. Perhaps, the long-term use of this sugar mill effluent for irrigation must be discouraged, as this improper wastewater usage results in the contamination of soils and water if released into water bodies [18].

Similar to this, unchecked human activities, industrial activities, and geological activities cause groundwater contamination in developing nations, including Ethiopia. It has been increasing and has less emphasis. For instance, the Lake Beseka expansion affects the surface and groundwater dynamics and soil properties of the region and the condition is specifically dangerous for the sustainability of Methara Sugar Estate, and Matahara town in particular, and the Awash Basin irrigation in general [19]. Protecting groundwater from diverse contamination sources necessitates an integrated approach, emphasizing the need for better data collection and a strategic framework for contamination prevention and management. In fact, once contaminated, groundwater presents a complex challenge for remediation, more so than surface water due to its relatively stable quality that does not fluctuate. Perhaps understanding and maintaining groundwater quality is crucial, particularly in regions experiencing significant pollution like the Awash Basin. However, comprehensive data on groundwater quality in Ethiopia are scarce, which complicates efforts to assess and manage this resource effectively [20].

Due to pollution in surface water and its shrinkage, unregulated groundwater abstraction, and contamination from both anthropogenic and geogenic sources, ensuring equitable access to safe and affordable drinking water in the Middle Awash Basin presents significant challenges, directly impacting the achievement of Sustainable Development Goal 6 (SDG6). Additionally, the goals of halving the proportion of untreated wastewater; eliminating the dumping, and minimizing the release of, hazardous chemicals, including heavy metals, into water bodies; and significantly increasing the recycling and safe reuse of water in Africa, as outlined in SDG 6.3, face substantial obstacles in regions like Ethiopia. Therefore, a comprehensive assessment of both groundwater and surface water quality in water-scarce areas such as the Middle Awash is essential to support sustainable development and maintain reliable water sources. The primary objective of this research is to evaluate the groundwater quality in the Middle Awash Basin, focusing on its suitability for both irrigation and drinking purposes. This study is critical due to the prevailing highly significant reliance on groundwater in regions where access to potable water is frequently unreliable. By analyzing a range of physicochemical and heavy metal parameters in boreholes and hand-dug wells, this research aims to provide a comprehensive assessment of groundwater quality. Both natural and anthropogenic causes of groundwater pollution were thoroughly analyzed. The findings are expected to inform the development of regulatory guidelines and risk reduction strategies that will ensure a reliable supply of clean drinking water.

2. Study Area

The Awash River Basin lies between 37°57’ E and 43°25’ E longitude, and between latitudes 7°53’ N and 12°00’ N (Figure 1). The Awash River is 1200 km long overall. It starts in Ethiopia’s central highlands at an elevation of 3000 m and passes through a number of locations before joining Lake Abe at a height of 250 m. The Awash River Basin, the basin where the study was undertaken, is divided into three sections: upper, middle, and lower. It is one of the most heavily utilized basins in the country, situated at a lower course of the most urbanized and industrialized Upper Awash. Middle Awash is known for having both large- and small-scale irrigation, as well as agroindustry and sugar factories (Wonji, Methara, and Kesem Sugar factories). The study area’s elevation gradient covered a range of elevations, from high mountains approximately 4199 m to low points 532 m above sea level (Figure 1). The Middle Awash Basin is primarily known for being water-scarce and occasionally flood-prone. There are tributary rivers, lakes, hot springs, and swamps in the Middle Awash Basin. One of the basin’s natural lakes, for example, is Lake Beseka,
Ethiopia’s Lake, which was a saline lake located in the East African Rift Valley (Middle Awash). It has no natural exits and has grown significantly since the 1960s as a result of subsurface flows bringing excess irrigation water into the lake from subterranean flows, hot-spring inflow, and GW discharge.

Figure 1. The study area map. N.B: GW1–GW7 are boreholes near Lake Beseka; GW8–GW13 are piezometers located in the Middle Awash; GW14 and GW15 are boreholes located near Awash 7; and GW16 is a borehole (Hot-spring) located near the Awash Basin Main Office.

2.1. Geological Setting and Structures

Ethiopia is home to a wide variety of volcanic, sedimentary, and metamorphic rocks, as seen in Figure 2 below. According to studies, there are four distinct rock groups that can be distinguished based on their coverage and extent. Precambrian basement complex, Paleozoic and Mesozoic sedimentary rock, territory volcanic rocks, and quaternary sediments and volcanic rocks can all be shown with percentage compositions of 18%, 25%, 40%, and 17%, respectively. But their presence might also differ from basin to basin or from one place to another. For example, the largest group of volcanic rocks in the study area is the Trap Series, which formed in the early and middle Tertiary when cracks opened up. In the Rift Valley, the Pleo-Quaternary volcanics are mostly contained. The geology of the study area surrounding the lake comprises volcanic rocks, mainly recent to sub-recent basalts, ignimbrite, rhyolite, and tuff. The floor and edges of Lake Beseka are constituted by Pleistocene lacustrine sediments [21]. Most of the volcano-tectonic process-controlled lakes found in the Ethiopian Rift Valley are found in the part of the Ethiopian Rift System located to the south of the Afar Triangle, called the MER [22,23]. The study area’s topography is a reflection of the Middle Awash Valley’s recent geomorphic history, which saw the
formation of a vast alluvial plain from deposits of the Awash River [24]. Slope gradients are often very low, with most of them falling between 1% and 2% [24]. Volcanic rocks make up the parent materials of the alluvial deposits in the study area’s Rift Valley. These comprise rhyolite parent materials; alkaline olivine and dolerite-andesite basaltic magmas; carbonatite; volcanic ash; tuff; pumice; and granites, feldspars, and aluminosilicates of sodium and potassium [25,26].

This area’s geological makeup includes volcanic ash and a variety of rock types, such as sedimentary and igneous rocks, which significantly contribute to groundwater contamination. For example, in the Afar section of the Rift and much of the adjacent plateau areas, the dominant basaltic rocks rich in Fe and Mn are often interbedded with sediments [27]. This interplay of volcanic activity and rifting has led to the formation of the low-lying Afar Depression. Additionally, young (Quaternary) unconsolidated alluvial and lake sediments within the Rift zone can further influence water quality [20]. Thus, both natural conditions and complex geological processes must be considered to fully understand and address the challenges of groundwater quality in Ethiopia.

Figure 2. Simplified Geological Map of Ethiopia (Adopted from the Water Information and Knowledge Management Project [11]).

2.2. Climate and Hydrology

The basin covers a wide climatic zone from humid subtropical to arid and has a relatively long-running and dense meteorological and hydrological observation network.
Climate variability is one of the severe environmental changes of the twenty-first century [28,29]. Thus, parts of the water cycle are probably accelerating due to climate change because rising global temperatures accelerate global evaporation. On average, there may be greater precipitation due to increased evaporation. In actuality, there are differences in the global distribution of higher rates of precipitation and evaporation. Some countries, like Ethiopia, such as the Upper Awash (Upper Awash > Middle Awash > Lower Awash), may have precipitation that is heavier than usual. As a result of the complex topography, the intertropical convergent zone (ITCZ) and associated atmospheric circulation are important contributors to the Awash River Basin climate [30]. Studies also revealed that the annual temperatures in the basin showed a significant increase [31]. The elevated temperatures in the research region linked to climate change may result in modifications to precipitation and evaporation patterns. For this reason, the rain fall in the Awash River Basin is highly variable in space and time [32] and thus the research area is extremely vulnerable to significant flooding as well as limited water access.

In fact, Ethiopia is one of the nations most susceptible to the effects of climate change. Regarding climate change, the Ethiopian governments have to carry out SDG Goal 13 (urgent action to address climate change and its consequences). However, groundwater quality is predominantly controlled by anthropogenic factors and natural activities, including volcanoes, which can be modified by climate change. Climate change can influence GW quality because of the composition of recharge water, which is modified, or because the proportions of water from a different origin change. Not only this, but also it can influence GW temperature in opposite directions. For instance, in areas dominated by infiltrating precipitation, the increase in air temperature will propagate to groundwater. However, if river water infiltration is a dominant recharge mechanism, the GW temperature can decrease due to higher fraction of recharge during winter. In fact, the occurrence of GW is mainly influenced by the geophysical and climatic conditions of the area. The difficulty in obtaining productive aquifers is a peculiar feature of Ethiopia, which is characterized by the wide heterogeneity of geology, topography, and environmental conditions [33].

2.3. Irrigation: Agroindustry and Sugar Plantation

The sugar industry, being an important player in foreign exchange earnings, also plays its part in polluting the vent with its discharges [34]. When sugar is made, a large amount of waste is produced, and this waste has a high pollution load, especially when it comes to organic matter, suspended particles, press mud, bagasse, heavy metals (Zn\textsuperscript{2+}, Ni\textsuperscript{2+}, Cu\textsuperscript{2+}, Mn\textsuperscript{2+}, Pb\textsuperscript{2+}, Cd\textsuperscript{2+}, Cr\textsuperscript{3+}, and Fe\textsuperscript{2+}) [35], and air pollutants [36]. The sugar industry uses a variety of chemicals, mostly for the purposes of refining final goods (i.e., sugar) and coagulating impurities. For instance, polyelectrolyte, H\textsubscript{3}PO\textsubscript{4}, and Ca(OH)\textsubscript{2} are some of several compounds used for a variety of applications. Irrigation raises local groundwater recharge and water tables, which could lead to pollution as well (Figure 3). Pesticides and herbicides, which are agricultural chemicals, can contaminate groundwater in a variety of ways. One of the potential dangers derived from the application of agrochemicals is the pollution of groundwater [37]. After their application to crops, they are observed by soil and percolate through the soil after rain or floods, carry the chemical with them, and are eventually leached to the underlying groundwater [38]. Sugar mill effluents are a source of groundwater contamination [39]. High concentrations of TDS, alkalinity, DO, BOD, and COD above the permissible limit were observed in groundwater around sugar industries in India [40]. In agricultural landscapes, topography plays an important role in the transport of chemicals to groundwater [37]. Consequently, the concentrations of chemicals associated with agricultural practices, such as nitrate nitrogen (nitrate), chloride, and sulfate are increasing at an alarming rate in water tables [41].
These samples were sourced from 16 locations across the Middle Awash Basin, including portable digital EC, TDS, and pH meter. Major ions and other physicochemical parameters, been measured ically, while kitchenware, includes stations, 3.

Figure 3. The groundwater productivity of the study area [42,43].

3. Materials and Methods

To evaluate groundwater quality, a total of 32 samples from boreholes, piezometers, and wells were collected during the dry (June 2021) and wet (November 2021) seasons. These samples were sourced from 16 locations across the Middle Awash Basin, including Addis Ketema, Merti camp, Abadir 4th camp, and Awash Sebat-kilo water supply (which includes two water supply wells), along with several piezometer sites (six piezometers) and one hot-spring well near the Awash Basin Office at Amibera Wereda, Ethiopia. While the bulk of sampled stations, eight, numbering 50%, are used for washing (clothes, kitchenware, and bathing uses) (near Merti and Addis Ketema), a fraction of sampling stations, two, numbering 12.5%, are used for drinking (Awash Sebat-kilo town). A total of six (or 37.5%) of the sampled stations are piezometer stations (Amibera state farm). Typically, half of the sample stations are located close to Lake Beseka. A total of eight sampled stations, or 50% of the sampling sites, are downstream of LB (@Awash-Halidebi) while the other 50% are close to Lake Beseka (@Awash-Awash).

A short length of plastic tubing was inserted into the piezometer, and samples were collected by sucking on the tube, pulling it out of the piezometer, and emptying it after kinking off the tube. When it hits the water, an alarm will sound, and once the level is measured again, it will be recorded. Samples were stored in polyethylene bottles that had been acid-washed and rinsed with the water to be tested. Immediately after collection, the bottles were transported to the laboratory and stored at 4 °C. On-site, parameters such as temperature, electrical conductivity, and pH were measured using a pre-calibrated portable digital EC, TDS, and pH meter. Major ions and other physicochemical parameters, including total hardness, alkalinity, calcium (as CaCO₃), magnesium (as MgCO₃), bicarbonates, carbonates, fluoride, chloride, sulfate, phosphate, nitrate, nitrite, and ammonium ions were analyzed using standard methodologies [44] with a Palintest 7100.
Heavy metal samples, filtered and acidified, were analyzed for over 24 metals and metalloids (including Al, Li, Mo, Ti, V, Mn, Ba, Ni, Cu, Zn, Sr, As, Rb, Cr, Zr, Nb, Ge, Co, Fe, Ga, Ag, Cd, Sn, and Sb) using ICP-MS/OES at the Oxford Analytical Laboratory in the UK. The following parameters were taken into consideration when setting up the instrument operating conditions (ICP-MS): RF power (1600), internal standard (Rn, In, Ir, and Re), modes of operation (Helium collision cell and standard operation), plasma gas flow (18 L/min), nebulizer gas flow (0.9–1.0 µL/min), sample uptake rate (250 µL/min), nebulizer (PerkinElmer micromist), and spray chamber (Quartz cyclonic at ambient temperature (ca 2 °C). Statistical analyses, including mean, standard deviation, and correlation, were conducted using SPSS version 26. The results were discussed using average values and 95% confidence intervals, with the least significant differences (LSDs) employed to evaluate statistical differences between means at a significance level of α ≤ 0.05. Data visualization was enhanced using Origin 2021 software and Minitab 19.

4. Results and Discussion

Understanding the main factors controlling groundwater chemistry is very important for sustainable groundwater development. Thus, for the purpose of evaluating the quality of groundwater and its suitability for drinking and agriculture, we have examined over twenty physicochemical parameters, including pH, electrical conductivity (EC), total dissolved solids (TDS), alkalinity, bicarbonate, carbonate, chloride, fluoride, sulfate, phosphate, nitrate, nitrite, ammonia, ammonium, and total hardness (TH) (Table 1) in Middle Awash groundwater (Figures 4 and 5). The study area’s groundwater resources have been subjected to an evaluation of their overall pollution level using twenty-four different heavy metals (metalloids) (Al, Li, Ti, Co, Cu, As, Mo, Mn, Cr, Ba, Cr, Sr, Fe, Mn, Ni, Ba, and the like) (Table 2). Multivariate statistical techniques (principal component analysis and Spearman’s correlation) are combined to determine the pollution status and likely sources of pollutants in the middle valley of Awash, thereby strengthening the results.

![Figure 4. The Spatial variability of physicochemical parameters in the study area (the unit of EC-µS/cm; Na in meq/L, whereas TDS, Alk, bicarbonate, carbonate, sulfate, and Cl, in mg/L).](image-url)
Table 1. The physicochemical statistical data (min, max, standard deviation, and mean) and Pearson correlation between variables.

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<td>−0.57</td>
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<td>−0.51</td>
<td>−0.52</td>
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<td>517</td>
<td>269</td>
<td>225</td>
<td>275</td>
<td>132.5</td>
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<td>4</td>
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<td>1.08</td>
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<td>15,645</td>
<td>10,826</td>
<td>1600</td>
<td>1925</td>
<td>607.5</td>
<td>200.5</td>
<td>69</td>
<td>105.2</td>
<td>379</td>
<td>17.6</td>
<td>0.18</td>
<td>412.5</td>
<td>18.2</td>
<td>188.5</td>
<td>2.43</td>
<td>6.53</td>
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<tr>
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<td>8.74</td>
<td>3152</td>
<td>2099</td>
<td>885</td>
<td>1079</td>
<td>529.1</td>
<td>191.1</td>
<td>38.8</td>
<td>41.28</td>
<td>46.73</td>
<td>1.82</td>
<td>4.48</td>
<td>0.04</td>
<td>244.8</td>
<td>7.85</td>
<td>135</td>
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<td>4.12</td>
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<td>0.46</td>
<td>3760</td>
<td>2625</td>
<td>415</td>
<td>503</td>
<td>249</td>
<td>167.6</td>
<td>49</td>
<td>13.05</td>
<td>23.7</td>
<td>0.78</td>
<td>4.24</td>
<td>0.06</td>
<td>105.6</td>
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<td>1500</td>
<td>1000</td>
<td>500</td>
<td>580</td>
<td>250</td>
<td>300</td>
<td>200</td>
<td>150</td>
<td>200</td>
<td>12</td>
<td>45</td>
<td>3</td>
<td>250</td>
<td>1.5</td>
<td>250</td>
<td>0.2/3</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

N.B: WQP: Water Quality Parameter; SD: Standard Deviation; Tur.: Turbidity: NTU: Nephelometric Turbidity Unit; the unit of EC is µS/cm; the unit of Na & K is meq/L; the unit of other parameters is in mg/L.
Table 2. Seasonal variability of iron and manganese in all sampled stations.

<table>
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<tr>
<th>HMs</th>
<th>Season</th>
<th>GW1</th>
<th>GW2</th>
<th>GW3</th>
<th>GW4</th>
<th>GW5</th>
<th>GW6</th>
<th>GW7</th>
<th>GW8</th>
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<td>BD</td>
<td>7.0</td>
<td>BD</td>
<td>BD</td>
<td>BD</td>
<td>BD</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>17.0</td>
<td>25.0</td>
<td>103.0</td>
<td>98.7</td>
<td>22.1</td>
<td>69.9</td>
<td>55.9</td>
<td>10.5</td>
</tr>
<tr>
<td>Mn</td>
<td>A</td>
<td>0.9</td>
<td>1.4</td>
<td>992.2</td>
<td>48.6</td>
<td>16.0</td>
<td>2.7</td>
<td>1.4</td>
<td>63.6</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>3.8</td>
<td>79.4</td>
<td>824.8</td>
<td>121.1</td>
<td>13.8</td>
<td>12.6</td>
<td>10.3</td>
<td>38.8</td>
</tr>
</tbody>
</table>

GW9  GW10  GW11  GW12  GW13  GW14  GW15  GW16

| Fe  | A      | BD  | BD  | 19.6| 741.9|109.4|12.8 |3.1  |16.3 |
|     | B      | 413.8|26.2|14.6 |-     |593.2|96.7 |71.8 |42.6 |
| Mn  | A      | 4.1 | 2.5 | 70.8|141.7|408.4|10.6 |2.9  |11.9 |
|     | B      | 178.4|9.3 |100.1|-     |127.9|259.4|19.5 |24.0 |

GW9  GW10  GW11  GW12  GW13  GW14  GW15  GW16

N.B: Units are in µg/L (A = June, 2021, end of dry season; B = end of wet season, November, 2021).

Figure 5. The spatial variability of physicochemical parameters in the study area (All units are mg/L).

4.1. Distribution of Physicochemical Parameters

4.1.1. Turbidity and pH

Turbidity is a measure of the degree to which the water loses its transparency due to the presence of suspended particulates [45]. One of the characteristics of groundwater that gives it certain advantages over the surface water is its clearness and colorlessness unless tainted with humic materials. It usually contains no suspended matters. However, due to the presence of humic materials, and colloidal and extremely fine dispersion of substances, some extremely high values of turbidity (NTU) were observed in the following sampled stations: GW8 (85.0), GW9 (28.8), GW10 (27.5), GW11 (183.0), GW12 (760.0, muddy), and GW13 (950). The very high values were recorded in piezometer stations (GW8–GW13), which might be due to organic matter such as the decay of plants, the presence of microorganisms, and/or mud formation. While the remaining ten stations (62.5%) show less than the WHO limit (5 NTU). Whereas, the power of hydrogen (pH) is a key indicator for water acidity and alkalinity. In the study, almost all of the water samples are alkaline due to the presence of carbonates and bicarbonates. As shown in Table 1, the pH values of water samples varied from 8.2 to 10.1 and it was found above the limit prescribed by WHO [46]. A total of ten stations (62.5%) exceeded the drinking water standard limit.
4.1.2. Electrical Conductivity (EC) and Total Dissolved Solids (TDS)

The electrical conductivity (EC) in GW samples, which indicates its salinity, is a useful tool for assessing whether water is suitable for agriculture and drinking. With an average of 3152 µS/cm, EC values range from 517 to 15,645 µS/cm. The influxes of saline lake water to groundwater may increase the salinity [20]. The maximum permissible limit of EC in drinking water, according to WHO standards, is 1500 µS/cm [46]. According to the results of the analysis, about 70% of the samples, or 11 samples, had EC values that were higher than the standard value; these high salinity values in the groundwater are apparent as a result of the influence of saline geothermal waters. High concentrations of dissolved salts in the GW from the sedimentary formations are also common as a result of the reaction of the often abundant evaporite minerals [20]. The range of TDS is 269 to 10,826 mg/L in the study area; the mean value is 2099 mg/L. The TDS was highest in sample GW11 (piezometer station).

4.1.3. Alkalinity, Bicarbonate (HCO$_3^-$), and Carbonate (CO$_3^{2-}$)

In the study area, the highest concentrations of alkalinity, carbonates, and bicarbonates were recorded at 1600 mg/L, 950 mg/L, and 1925 mg/L in the same station, respectively. Alkalinity, bicarbonate (HCO$_3^-$), and carbonates (CO$_3^{2-}$) range from 225 to 1600 mg/L; 275 to 1925 mg/L; and 132.5 to 950 mg/L, respectively. Perhaps the source of the alkalinity, bicarbonates, and carbonates in the groundwater might be natural activities (near LB) and various human activities (downstream of Beseka). As seen in Table 1, the majority of sampled water exceeded the maximum allowable limit of alkalinity (500 mg/L), bicarbonates (580 mg/L), and carbonates (250 mg/L). Bicarbonate (HCO$_3^-$) was the dominant anion; it might be due to the topology and geology of the study area.

4.1.4. Fluoride (F$^-$) and Chloride (Cl$^-$)

As shown in Table 1, the highest level of fluoride (18.2 mg/L), more prominent than the WHO limit (1.5 mg/L), was found in GW1. All inspecting stations, including GW15 (1.96 mg/L), exceeded the WHO limit, which is subsequently a recognized major issue, particularly for the communities using the water for drinking (GW15 and GW16). One hundred percent of the tests exceed the standard, and the most noteworthy concentration was 18.2 mg/L, which is indeed higher than a few Rift Valley nations in Africa including Kenya and Tanzania [47]. In fact, studies also revealed that about 30% of Ethiopia’s groundwater is naturally contaminated with high salinity and fluoride [48]. It might be due to the weathering of the volcanic bed rocks interaction. In the research location, almost 37% of the GW samples have chloride WHO concentrations above the limit of 250 mg/L. The concentration of chloride ranges from 117.5 mg/L to 412.5 mg/L. The main source of chloride in the GW is the result of erosion and weathering of crystalline rocks. The anion is derived from minerals such as sodalite, apatite, micas, and hornblende in the rock matrix. In fact, chloride (Cl$^-$) is a highly mobile anionic species. The chloride limits were established mostly based on taste preferences. However, in this study, the highest concentration was found at 412.5 mg/L (GW1). However, using water with high chloride concentrations has not been found to have any negative health impacts on humans [49].

4.1.5. Total Hardness (TH), Calcium (Ca$^{2+}$), and Magnesium (Mg$^{2+}$)

The amount of dissolved calcium and magnesium, in addition to a range of other metals in the water, is the basic definition of water hardness (reference). There are a lot of dissolved minerals in hard water, mostly calcium and magnesium. One water-quality indicator that was investigated was water hardness; the results are displayed in Figures 4 and 5. Since water dissolves trace amounts of naturally occurring minerals as it passes through soil and rock and transports them into the GW supply, water systems that use GW as a source are concerned about water hardness. Hard water may be seen around a water supply well if the minerals Ca and Mg are present in the surrounding soil.
Water hardness in the research area varies considerably and is categorized into four classes based on basic guidelines: less than 75 mg/L is classified as soft due to calcium carbonate content; 75 to 150 mg/L is considered moderately hard; 151 to 300 mg/L is categorized as hard; and more than 300 mg/L is classified as extremely hard. According to the study’s findings, the distribution of water hardness among the subsurface waters sampled was evenly spread, with 25% falling into each category: very hard, hard, moderately hard, and soft. As depicted in Figures 4 and 5 and detailed in Table 1, the highest recorded levels of calcium (Ca), magnesium (Mg), and total hardness (TH) were 200.5 mg/L, 69 mg/L, and 607.5 mg/L, respectively. These results suggest a common geological origin for these elements. The solubility of Ca and Mg in saline-alkaline groundwater is influenced by the presence of their respective carbonates and bicarbonates.

4.1.6. Sodium (Na\(^+\)) and Potassium (K\(^+\))

Sodium (Na) is a naturally occurring element that is most frequently found in combination with chloride to produce salt. There are several reasons why groundwater may include sodium, including naturally occurring brackish water, sodium-bearing rock minerals, salt-containing geological formations, and the weathering of soil minerals. Actually, the salt content of groundwater is normally quite low, although it can rise in Rift zones and locations close to volcanoes (reference). In the study area, the concentration of Na\(^+\) in groundwater ranges from 17.02 meq/L (GW15) to 105.2 meq/L (GW11). High concentrations of Na\(^+\) and Ca\(^{2+}\) in the groundwater were attributed to cation exchange capacity among minerals. The concentration of K in all groundwater samples is within the allowable limit. For instance, the highest (3.79 meq/L) and lowest (1.02 meq/L) concentration of K was observed in GW1 and GW13, respectively. The sources of K are probably the silicate minerals found in igneous and metamorphic rocks, such as orthoclase, microcline, hornblende, muscovite, and biotite, as well as evaporate deposits of sulphate and gypsum that release a significant amount of potassium into the groundwater. The primary cause of rising GW potassium levels is an agricultural practice [50].

4.1.7. Sulfate (SO\(_{4}^{2-}\)) and Phosphate (PO\(_{4}^{3-}\))

A high concentration (above 100 mg/L) of sulfate was observed in 12 stations out of 16 sampled subsurface waters, but this did not exceed the WHO limits. Mostly sulfate can exist in GW in the form of Ca, Mg, and Na soluble salts. A study indicates that still little is known about the direct health impacts of elevated sulfate intake, particularly through drinking water. Sulphate does not contribute to toxicity [51]. Elevated phosphate concentrations (0.3 to 2.4 mg/L) were detected in the groundwater. The highest value, which is 188.5 mg/L, was recorded in the GW4 station near LB. These values might come from the geology of the study area. Meanwhile, the phosphate concentration ranged between 0.3 mg/L (GW7) and 2.4 mg/L (GW8). As an example, Awash Basin Agricultural nitrate is the most prevalent chemical pollution found in GW aquifers basin-wide. The increase in agricultural output worldwide has been made possible by the extensive use of chemicals, including chemical fertilizers and insecticides. A higher concentration of sulphate is observed in the downstream part, which could be due to excessive use of fertilizers or use of soil amendments. Excess phosphates and nitrogen can seep into GW or be carried into water bodies by surface runoff. Because phosphate is not as soluble as nitrate, it seeps into the soil and is subsequently carried there by soil erosion [52].

4.1.8. Ammonia (NH\(_{3}\)), Ammonium (NH\(_{4}^{+}\)), Nitrate (NO\(_{3}^{-}\)), and Nitrite (NO\(_{2}^{-}\))

Ammonia is released into the atmosphere by industrial, agricultural, and metabolic processes as well as by using chloramine for disinfection. Surface and groundwater naturally occur at concentrations of less than 0.2 mg/L. Groundwater devoid of oxygen can have as much as 3 mg/L. Elevated amounts in surface water can result from intensive farm animals rising. Water containing ammonia may be contaminated by bacteria, sewage, or animal waste. Ammonium, nitrate, and nitrite play the most important role in biochemical
processes, but some organic nitrogen compounds in water may also be of significance. Nitrate (NO$_3^-$) is a very soluble nitrogen anion, and the most mobile form of nitrogen, which is not easily absorbed by mineral soils [53]. Various sampling stations located both nearby and downstream of LB show high nitrate concentrations in the groundwater as a result of intensive farming practices that alter natural drainage patterns by using nitrogen fertilizers. When drinking water contains more than 45 mg/L of nitrate, it can cause harmful health effects in people, such as stomach cancer [54] and methemoglobinemia, sometimes known as “blue baby syndrome,” which typically affects infants [49].

All of the samples have nitrate contents between 1.1 mg/L (in stations GW11, GW13, & GW16) and 17.6 mg/L (GW1), which is under the WHO acceptable limit. However, relatively high concentrations of nitrate were recorded near LB. As shown in Figure 5, an elevated level of turbidity was observed in GW13; EC and TDS in GW11; TH, alkalinity, bicarbonate, and carbonate in GW9; Ca-CO$_3$, Mg-CO$_3$, Mg, and Ca in GW9; Na$^+$ in GW11; K$^+$ in GW1; NO$_3$-N in GW1; F$^-$ in GW1; Cl$^-$ in GW13; SO$_4^{2-}$ in GW4; PO$_4^{3-}$ in GW8; and NH$_3$ and NH$_4^+$ in GW14. The findings also revealed that relatively high concentrations of physicochemical parameters were observed in shallow GW (Piezometer) than deep GW (Lake Beseka catchment). The water type in the study area is ascertained using the Piper diagram [55]. The hydro-chemical composition of the groundwater samples that were obtained in the study area, specifically both the Lake Catchment and Amibera irrigation field, is predominantly the Na-HCO$_3$ type, as per the analytical data. In general, sodium is a dominant cation and bicarbonate is a dominant anion. Over 81% of the sampled GW samples show the HCO$_3$-Na type of water due to carbonate rocks, such as limestone and dolomite, and the weathering of carbonaceous rocks.

![Figure 6. Piper diagram of water chemistry for groundwater in the study area.](image)

4.2. Distribution of Heavy Metals

This section presents the summary statistics of heavy metals (metalloids) concentration in the study area. For instance, Table 3 and Figure 7 illustrate that a high concentration of As above the permissible limits of WHO was observed in different stations (including
GW1, GW2, GW3, GW5, and so on) in the GW samples. The highest concentration of As, 201 µg/L, was determined in GW8 (around), which is excessively high, or 20 times higher than the allowable limit of WHO, 10 µg/L [46]. Near the Merti Kera complex, station GW7 (11.1 µg/L) and Merti camp near Shibo-gebi, station GW5 (18.1 µg/L), both had very high concentrations of As (above 10 µg/L) [46]. About half (50%) of the samples revealed very high concentration of As (above 10 µg/L) recorded in stations GW7 (11.1 µg/L) (Merti camp near Shibo-gebi), GW5 (18.1 µg/L) (Merti Kera compound), GW3 (34.3 µg/L) (Merti Beret house), GW6 (41.9 µg/L) (Abadir 4th camp), GW2 (83.1 µg/L) (Merti near Buret area), GW1 (116.1 µg/L) (Addis Ketema Mosque), GW12 (117.2 µg/L) (AIP-10.2), and GW8 (210 µg/L) (AIP-41). Among the sampled stations, six sites are located around Lake Beseka. Almost all are deep wells, while the remaining two sites are piezometers and were showing extremely high values. These stations are found in Amibera irrigation (state) farms. Both are piezometer stations and their water levels at the time of sampling were 1232 cm (AIP-10.2) and 167 cm (AIP-41) meters. Arsenic may also be present in some GW sites within the southern Rift where sodium-bicarbonate geothermal waters exert an influence on GW quality, although no data are available to substantiate this.

![Pie Chart of HMs in sampling stations](image)

Figure 7. Pie chart of heavy metals sampling stations.
Table 3. Correlations between heavy metals (metalloids) and statistical summary of heavy metals concentration in groundwater (in \( \mu g/L \)).

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<th>Cu</th>
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4.2.1. Aluminum (Al), Iron (Fe), and Manganese (Mn)

The concentration of Al varied from 20.3 to 2615 µg/L; a low concentration of Al was observed at site GW10 (20.3 µg/L), whereas the highest Al concentration was found at GW12. The major source of Al in GW might be the volcanic ash, weathering of aluminum-containing rocks such as bauxite. The highest concentration of Al was found below LB at station GW12 (AIP12). Aluminum ions in other compounds also hydrolyze, and this continues until the cationic charge has run out, ending the reaction by hydroxide formation. The beginning of the hydrolysis reaction is as follows (Equation (1)):

$$\text{Al}^{3+} \text{(aq)} + 6\text{H}_2\text{O} \text{(l)} \rightarrow [\text{Al(H}_2\text{O})_6]^{3+} \text{(aq)}$$  

(1)

Aluminum mainly occurs as $\text{Al}^{3+}$ (aq) under acidic conditions and as $\text{Al(OH)}_4^{-}$ (aq) under neutral to alkali conditions. Other forms include $\text{AlO}_2^{2-}$ (aq) and $\text{Al(OH)}_3$ (aq). The regular aluminum concentration expected in groundwater is 4 µg/L because it is present in soils as water-insoluble hydroxide. Depending on the variability of pH values, the solubility of Al might rapidly increase, causing aluminum concentrations to rise above 5 µg/L. However, elevated levels of aluminum (>200 µg/L) have an impact not only on fish but also on birds and other species that eat tainted fish and insects, as well as on animals that inhale the metal through the air. When birds eat infected fish, their eggshells thin and their offspring are born with low birth weights. Animals that inhale Al through the air may experience respiratory issues, lose weight, and become less active. The effects of Al have drawn our attention, mainly due to the acidifying problems. It may accumulate in plants and cause health problems for animals that consume these plants.

Metals that are found naturally in rocks, minerals, and soils are iron (Fe) and manganese (Mn). When these solid materials enter the aquifer, groundwater in it starts to disintegrate them. This causes their contents, such as manganese and iron, to be released into the water. The concentration of Fe varied from 6.20 to 741.9 µg/L; the lowest concentration of Fe was observed at different sites, including GW8 (6.20 µg/L), whereas the highest Fe concentration was found at GW12 (741.9 µg/L). As iron-bearing minerals and rocks weather, iron is naturally added to groundwater. The World Health Organization (WHO) establishes 300 µg/L as the maximum permitted concentration of iron in drinking water. In the study, high concentrations of iron above the maximum permitted limit were recorded in stations.

Meanwhile, the concentration of Mn varied from 2.4 µg/L to 908.5 µg/L; a low concentration of Mn was observed at site GW1 (2.4 µg/L), whereas a high Mn concentration was found at GW3 (908.5 µg/L). As shown in Table 2, for a particular well, the amount of dissolved iron and manganese in the groundwater changes seasonally. For instance, high concentrations of Fe (in 14 stations, or 87.5%) and Mn (in 11 stations, or 69%) were recorded in the partly wet season (10 November 2021). This variance is typically linked to the surface bringing in oxygenated water during times of strong recharge. The oxygenated water will keep the iron and manganese from dissolving, resulting in low quantities of these metals in the water drawn from the wells. Iron and manganese will dissolve once more in the recharge water when the oxygen has been used up, giving the water dissolved iron and manganese properties.

4.2.2. Arsenic (As), Molybdenum (Mo), and Vanadium (V)

Numerous human activities, such as mining, farming, landfills, and urban expansion, release heavy metals into groundwater [56]. In the research area, geological and anthropogenic processes have the potential to introduce heavy metals and As into water bodies (GW & SW). For example, As can occur in water bodies from various sources in various forms. Arsenite (As(III)) and arsenate (As(V)) are both soluble in water as species and can exist in both inorganic and organic forms. High levels of chloride have an impact on the solubility and mobility of metals, including As, as Table 1 illustrates. Chloride complexes have the ability to make metals more soluble when they are desorbed and change into a soluble phase, which prolongs their persistence in soil and freshwater environments [57].
Both organic and inorganic arsenic species (As(iAs)) are water-soluble arsenic found in natural water sources.

When choosing and analyzing the most dominant form of As in water, the most present is inorganic As as As(V). If As(III) is present, there are two important things that need to be taken into account; firstly, As(III) is more poisonous (even at low concentrations) than As(V). Besides the severe toxic effect, As(III) is easily oxidized. Arsenic species can be transformed into insoluble compounds in combination with other elements, such as iron and sulfur [58]. Most of the time, As is mobilized by displacement from the sediment surface [59].

Molybdenum is a Group VIB HMs, and Mo(IV) and Mo(VI) are predominant states in nature. The most common oxidation states are $4^+$ and $6^+$ [60]. It occurs as molybdenite ($\text{MoS}_2$) and moly dates ($\text{MoO}_4^{2-}$) in igneous or sedimentary rocks. Even though most Mo compounds are not very soluble in water, the molybdate ion, $\text{MoO}_4^{2-}$, forms when Mo-containing minerals come into contact with oxygen and water is soluble (Equations (2) and (3)).

$$2\text{MoS}_2 + 7\text{O}_2 \rightarrow 2\text{MoO}_3 + 4\text{SO}_2$$  \hspace{1cm} (2)  

$$\text{MoO}_3 + 2\text{NH}_3 + \text{H}_2\text{O} \rightarrow (\text{NH}_2)_2\text{(MoO}_4\text{)}$$  \hspace{1cm} (3)

Strong alkaline molybdates have a high solubility for Mo(VI) oxides ($\text{MoO}_4^{2-}$). Mo can exist in a wide variety of oxidation states, which are discussed in numerous Mo chlorides. Molybdenum (Mo) may be transformed in the LB catchment because of the hot weather, temperature, and volcanic factors around the lake. In Lake Beseka, under physiological conditions (at pH > 6.5), the molybdate anion, $[\text{MoO}_4]^{2-}$, is the sole molybdenum species in aqueous media [61,62]. Molybdenum compounds, including molybdenum trioxide and polymolybdates, transform rapidly to the $[\text{MoO}_4]^{2-}$ ion under environmentally relevant test conditions. Protonated forms, such as $[\text{HMoO}_4]^{-}$ and $\text{H}_2\text{MoO}_4$, are found at pH < 5 [60]. Molybdenum tends to be more mobile under alkaline conditions, but adsorption increases with decreasing pH [63]. In the study, we found that the highest concentration of Mo varied from 2.6 to 802.4 µg/L; a low concentration of Mo was observed at site GW15 (2.6 µg/L), whereas the highest concentration was observed in GW11 (802.4 µg/L).

In water, V(IV) is commonly present as a vanadyl cation ($\text{VO}_2^+$, $\text{VO(OH)}_2^+$), whereas V(V) exists as a vanadate oxyanion ($\text{H}_2\text{VO}_4^-$, $\text{HVO}_4^{2-}$) [64]. $\text{VO}_2^+$ is strongly adsorbed on solid phases, including organic and oxyhydroxide phases [65]. Vanadium varies in concentration around the world, and it is usually found associated with iron-bearing water [66]. Vanadium was found in groundwater samples. The minimum and maximum vanadium concentrations found were 1.7 µg/L and 528 µg/L, respectively. Vanadium (V) is significantly correlated with other trace elements such as arsenic, fluoride, and boron [67]. As seen in Table 4, it is mostly found associated with As ($r = 0.91$).

### Table 4. Comparison of HMs in Lake Beseka’s surface water and groundwater.

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<th>Ti µg/L</th>
<th>V µg/L</th>
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<td>116</td>
<td>10.7</td>
<td>0.5</td>
<td>11.2</td>
<td>BD</td>
</tr>
<tr>
<td>GW2</td>
<td>57.2</td>
<td>104.6</td>
<td>1.2</td>
<td>97.0</td>
<td>40.4</td>
<td>28.0</td>
<td>112.5</td>
<td>123.6</td>
<td>548.4</td>
<td>83.1</td>
<td>1.6</td>
<td>0.5</td>
<td>BD</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GW3</td>
<td>128.6</td>
<td>33.7</td>
<td>1.9</td>
<td>92.3</td>
<td>908.5</td>
<td>31.6</td>
<td>176.4</td>
<td>67.4</td>
<td>525.2</td>
<td>34.3</td>
<td>0.4</td>
<td>0.3</td>
<td>55.0</td>
<td>BD</td>
<td></td>
</tr>
<tr>
<td>GW4</td>
<td>142.1</td>
<td>20.8</td>
<td>2.5</td>
<td>30.8</td>
<td>80.4</td>
<td>21.0</td>
<td>114.4</td>
<td>26.2</td>
<td>631.8</td>
<td>9.0</td>
<td>1.9</td>
<td>0.2</td>
<td>BD</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GW5</td>
<td>46.9</td>
<td>17.6</td>
<td>0.8</td>
<td>56.6</td>
<td>14.9</td>
<td>44.4</td>
<td>94.9</td>
<td>36.7</td>
<td>842.2</td>
<td>181.1</td>
<td>1.3</td>
<td>0.2</td>
<td>BD</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GW6</td>
<td>97.2</td>
<td>55.1</td>
<td>1.5</td>
<td>71.8</td>
<td>7.6</td>
<td>12.8</td>
<td>55.7</td>
<td>16.8</td>
<td>202.5</td>
<td>41.9</td>
<td>2.1</td>
<td>BD</td>
<td>BD</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GW7</td>
<td>65.2</td>
<td>32.1</td>
<td>1.2</td>
<td>36.5</td>
<td>5.9</td>
<td>8.0</td>
<td>61.1</td>
<td>15.7</td>
<td>181.8</td>
<td>11.1</td>
<td>3.5</td>
<td>BD</td>
<td>BD</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Surface water</td>
<td>SW1</td>
<td>816.0</td>
<td>88.9</td>
<td>50.6</td>
<td>69.9</td>
<td>22.9</td>
<td>24.0</td>
<td>54.3</td>
<td>21.4</td>
<td>56.4</td>
<td>57.2</td>
<td>1.4</td>
<td>0.3</td>
<td>631.3</td>
<td>BD</td>
</tr>
<tr>
<td>SW2</td>
<td>758.8</td>
<td>91.0</td>
<td>45.2</td>
<td>72.8</td>
<td>19.0</td>
<td>14.8</td>
<td>49.6</td>
<td>11.5</td>
<td>54.4</td>
<td>43.4</td>
<td>1.4</td>
<td>0.3</td>
<td>598.7</td>
<td>BD</td>
<td></td>
</tr>
<tr>
<td>SW3</td>
<td>556.2</td>
<td>116.7</td>
<td>35.2</td>
<td>71.3</td>
<td>12.7</td>
<td>13.5</td>
<td>45.5</td>
<td>8.1</td>
<td>42.6</td>
<td>35.1</td>
<td>1.1</td>
<td>0.3</td>
<td>459.4</td>
<td>BD</td>
<td></td>
</tr>
<tr>
<td>SW4</td>
<td>134.2</td>
<td>111.7</td>
<td>9.9</td>
<td>62.0</td>
<td>7.5</td>
<td>11.9</td>
<td>58.4</td>
<td>8.1</td>
<td>42.2</td>
<td>45.6</td>
<td>0.6</td>
<td>0.2</td>
<td>108.7</td>
<td>BD</td>
<td></td>
</tr>
<tr>
<td>SW5</td>
<td>188.5</td>
<td>91.9</td>
<td>14.4</td>
<td>94.2</td>
<td>7.9</td>
<td>10.6</td>
<td>15.6</td>
<td>8.2</td>
<td>67.0</td>
<td>61.2</td>
<td>7.9</td>
<td>0.1</td>
<td>150.7</td>
<td>BD</td>
<td></td>
</tr>
</tbody>
</table>

N.B: SW1: Lake Beseka at canal; SW2: Lake Beseka at intake; SW3: Lake Beseka at the left side of the old road; SW4: Lake Beseka at the right side of the old road; SW5: Lake Beseka at new lodge; BD: below detection limit.
4.2.3. Barium (Ba), Lithium (Li), and Strontium

The concentration of barium in groundwater is regulated by barite (BaSO$_4$) solubility. The relationship between strontium and barium in groundwater is controlled by the dissolution of sulfate salts containing strontium and the precipitation of barite. Surprisingly, groundwater with low SO$_4^{2-}$ concentrations (or less than 10 mg/L) could be predicted to have high Ba contents [69]. As a result, only very low concentrations of Ba (ranging from 6.8 to 76.2 µg/L) were found in the investigated sites. This could be because the groundwater samples had significant concentrations of SO$_4^{2-}$ (188.5 mg/L). Although barium compounds are utilized in many industrial applications and can be found as trace elements in both igneous and sedimentary rocks, the majority of Ba in water comes from natural sources. Barium may be a connection between cardiovascular illnesses [70]. Nearly all (100%) of the samples in the research area had results (Ba) below the WHO standards (700 µg/L).

Like all alkali metals, lithium reacts easily in water and does not occur freely in nature due to its activity. Lithium compounds such as lithium chloride, lithium carbonate, lithium phosphate, lithium fluoride, and lithium hydroxide are more or less water soluble. In the study, the highest concentration of Li 68 µg/L was observed in GW8. Most sampling stations do not exceed the WHO standard [46]. However, too much lithium may be toxic.

In fact, strontium (Sr) and barium (Ba) are alkaline-earth metals that are a common trace element in most rocks, soils, sediments, and waters. Both rock weathering and soil erosion can lead to strontium contamination of water supplies. Because many strontium compounds react violently with water, they can travel across the environment rather easily. The groundwater sites that were analyzed showed Sr concentrations ranging from 71.1 µg/L to 1236 µg/L, with the lowest concentration being seen there. Some stations, including GW, recorded above the 700 µg/L or Canadian water requirements [71]. In general, carbonates have higher strontium contents than ultrabasic rocks and sandstones. There are many sedimentary basins (which frequently contain evaporites) and carbonates that could be sources of sulfur or are probably connected to sulfur minerals [72].

4.2.4. Chromium (Cr), Cadmium (Cd), and Zinc (Zn)

Cadmium (Cd) is expected in high concentrations at low pH; however, it is not valid for the Rift Valley groundwater system [69]. For instance, high pH wells (piezometer stations) also showed high Cd at station GW11 at 210 cm (2.1 m). In the study, at GW11, partly in dry and wet seasons, 4.6 µg/L (pH = 8.44) and 0.62 µg/L (pH = 9.06) were recorded, respectively. The highest mean concentration of Cd-values is found in the alkaline groundwater samples at very high pH values (Cd = 2.62 µg/L). The source might be anthropogenic (might be fertilizers and pesticides). Chromium (Cr) is a well-known cancer-causing element. Anthropogenic sources like the tanning industry pollute water bodies in the Awash Basin [68]. Meanwhile, the concentration of Cr exhibited in all samples was below the maximum allowable limit (50 µg/L) noted by WHO [46, 73]. Arguably, the previous studies conducted in the Rift Valley found the highest value of Cr in GW was 21 µg/L [69]. Similarly, the highest concentration of Cr recorded in this study was 10.7 µg/L in GW1 (at Addis Ketma, near LB).

Zinc (Zn), across all sampling stations, ranged from 10 to 6060 µg/L. In groundwater, the concentration of zinc (Zn) is usually expected to be between 10 and 40 µg/L. However, the highest concentration of Zn, 6060 µg/L, was recorded in the groundwater sample collected in the piezometer station (GW11). In the study, the concentration of Zn was recorded between 871 µg/L and 6000 µg/L in the Amibera irrigation fields, or piezometer stations. Surprisingly, the highest concentration of Zn was recorded in all piezometer stations; this might be associated with the fertilizers and chemicals (pesticides, herbicides, or else) used for cotton production or sugar cane plantation.
4.2.5. Silver (Ag), Antimony (Sb), and Tin (Sn)

Silver (Ag) is considered to be less toxic to humans. The main natural source of Ag is sulphidic ores. Its mobility is very low under alkaline conditions. Silver (Ag) ranged from 0.1 to 0.2 µg/L. The concentration of antimony (Sb) varies between ND to 5.3 µg/L across all sampling stations. Tin (Sn), across all sampling stations, ranged from 0.1 to 3.5 µg/L. The highest concentrations of Sb and Sn were recorded in GW11 with the values of 5.3 µg/L and 3.5 µg/L, respectively. It might be from organo-tin compounds or chemicals used for biocides in the Amberra state farm. Of the various tin-bearing minerals, cassiterite is an oxide, while the remainder is complex sulfides. The concentration of Sb in GW was expected to be 0.001 µg/L; however, in the study, a value of above 5 µg/L was recorded in station GW11 [70], which is still less than the WHO's 20 µg/L limit [46].

4.2.6. Copper (Cu), Cobalt (Co), and Nickel (Ni)

Copper (Cu) is a trace metal. According to the result of Table 3, the minimum and maximum concentrations of Cu were recorded from 47.7 µg/L to 369.7 µg/L. The mobility of Co strongly depends on the geochemical conditions [69]. Cobalt concentrations observed in the Rift Valley drinking water range from less than 0.002 to 3.1 mg/L [69]. However, the highest Co value was recorded in station GW (1.6 µg/L).

4.2.7. Niobium (Nb), Gallium (Ga), and Germanium (Ge)

Niobium (Nb) is a member of the fifth group of the periodic table. Niobium typically forms compounds with an oxidation state of +5. Niobium is closely associated with titanium in ores. Niobium can best be dissolved in a mixture nitric acid and hydrofluoric acids, completely miscible with iron. Its most common oxide is Nb2O5, which is produced by heating the metal in an oxygen environment. In a study of groundwater samples from LB and Amiberra irrigation farms, Middle Awash, the typical range for naturally occurring Nb concentrations in groundwater was measured to be from 0.1 to 3.5 µg/L. A high level of interaction between Al and Nb (r = 1.0) was found in studied groundwater, which might be predominantly of a natural origin [74]. Gallium (Ga) is the 34th most abundant element found in Earth’s crust, and it is widely distributed in low amounts in many rock types. The results of this study showed that the minimum and maximum level of Ga was observed at 0.1 µg/L and 10.3 µg/L, respectively. The ecological effects of gallium may be similar to those of aluminum given their similar behavior in the environment. Germanium (Ge) is a non-essential and non-harmful element.

An increased germanium level is mainly associated with thermal waters, waters with either very low or very high pH, and saline waters [75]. The highest concentration (1.5 µg/L) of Ge was recorded in GW16. Ge was found in increased amounts in CO2-rich thermal waters and alkaline sodium-dominated thermal waters [76].

4.2.8. Rubidium (Rb), Titanium (Ti), and Zirconium (Zr)

The higher concentrations of Rb, Ti, and Zr were found in stations GW4, GW12, and GW12 with levels of 35 µg/L, 171.3 µg/L, and 20.2 µg/L, respectively. Titanium (Ti) is a chemical element and is found in nature only as an oxide. Titanium (Ti), across all sampling sites, ranged from 0.5 to 171.3 µg/L. Zirconium (Zr), ranged from 0.4 to 20.2 µg/L across all sampling stations. The concentration of Rb ranged from 2.2 to 35 µg/L. The concentrations of Ti do not exceed the standard limits of WHO.

4.3. Pearson Correlation (r) Analysis

Distinguishing between different types of groundwater samples can be achieved by applying multivariate statistical techniques to the interpretation of analytical results and Pearson’s correlation coefficient (r) between potential variables computed. To determine the inter-correlational relationship between the chosen parameters, a correction matrix consisting of twenty-two groundwater quality parameters was generated. Table 1 illustrates that there was a significant correlation (r > 0.9) between the Na, EC, and TDS. Even additional
parameters show a good link (r > 0.75), such as Na with Cl, F, alkalinity (alk), bicarbonate, and carbonate. Observed pH showed a weak correlation with all measures, with the exception of turbidity.

Table 3 revealed a positive correlation between heavy metals (metalloids) such as Al and Ni (r = 0.94), Al and Cu (r = 0.86), Al and Zr (r = 0.86), Al and Co (r = 0.94), Al and Fe (r = 0.93), Al and Ag (r = 0.71), Al and Sn (r = 0.85), Al and Sb (r = 0.83), and Al and Nb (r = 1.0), while a similar result was observed with Ti. For instance, Ti and Ni (r = 0.95), Ti and Cu (r = 0.83), Ti and Zr (r = 0.87), Ti and Co (r = 0.94), Ti and Fe (r = 0.91), Ti and Ag (r = 0.71), Ti and Sn (r = 0.86), Ti and Sb (r = 0.83), and Ti and Nb (r = 1.0) were recorded due to a similar geogenic source. This fact is supported by Figure 8 Cluster 1 (Al, Ti, Ba, Ni, Cu, Zn, Zr, Nb, Ge, Co, Fe, Ga, Ag, Sn, and Sb might have the same origin). Surprisingly, Ni has strongly positive similarities with Al and Ti; Ti and Cu (r = 0.84), Ni and Zr (r = 0.91), Ni and Nb (r = 0.95), Ni and Co (r = 0.97), Ni and Fe (r = 0.89), Ni and Ag (r = 0.83), Ni and Sn (r = 0.87), and Ni and Sb (r = 0.73) arguably had a similar origin. While some other metals, including As, Ba, Cd, Ba, Fe, Ga, Ag, and others revealed strongly positive relations. For instance, if we compare Cluster 2 heavy metals (Mo, Li, Sr, and Cd), for Mo and Zn (r = 0.85), Mo and Ag (r = 0.79), and Mo and Cd (r = 0.97), high positive correlations were recorded. In Cluster 3 (V, As, Rb, and Cr), similarities in origin were recorded between V and As (r = 0.91).

4.4. Multivariate Statistical Analysis

Principal component analysis (PCA): PCA is a linear analytical technique used to reduce a data set’s dimensionality while trying to guarantee that associations remain within the original data. Speaking to a large data set in less estimation may be interesting in data representation and compression tasks, where it is frequently used. In this study, the PCA analysis (Figure 9) indicates that while the Ambiera irrigation schemes (from GW9–GW13) may be the result of anthropogenic factors such as excessive use of pesticides and agricultural inputs or groundwater salinization, the main reasons for the heavy metal pollution near the LB GW (from GW1–GW8) may be geogenic. Al, Ti, Ba, Ni, Cu, Zn, Zr, Nb, Ge, Co, Fe, Ga, Ag, Sn, and Sb might have the same origin. As illustrated in Figure 8, the correlation type of matrix was chosen to weigh all parameters equally. As a result, the plot displayed the quantity of main components, or uncorrelated variables, in the heavy metals data sample. A short distance indicates the closure of two chemical parameters, while a high distance shows the dissimilarity in the parameters. For example, the first component has substantial positive loadings for Co, Ni, Zr, Nb, Cu, Sn, Sb, Ti, Fe, and Al. Conversely, the second component has significant negative loadings for As and Cr. All things considered, the biplot and dendrogram plots (Figure 8) show that variations in the concentration of heavy metals in the groundwater aquifer under study may have both geogenic (such as rock water interactions) and anthropogenic (such as surface runoff and fertilizers used in agriculture) causes.

4.5. Comparison of Surface Water and GW HMs Data in the Lake Beseka Catchment

Water testing examined surface water and boreholes within the LB watershed (Beseka’s HMs data) [68] in order to investigate potential heavy metal sources in both the groundwater and surface water. Water quality data were computed as indicated in Table 5. To concentrate on examining how the basin’s topography and volcanic activity affect nearby bodies of water, such as the LB region, calculations were made. Furthermore, as Table 4 illustrates, the results show the degree of high concentration of HMs.
Figure 8. The similarity plot of heavy metals in the dendrogram. NB: The blue line represents the parameters' similarity under cluster number one; cluster two is shown by the red line; cluster three is indicated by the purple line; and cluster four is represented by the green line.

Figure 9. The principal component analysis (PCA) biplot of heavy metals.

Table 5. Functional piezometer stations in Amibera irrigation schemes (SCD: sample collected at the depth of).

<table>
<thead>
<tr>
<th>No.</th>
<th>Location Description</th>
<th>Piezometer</th>
<th>SID</th>
<th>SCD</th>
<th>Soil Type</th>
<th>Field Cover</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Shelko near new Asphalt Road</td>
<td>AIP-41</td>
<td>GW-8</td>
<td>167 cm</td>
<td>Fluvisols</td>
<td>Sugarcane</td>
</tr>
<tr>
<td>2.</td>
<td>Ambash near new settlement DC</td>
<td>AIP-40</td>
<td>GW-9</td>
<td>135 cm</td>
<td>Fluvisols</td>
<td>Sugarcane</td>
</tr>
<tr>
<td>3.</td>
<td>Near to Bolhamo village</td>
<td>AIP-62</td>
<td>GW-10</td>
<td>95 cm</td>
<td>Fluvisols</td>
<td>Sugarcane</td>
</tr>
<tr>
<td>4.</td>
<td>Melka-Sedi farm near 4th camp</td>
<td>AIP-10-1</td>
<td>GW-11</td>
<td>210 cm</td>
<td>Fluvisols</td>
<td>Trees and shrubs</td>
</tr>
<tr>
<td>5.</td>
<td>Melka-Sedi farm near 4th camp</td>
<td>AIP-10-2</td>
<td>GW-12</td>
<td>1232 cm</td>
<td>Fluvisols</td>
<td>Trees and shrubs</td>
</tr>
<tr>
<td>6.</td>
<td>Melka-Sedi farm near 4th camp</td>
<td>AIP-10-4</td>
<td>GW-13</td>
<td>215 cm</td>
<td>Fluvisols</td>
<td>Trees and shrubs</td>
</tr>
</tbody>
</table>

N.B: Amibera Irrigation Project (AIP); Sources: from field visits and study [24].
Comparing the HMs content of the two types of water and their potential sources was the goal of the above Table 4 and the figures below (Figures 10 and 11). Moreover, to investigate the water chemistry of surface water interaction across catchments. Table 4 illustrates that similar sources led to significant quantities of heavy metals and arsenic in both SW and GW samples. In a few cases, such as GW4, elevated levels of arsenic were observed exceeding the WHO-endorsed threshold of 10 µg/L. Conversely, comparatively low concentrations of Fe and Al were found in the Beseka catchment, whereas extraordinarily high concentrations of both were found in the SW of LB [10,77]. It could be caused by man-made sources or by the catchment’s rock deterioration. In both cases, Mo concentrations were found to be quite similar, which may be because of similar sources.

**Figure 10.** Comparison of the concentration of As and Mo in both water types sampled in the same area.

**Figure 11.** The concentration of HMs and As in SW and GW samples collected in the LB catchment.
4.6. Comparison of Water Level and Some Physicochemical Change

For example, an observation borehole is one that is drilled especially to record water level (Table 5). An observation borehole’s water level is a combination of all the aquifers the drill has entered. It is referred to as a piezometer if it is drilled to measure the water quality and quantity in a certain horizon and other horizons are cased off. Where piezometric levels are greater than the lake stage area, groundwater flow is directed towards the lake [78]. Current piezometric values at Melka Worrrer show that shallow groundwater flows mostly into the River Awash. In many areas of the irrigation area, groundwater levels are shallow, typically less than three meters below the surface. The study by [78] indicates that the direction of GW flow is towards the lake, suggesting that the groundwater–surface water interaction may be the source of the high concentration of heavy metals in the LB. Heavy metals from ground sources or water flowing into the lake may pollute the water. Therefore, the interaction may be the cause of the change in water chemistry.

A piezometer, also known as a tube well, is primarily used for measuring subsurface water pressure. Since the 1970s [78], more than fifty piezometer stations have been installed in the study area, with at least 25 of these used to monitor subsurface water quality and water level changes in the Middle Awash irrigation schemes. According to [24], all piezometers monitored in their studies have shallow water tables [78] and piezometers are mostly used to monitor shallow wells [79]. Currently, over half of these piezometer stations are non-functional, primarily due to damage from machinery, while others suffer from lack of maintenance. This presents significant challenges due to limited information on their functionality, compounded by inadequate regulation and monitoring. The neglect of these valuable resources is notable. For this study, six sites were selected to assess the water quality and water level changes in the GW of Middle Awash.

About six piezometers were used to compute the water quality of the groundwater in the Amibera irrigation farms in order to look at the patterns in changing water levels. The secondary data from the Awash Basin Administration Office, MoWE; the water level change; and the water quality were computed based on the study’s findings, as shown in Figure 12a,b. The results showed that the quality and level of the water had changed. For example, in 2009, a groundwater sample was taken at the following levels: 5.61 m (GW10), 2.5 m (GW11), and 2.75 m (GW9). However, in 2021, the levels were 1.35 m, 2.1 m, and 0.95 m, respectively. Electrical conductivity (EC) also changed in 2021, rising from 8850 µS/cm (GW9), 15,390 µS/cm (GW10), and 9650 µS/cm (GW13) to 1702 µS/cm, 2074 µS/cm, and 4985 µS/cm, respectively.
Awash-Awash and Awash Halidebi sub-basins) were confirmed. Exceeding values of pH (10.15), turbidity (950 mg/L, turned into muddy), electrical conductivity (15,645 µS/cm), total dissolved solids (10,826 mg/L), alkalinity (1600 mg/L), bicarbonate (1925 mg/L), carbonate (950 mg/L), total hardness (607.5 mg/L), sodium (105.2 meq/L), chloride (412.5 mg/L), and fluoride (18.2 mg/L) were detected in a few groundwater stations. Since the 1970s, the LB watershed’s groundwater is seriously contaminated by arsenic and other heavy metals between boreholes and Lake Beseka after first characterizing the physicochemical and heavy metal characteristics of both.

The physicochemical properties of GW samples in both study areas, near and downstream of Lake Beseka, and the spatial and temporal differences between the two basins (at Awash-Awash and Awash Halidebi sub-basins) were confirmed. Exceeding values of pH (10.15), turbidity (950 mg/L, turned into muddy), electrical conductivity (15,645 µS/cm), total dissolved solids (10,826 mg/L), alkalinity (1600 mg/L), bicarbonate (1925 mg/L), carbonate (950 mg/L), total hardness (607.5 mg/L), sodium (105.2 meq/L), chloride (412.5 mg/L), and fluoride (18.2 mg/L) were detected in a few groundwater stations.

Our findings indicate that the LB watershed’s groundwater is seriously contaminated with heavy metals. The primary sources of the contaminants are most likely geogenic and anthropogenic. Examples of naturally occurring sources of pollution include geological processes, volcanic ash eruptions, changes in the climate, and interactions between surface and groundwater. On the other hand, anthropogenic activities include waste from urban and rural regions, hazardous chemical discharge, sugar plantations, inadequate sewage systems, industrial use, and agricultural practices which all contribute to groundwater pollution problems.
Our results show that groundwater wells near LB are enriched in As (GW8), V (GW8), Ga (GW8), Li (GW8), Rb (GW4), Cr (GW1), and Mn (GW3). Piezometer stations in the Amibera irrigation schemes display high concentrations of Cu, Sb, Sn, Co, Fe, Zr, Nb, Ni, Ti, and Al, with Ba found in GW9, and Mo, Zn, Ag, and Cd in GW11. Certain elements, such as Al, As, Mo, Mn, Cu, and V, exceed WHO limits at various sampling locations. However, groundwater quality at some stations (GW15 and GW16) is suitable for drinking. Conversely, 87.5% of sampled groundwater sources in the Beseka catchment and Amibera farm states are unsuitable for drinking. More than half of the sampled wells serve as primary household water sources for washing and cleaning, necessitating risk assessment tests due to frequent human contact, despite being unsuitable for ingestion.

The physical and chemical characteristics of both boreholes and surface water (Lake Beseka) might be associated by exchange subsurface flows, which are impacted by groundwater–surface water (Lake Beseka) (GW-SW) interaction. In groundwater, the main cations are Na\(^+\) > K\(^+\), and the principal anions predominantly observed are HCO\(_3^−\) > Cl. Similarly, the recent studies conducted on Lake Beseka revealed that the major cations and anions had the following order of abundance Na\(^+\) > K\(^+\) and HCO\(_3^−\) > Cl\(^−\), respectively. It is possible that the Beseka catchment, boreholes, and Lake Beseka primarily produce sodium bicarbonate water (Na-HCO\(_3^−\)). This implies that there are interactions between surface water and ground water (SW–GW) in the study area.

Only two stations near Awash 7 town are designated for drinking purposes. Residents near the study area, particularly in Addis Ketema and Werrer Office, occasionally face difficulties accessing clean tap water, relying heavily on groundwater resources for drinking despite mechanical, electrical, and pipe issues.

The Ministry of Water and Energy (MoWE) and other related authorities (MoILLs, MoA, EPA) should assess how land cover changes, river rejuvenation, and climate change affect groundwater systems. Intensive efforts are needed basin-wide and nationwide to account for groundwater interactions with other hydrological systems, such as rivers and lakes, and to ensure comprehensive groundwater services. Protecting groundwater from pollution is crucial, particularly in areas resistant to climate change. Further assessment of sugar plantations is also required. While this study is a good indicator of groundwater pollution, more comprehensive data collection in the upper, middle, and lower Awash is necessary to enhance current research findings. This includes testing wastewater quality and leachates from all sugar factories (Wonji, Methara, and Kesem Sugar factories), as well as rural sewage wastes within the study area.

In summary, the extent and sources of heavy metal (including As) and physicochemical contamination are investigated in this study, primarily with regard to groundwater quality and its relationship to surface water bodies (LB). Extensive studies on groundwater quality and quantity are desperately needed. Furthermore, vulnerable communities in the research region may benefit from the implementation of promising removal methods such as adsorption, reverse osmosis, and bioremediation.

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