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Chemical guality assessment of major brands of bottled mineral water available in the **Ethiopian market**

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| ARTICLE INFO | ABSTRACT | | | | | |
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| Article history: Received 02 Jul. 2022 Received in revised form 20 Sep. 2022 Accepted 27 Sep. 2022 | Assessing bottled mineral water with drinking water guidelines set by the World Health Organization (WHO) and the Ethiopian Standard Agency (ESA) are highly relevant for practitioners, bottling companies, managers, regulators, and policymakers regarding water supply particularly bottled water. The present study was carried out to report the physicochemical quality of six branded bottled mineral water widely available in the Ethiopian market and compare them with drinking | | | | | |
| Keywords: Bottled mineral water; Quality parameters; TDS; PH; Chemical quality | water standards. The investigated physicochemical parameters were pH, electrical conductivity (EC), total dissolved solids (TDS), chloride ion (CL [*]), nitrate ion (NO ₃ [*]), potassium (K ⁺), sodium (Na ⁺), zinc (Zn ⁺), iron (Fe ³⁺), calcium (Ca ²⁺) and magnesium ion (Mg ²⁺) using standard analytical techniques. Flame Atomic Absorption Spectroscopy (FAAS) was used to determine the number of metal elements. The Ultra Violet-Visible Spectrophotometer (UV-VIS) analysis was used to determine the amount of NO- in the bottled mineral water. The TDS and CL-values were determined by using gravimetric and volumetric methods. The study results revealed that the values of the quality parameter concentrations measured experimentally were slightly varied from the labeled values on the bottle. However, all brands were within EAS and WHO limit values for drinking water. The calculated correlation coefficient between the bottled mineral water, and between TDS and the pH concentration in bottled mineral waters was 0.99, 0.77 and 0.94, respectively. The study also verified that all the studied bottled water brands are safe for human consumption. | | | | | |

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1. Introduction

Bottled mineral water is defined as any potable drinking water packaged in plastic or glass water bottles for sale that is sealed in food-grade bottles or other sanitary containers and intended for human Bottled mineral water is water from a mineral spring that contains various minerals, and its use has increased even in countries where clean tap water is available. The bottled water industry began in 1970, and with the promotion of this product, the bottled

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consumption.

water market grew to three times the size of the soft drink market bv late 1990. Humans consume water in a variety of forms, one of which is bottled water, which comes from a variety of sources (1). Because of health concerns and the limited availability of freshwater resources in many parts of the world, consumers prefer bottled water. It is well understood that clean water is necessary for healthy livelihoods (2-4). Bottled mineral water is generally regarded as safe for human consumption, especially for longdistance travelers. It serves as the only reliable source of drinking water. However, several studies have found that bottled water does not acceptable standards. Mineral always meet bottled water typically contains minerals such as magnesium, calcium, sodium, and zinc, and according to recent research, they're a fairly effective wav to increase mineral your intake. According to the latest report, mineral water has some legitimate health benefits. It is widely accepted as potable, which means it is free of physical, chemical, and microbiological contaminants that could cause adverse health effects on humans if consumed (5, 6). Bottled mineral waters are becoming more popular all over the world (7). According to surveys, consumers are turning to bottled mineral water as a healthier alternative to soft drinks 9). (8, For ingesting-water quality, verification is the use of methods, tactics, or exams similar to those utilized in operational tracking to determine whether the overall performance of the ingesting-water delivery is in compliance with the stated targets mentioned by way of the healthprimarily based goals.

With the intention of determining which parts are certainly of challenge, it will likely be vital to adopt an ingesting-water great evaluation. The guiding principle values are established on the basis of global risk assessments of the health outcomes associated with exposure to chemicals in water. Those guidelines provide tenet values for a plethora of additional chemical contaminants that may or may not affect any particular water supply. In controlling consuming-water components, trying out approaches normally checks whether the product meets the specifications. Wellness targets, incorporating numeric recommended limits and other targets described in drinking-water quality guidelines, are provided as the scientific basis for developing national or regional numerical drinking-water quality standards (10, 11). There is no universally applicable approach, and the nature and form of drinking-water standards may differ across regions. This may result in national standards that differ significantly from these guidelines, both in scope and risk targets. Communities served, as well as major water users, should be involved in standard-setting to ensure that standards are acceptable to consumers (12). People living in developing countries lack access to clean water due to environmental pollution and most diseases are caused by the consumption of contaminated water (13).The chemical contaminants in potable water include: some heavy metals, non-metals, disinfection by-products, nitrate, nitrite, pesticides and sulfate (14-17).

The levels of chemicals in drinking water are sometimes high enough to cause acute health effects. Polluted drinking water causes many diseases such as diarrhea, vomiting, gastroenteritis, dysentery and kidney problems (18-21). Several studies on the determination of water quality indexes for various water bodies in various countries around the world have been publicly released. Momani (22) examined the chemical evaluation of bottled drinking water using IC, GC, and ICP-MS; Sasikaran et al (23) assessed the quality of bottled drinking water sold in the Jaffna peninsula by analyzing the physical, chemical, and microbial contents and comparing them to the recommended Sri Lankan Standard (SLS) values. Mihayo and Mkoma (24) investigated the chemical water quality of bottled drinking water brands sold in Mwanza, Tanzania; and Dinelli et al (25) conducted a comparison study in Italy between bottled mineral water and tap water. Ghrefat (14) investigated the classification and evaluation of commercially bottled drinking water in Saudi Arabia; Toma et al (26) investigated the use of a water quality index to assess water quality in some bottled water in Erbil City, Kurdistan Region, Iraq; and Bolawa and Adelusi (17) determined the heavy metal profile in bottled water samples obtained from various markets in Lagos, Nigeria. Akoteyon et al (27) investigated the determination of water quality parameters and suitability of underwater bodies in Shimago Town, Karnataka, India; Boah et al (28) investigated the mathematical

computation of the water quality index of Vea Dam in Ghana's Upper East Region; and Khare et al (29) investigated the assessment of the water quality index of Robertson Lake in Jabalpur, India, and the use of test results in remote sensing applications. Bouslah et al (30) used the weighted arithmetic index method to assess the water quality index of Koudiat Medouar Reservoir in Northeast Algeria; Ansari and Hemke (31) evaluated the water quality index for assessment of water samples from in Chandrapur City, India. different zones Akhbarizadeh et al (32) concentrated on emerging contaminants and contamination linked to the types of plastic used in China for water bottles. Alasdair et al (33) conducted a systematic review and meta-analysis of publicly available studies on bottled water quality and associated health outcomes in China published between 1995 and early 2016.

The chemical quality of drinking bottled mineral water has also been investigated in order to assess the quality of drinking water in Ethiopian regions (6, 34-42). Several studies on the quality of bottled water in Ethiopia have been conducted, including: Seda et al (43) investigated the levels of common ions in bottled mineral waters consumed in Addis Abeba; Mekonnen et al (20) evaluated the chemical quality of major brands of bottled water sold in Gondar Town, Ethiopia. Elisabet et al (44) determined the water quality index of bottled water sold in Addis Abeba, Ethiopia, and compared them to WHO values.

Mekuanint (45) investigated the drinking water quality of the north Mecha district, Amhara Region, Ethiopia, using 26 drinking water samples collected from dweller community water points during the dry seasons of 2020 and subjected to analysis of physicochemical parameters, bacteriological parameters, and trace metal levels.

Many researchers have studied the qualities of bottled mineral water using various parameters. Horton (46) developed the water quality index, which was later used by several workers to assess the quality of various water resources. Boyd (47) investigated the contaminants in drinking water and discovered that microbiological pathogens are the most important and necessary risk exhibited by drinkable water. Venturini and Frazo (48) conducted a systematic review that only looked at fluoride concentrations in bottled water. Rosinger et al (49) studied the parameters of bottled water and discovered that a lack of fluoride concentration in drinking water is detrimental to health. Klevay (50) also came to the conclusion that the hardness of bottled water is important for human health. Harmon et al (51) investigated the taste-related chemical composition causes of tap, bottled, and recycled water. Font-Ribera et al (52) investigated trihalomethane concentrations in tap water as a determinant of bottled water and concluded that it is unpleasant and that the differences are not always discernible.

As stated above, the researchers made an assessment of the chemical quality of bottled water marketed in a specific town or region of Ethiopia, but they didn't consider the nationally distributed brands of bottled mineral water marketed in most areas of Ethiopia. Additionally, they don't consider all these water quality parameters: pH, TDS,

cations (Ca²⁺, Mg²⁺, K⁺, Na⁺) and anion (Cl⁻, NO₃-) and most of their measurements are only on the packaged bottled water, and they don't compare the quality parameters with the original in the soil. This study was conducted to assess the quality of bottled mineral waters in Ethiopia on selected nationally distributed six brands of bottled mineral water. The water quality parameters of pH,

TDS, Ca²⁺, Mg²⁺, K⁺, Na⁺, Cl⁻ and NO₃⁻ were assessed to evaluate the quality of bottled mineral waters in Ethiopia. Therefore, the aim of this study is to assess the physico-chemical quality parameters of bottled mineral water consumed in Ethiopia and compare the results with the labels by the manufacturers, WHO and Ethiopian Standard Agency (ESA) standards and establish relationships between the various parameters that may help estimate the validity of the labeled results.

2. Materials and Methods

2.1. Collection and Preparation of Samples Six brands of bottled mineral water samples (brands 1, 2, 3, 4, 5 and 6) that are often consumed in Ethiopia were acquired at random from local marketplaces and were chosen based on the pH

value of seven observables, TDS value, and public interest. Table 1 presents the classification of the bottled water samples in terms of brands, types, quantity, volumes and manufacture. All sample bottles were kept sealed and refrigerated at 4°C until the time of analysis. Then, the instrument was calibrated while instrumental procedures were used and recorded with the result of the analysis. The results of the tests on bottled mineral water for each sample have been reported, and the mean value of triplicate was collected.

2.2. PH, EC and TDS Determination Procedure

The pH, which is affected by carbon dioxide and the carbonate-bicarbonate equilibrium, is a key indicator of water quality. pH is an important variable in assessing water quality because it influences many biological and chemical processes within a body of water, as well as all processes associated with water supply and treatment.

The WHO has recommended a pH range of 6.5 to 8.5 as a safe limit. After calibrating the pH meter, the pH values were estimated. A total of 250 mL of samples were collected and transferred into six different clean beakers, and the pH of the water samples was measured using a pH meter model 2432. The pH meter was calibrated with buffers 4 and 7 which had been prepared ahead of time. Conductivity was measured using a conductivity meter. The total dissolved solids (TDS) was measured using a gravimetric method. The TDS was calculated by weighing a known volume of the sample before and after drying at 103°C. The liquid sample values and solids levels were all reported in milligrams per liter. The weight of the 250 mL clean, dried glass beaker was measured.

Then, using a measuring cylinder, measure 100 mL of bottled water and transfer it to a clean, dried beaker. After that, put the beaker on the hot plate maintained at 103°C until the evaporation completely finished and cooled the beaker.

Also measured was the weight of the cooled beaker. Finally, find out the weight of solids in the beaker by subtracting the weight of the clean beaker from the weight of the cooled beaker and the total dissolved solids (TDS) calculated by the formula:

$$TDS (mg/L) = \frac{mg(solid) \text{ of beaker } x1000}{\text{volume of sample}}$$

2.3. Reagent Preparation and Chloride Ion Estimation Procedure

The 0.412 g of sodium chloride (NaCl) was measured by an electronic balance and it was transferred to the beaker that contained distilled water and mixed by a glass rod.

Then the standard NaCl solution was transferred to a 250 mL volumetric flask and filled up to its marks. The 1.1985 g of silver nitrate was measured by electronic balance and transferred to silver nitrate in 250 volumetric а mL. flask It was filled with distilled water up to its marks. Then they standardized it against 0.0282 M of NaCl solution and stored it in an amber bottle. After that, the 25 g of potassium chromate was measured by an electronic balance and transferred to the beaker containing distilled water.

A few drops of silver nitrate solution are added until a slightly red precipitate is formed. Then they allowed it to stand for 12 h. After 12 h, they filtered the solution using filter paper and diluted the filtrate with 1000 mL of distilled water.

The amount of chloride present in water was determined by titration of the water sample with silver nitrate solution (53, 54).

The silver nitrate reacted with chloride ions in a 1:1 mole of AgNO₃ and chloride. Silver chloride precipitates quantitatively before red silver chromate is formed.

The end of the titration was indicated by the formation of red silver chromate from excess silver nitrate. The results were expressed in mg/L of chloride ions. The burette was rinsed with silver nitrate solution and filled with silver nitrate solution to a concentration of 0.0282 N. It was also set to zero and secured to the burette in the stand before extracting 20 mL of bottled mineral water from a sample of a 250 mL conical flask. A potassium chromate indicator was added to get a light yellow color and the sample was titrated against a silver nitrate solution until the color was changed to a brick-red color. Finally, the volume of silver nitrate that was used for the sample was titrated and repeated the procedure for concentrated values. Then the chloride ion concentration was calculated by the formula:

Chlorides (mg/ L) =
$$\frac{(VS-VB) \times \text{Normality } x 35.45 \times 1000}{\text{Volume of sample taken}}$$
 (2)

Where, VS is the volume of sample and VB is the volume of blank.

2.4. Nitrate Test Procedure

When a water sample containing nitrate ions is treated with Nitra Ver 5 Nitrate Reagent Powder Pillow, a yellow-reddish compound is created. The quantity of nitrate nitrogen can be determined by a UV-Spectrophotometer using Nitra Ver 5 Nitrate Reagent powder. All test tubes were washed, rinsed by the samples and filled with 10 L of bottled water samples. One Nitra Ver 5 nitrate reagent powder was added to test tube samples, a stopper was applied, the instrument timer was started, and the cell was vigorously shocked until the timer expired. Again, the timer started and it was shocking that the reaction period would begin up to five min after an amber color was developed if nitrate was presented. Then a blank was prepared, the other test tube was filled with 10 mL of bottled water samples, and they wiped the blank test tube clean and it was inserted into the cell holder. The instrument was displaying that it would show 0.0 mg/L NO₃. Finally, within one min of the timer expiring, I wiped the prepared samples and inserted them into the cell holder. The result was read as X mg/LNO_3 , where X represents the nitrate

concentration of each sample (see Table 1).

2.5. Analytical Procedures for Metal Analysis

The 100 mL of water sample was measured into a beaker, and then 1.5 mL of concentrated HNO_3 acid was added and slowly boiled on a hot plate until the solution evaporated to about 20 mL. Also, 1.5 mL of concentrated HNO_3 acid was added and the beaker was covered and heated.

The solution is then heated continuously until it appears light-colored and clear, indicating that digestion is complete. During digestion, the material was not permitted to dry out. Furthermore, 1 mL of concentrated HNO₃ was further added to dissolve the

remaining residue. The beaker walls and the watch glass were washed with distilled water and then transferred into a 50 mL plastic bottle and made to the mark with distilled water. For intermediate standard solutions (10 mg/L) in a 100 mL volumetric flask and working standards using deionized water, atomic absorption spectroscopic standard solutions of 1000 mg/L were utilized. Working standards of metal solutions were produced by dilution with deionized water in a 50 mL volumetric flask. By placing the produced standard solutions through an atomic absorption spectrometer, four points of the calibration curve were generated. The sample solutions were sucked into the AAS instrument immediately after calibration, and direct observations of metal concentrations were obtained. On each sample, three replicate determinations were performed. The analytical procedures were employed for the determination of elements in six blank samples.

2.6. Statistical Analysis

The science of collecting data and uncovering patterns and trends is known as statistical analysis. In statistics, Pearson correlation is the most commonly used. The Pearson correlation coefficient (R) was used to assess the chemical qualities of major brands of bottled mineral water and compare them to WHO and ESA drinking water guidelines. The correlation coefficient is a statistical measure of the strength of the relationship between two variables' relative movements. A correlation of -1.0 indicates that there is a perfect negative correlation, whereas a correlation of 1.0 indicates that there is a perfect positive correlation. The form of the relationship between the independent and dependent variables is expressed by the correlation expression, whereas the regression expression expresses the degree of association between two variables.

3. Results

3.1. Classification of bottled water brands based on TDS, pH and EC perspectives

To classify water types, various hydro-chemical classification systems are available. The European Union (EU) mineral water directive was used in this case to classify the investigated water by evaluating the obtained TDS. Classification systems are also used to identify chemical similarities and differences between water brands. The chemical composition criteria for the EU mineral water directives are very low mineral concentration (TDS<50 mg/L), low mineral concentration (TDS 50-500 mg/L), intermediate mineral concentration (TDS 500-1500 mg/L), and high mineral concentration (TDS>1500 mg/L) (55). The classification of currently observed data for bottled water is shown in Table 1, which is organized according to the EU mineral water directive. It may be seen that the coded brand 2 is falling into the "very low mineral concentration" class as the TDS value was found to be 14.33 mg/L, whereas the coded brands (brand1, brand 3, brand 4, brand 5 and brand 6)

are falling into the low mineral concentration class as the TDS value was found to be 72.67 mg/ L, 80.31 mg/L, 56.67 mg/L, 99.58 mg/L and 157.84 mg/L, respectively.

The pH of six branded samples of mineral drinking water was measured using а standardized digital pH meter. The 250 mL of each mineral drink sample was placed in a beaker, and the pH of the samples was determined by dipping the glass electrode in the samples. The observed pH values, including other data, are tabulated in Table 1. From Table 1, it is noticed that the pH values appeared in the range of 7.11-7.68. The result suggests that all the water samples are slightly basic. Table 5 represents the values of different parameters of drinking water from ESA and WHO. From Tables 1 and 5, it may be seen that all the water of the coded brands (brand1, brand 2, brand 3, brand 4, brand 5 and brand 6) stands at the recommended pH value of ESA and WHO, whereas the analyzed water samples of the coded brands (brand 2, brand 3, brand 4, brand 5 and brand 6) stand slightly different from the labeled values, but all are accepted values. Bottled water EC values were found to be in the range of 31.8-266.7 S/cm. The difference between the lowest and highest EC values is significant, and the average is 149.25 S/cm. It is well understood that EC measures a specimen's natural salt concentrations. As a result, it was determined that sample code brand 2 contains low ionic concentrations, whereas sample code brand 6 contains high ionic concentrations. Looking at the obtained TDS values, it can be seen that the values

were estimated to be in the 14.33-157.67 mg/L range. The remarkable fact is that brand 2 bottled water had the lowest EC and TDS values, while brand 6 bottled water had the highest EC and TDS values. Such coincidences between the EC and TDS values may be taken as the accuracy of the measurements. Therefore, total dissolved and electrical conductivity have a direct proportionality.

3.2. Chloride and Nitrate Ions

The volumetric titration method with potassium chromate indicator was used to determine the chloride concentration in the sample. The chloride concentration of bottled mineral water samples was determined by pouring 20 mL of sample into a conical flask, adding 2-3 drops of potassium chromate indicator, and titrating against 0.0282 M of silver nitrate until the solution turned brick-red. As the silver nitrate solution is gradually added, a silver chloride precipitate forms, as shown in the equation below:

 $Ag^{+}(aq)+Cl^{-}(aq) \rightarrow AgCl$ (3) When all of the chloride ions have precipitated, the titration is complete. Further silver ions react with the chromate ions in the indicator, potassium chromate, to form a red-brown silver chromate precipitate as shown in the equation below:

$$2Ag+(aq)+CrO^{2} \rightarrow 2AgCrO \quad (s) \tag{4}$$

As shown in the equation below the concentration of silver ions rises, a reddish-brown silver chromate precipitate is formed.

| Brands Code | рН | TDS (ppm) | EC (µS/cm) | Cl ⁻ (ppm) | NO ₃ - (ppm) |
|----------------|------|-----------|------------|-----------------------|-------------------------|
| Brand1 | 7.26 | 72.67 | 143.50 | 21.50 | 7.40 |
| Brand2 | 7.11 | 14.33 | 31.80 | 7.98 | 1.06 |
| Brand3 | 7.41 | 80.01 | 98.90 | 7.99 | 1.66 |
| Brand4 | 7.16 | 56.67 | 80.30 | 6.98 | 2.63 |
| Brand5 | 7.56 | 99.58 | 125.60 | 12.99 | 1.60 |
| Brand6 | 7.68 | 157.67 | 266.70 | 10.89 | 1.70 |

Table 1. Analysis value of pH, TDS, EC, Cl- and NO -

Table 2. Analyzed concentration of metals in the samples (ppm).

| Brands Code | Mg | Ca | K | Na | Fe | Zn |
|-------------|------|------|------|-------|------|------|
| Brand1 | 0.64 | 2.56 | 6.44 | 7.24 | 0.03 | BLD |
| Brand2 | BDL* | 0.27 | 0.82 | 3.41 | 0.03 | BLD |
| Brand3 | 0.90 | 2.52 | 2.04 | 5.40 | 0.12 | 0.02 |
| Brand4 | 0.73 | 2.02 | 2.38 | 3.50 | 0.03 | BLD |
| Brand5 | 3.01 | 0.15 | 5.05 | 17.00 | 0.03 | BLD |
| Brand6 | 2.91 | 8.64 | 2.45 | 7.88 | 0.03 | BLD |

Table 3. The physical and aggregate properties of the investigated bottled water brands, as well as the documents associated with the brands' labels.

| Brands | pН | | TDS (ppm) | | EC (μS/cm) | | Cl- (ppm) | | NO ₃ -(ppm) |
|--------|------|------|-----------|--------|------------|---|-----------|-------|------------------------|
| Code | М | L | М | L | М | L | М | L | М |
| Brand1 | 7.26 | 7.00 | 72.67 | 72.00 | 143.50 | - | 21.50 | 10.00 | 7.40 |
| Brand2 | 7.11 | 7.20 | 14.33 | 8-17 | 31.80 | - | 7.98 | - | 1.06 |
| Brand3 | 7.41 | 7.92 | 80.01 | 54.50 | 98.90 | - | 7.99 | 1.70 | 1.66 |
| Brand4 | 7.16 | 7.10 | 56.67 | 70.00 | 80.30 | - | 6.98 | 4.00 | 2.63 |
| Brand5 | 7.56 | 7.20 | 99.58 | 89.00 | 125.60 | - | 12.99 | 6.63 | 1.60 |
| Brand6 | 7.68 | 7.37 | 157.67 | 170.00 | 266.70 | - | 10.89 | 5.67 | 1.70 |

This is considered an indication that all of the chlorides has precipitated. When compared to the other samples, the examined samples of brand 4 bottled mineral water quickly display color changes. It demonstrates that the chloride content of brand 4 bottled mineral water is low. In comparison to other bottled mineral waters, brand 1 bottled mineral water has high chloride content. The concentration of nitrates in the samples is detected spectrophotometrically. Detection of nitrates from water samples is analyzed by taking 10 mL of sample in a test tube, adding one NitraVer 5 Nitrate reagent powder to it, and reading the results in mg/L NO₃ used as a spectrophotometer. The results confirmed that brand 1 bottled mineral water showed that high visible amber color compared to other bottled mineral water before determining the value of nitrate concentration. The analyzed values of nitrate concentration the highest value was obtained in brand 1 water and the lowest value was obtained in brand 2 bottled mineral water. It showed that brand 1 bottled mineral water was contaminated by nitrate compared to other bottled mineral water samples.

3.3. The Concentration of Metals in the Samples

The samples were analyzed for Zn, Fe, Na, K, Mg and Ca metal elements using an atomic absorption spectrometer. The results were presented as the average of the determination of triplicate records of the three sample solutions for each water sample. The results of metal concentration parameters are given in Table 2. The concentration levels of the ionic components present in the water samples are: 0.15-8.64 mg/L for Ca; BLD-3.01 mg/L for Mg; 0.03-0.12 mg/L for Fe; 0.82-6.44 mg/L for K; 3.50-17.0 mg/L for Na and BLD-0.02 mg/L for Zn. The main compositions of mineral water, such as calcium, sodium and potassium, were obtained at large values compared to other metal compositions.

3.4. A Comparison of the Analyzed and Labeled Values

As shown in Table 5, the majority of bottled mineral water factories did not label the following water quality parameters: EC, Fe, NO3, and Zn. It should be noted that the information contained in the packages varies depending on the results obtained.

3.5. The Comparison of Analyzed Values with ESA and WHO

The WHO recommends that social, economic and environmental factors be taken into account through a risk-benefit approach when adapting the guideline value to national standards. Because the WHO guidelines for drinking water quality are intended to be the scientific place to start for standards development, including bottled water, actual standards may deviate from the guidelines from time to time. The Ethiopian standard was developed in March 2001 for drinking water, depending on the WHO guidance and considering the geographical, economic and cultural values of the country. To compare the study's results, national and international guidelines developed in accordance with WHO and ESA guidelines were used in the current study (see Tables 3 and 4).

| Brands Code | Mg | Mg | | Ca | | K | | Na | | | Zn) | |
|----------------|------|------|------|------|------|------|------|------|------|-------|------|--|
| | М | L | М | L | М | L | М | L | М | L | М | |
| Brand1 | 0.64 | 7.34 | 2.56 | 13.9 | 6.44 | 3.30 | 7.24 | 8.9 | 0.03 | - | BDL | |
| Brand2 | BDL | 0.40 | 0.27 | 4.20 | 0.82 | 0.18 | 3.41 | 0.44 | 0.03 | - | BDL | |
| Brand3 | 0.90 | 1.39 | 2.52 | 5.74 | 2.04 | 0.39 | 5.40 | 2.6 | 0.12 | - | 0.02 | |
| Brand4 | 0.73 | 5.00 | 2.02 | 10.5 | 2.38 | 1.20 | 3.50 | 4.8 | 0.03 | - | BDL | |
| Brand5 | 3.01 | 6.63 | 0.15 | 1.95 | 5.05 | 7.23 | 17.0 | 2.9 | 0.03 | - | BDL | |
| Brand6 | 2.91 | 3.30 | 8.64 | 23.5 | 2.45 | 5.0 | 7.88 | 8.4 | 0.03 | 0.005 | BDL | |

Table 4. Concentrations of major metals in investigated bottled mineral water brands with label's document (BDL=Below Detection Limit), units in ppm.

Table 5. The comparison of current results with some national and international guidelines (57, 58) (BDL=Below Detection Limit), units in ppm.

| Brand code | pН | TDS ppm | EC µS/cm | Mg | Ca | K | Na | Fe | Zn | Cl- |
|------------|---------|---------|----------|------|------|------|-------|------|------|-------|
| WHO | 6.5-8.5 | 1000 | - | - | - | - | 200 | 0.3 | 3-5 | 250 |
| ESA | 6.5-8.5 | 1000 | - | 50 | 75 | - | 200 | 0.3 | 5 | 250 |
| brand6 | 7.68 | 157.7 | 266.70 | 2.91 | 8.64 | - | - | 0.03 | BLD | 7.88 |
| brand1 | 7.26 | 72.67 | 143.50 | 0.64 | 2.56 | 6.44 | 7.24 | 0.03 | BLD | 21.5 |
| brand2 | 7.11 | 14.33 | 31.80 | BLD | 0.27 | 0.82 | 3.41 | 0.03 | BLD | 7.89 |
| brand3 | 7.41 | 80.01 | 98.90 | 0.90 | 2.52 | 2.04 | 5.40 | 0.12 | 0.02 | 7.99 |
| brand5 | 7.56 | 99.58 | 125.60 | 3.01 | 0.15 | 5.05 | 17.00 | 0.03 | BLD | 12.99 |
| brand4 | 7.16 | 56.67 | 80.30 | 0.73 | 2.02 | 2.38 | 3.5 | - | BLD | 6.98 |

3.6. The Relationship between Metal Concentrations in Bottled Water and Soil Samples The correlation of the concentration of metal in bottled water with soil samples showed significant differences between the concentrations of the metal in the determination for all the analyzed. As shown in Fig. 1, the Zn concentration in the bottled water and Fe in the soil samples have the smallest concentrations of the other metals. Na has observed the highest concentration of other metals in both bottled water and soil samples. All bottled mineral water concentrations are slightly higher than all soil samples' metal concentrations.

Fig. 2 shows the correlation coefficient (R) between the metal concentration of bottled water and the soil sample. By using Pearson's correlation coefficient, the calculated correlation coefficient between the bottled water and the soil sample was obtained to be a strong positive correlation of value 0.99. This showed that there was a strong positive relationship between bottled water and soil sample parameters. As shown in Fig. 3 and 4, the correlation of

some dissolved solids (Ca, Na and K) and TDS concentration in bottled mineral water was determined for six branded bottled mineral water. The correlation coefficient (R) between some dissolved solids and the TDS concentration in bottled mineral water was 0.77, and this correlation coefficient was slightly positive. This showed that there was a slightly positive match between some dissolved solids and the TDS of water quality parameters.

3.7. The Correlation of TDS and pH Total Dissolved Solids (TDS) had a significant positive correlation with pH. For a variety of reasons, it was critical to keep a check on the TDS and pH of drinking water. According to Fig. 5, the TDS values increase as long as the pH values slightly increase. The pH value of mineral water is greater than seven because, in the case of alkali and alkaline metals, water from natural springs is called alkaline water, which is rich in alkali. The branded bottled mineral waters of brands 2 and 6 have the smallest and highest values for both TDS and pH, respectively. As shown in Fig. 6, the correlation coefficient (R) between TDS and pH concentration in bottled mineral waters was 0.94, and this correlation coefficient was a significant positive correlation. This showed that there was a significant positive correlation match between the TDS and pH values of bottled mineral water.

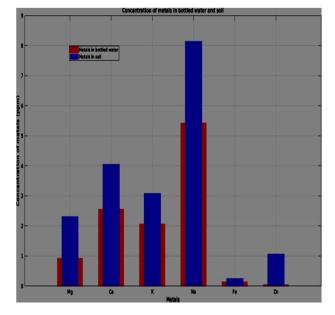


Figure 1. The comparison of metals concentration between bottled water and soil samples

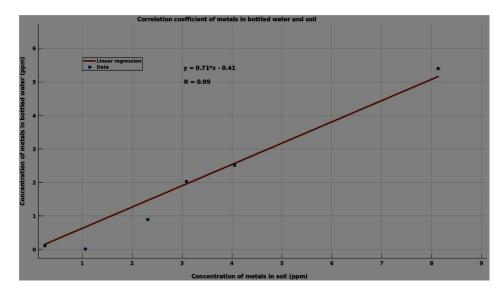


Figure 2. The correlation coefficient between the bottled water and the soil sample of metal concentrations.

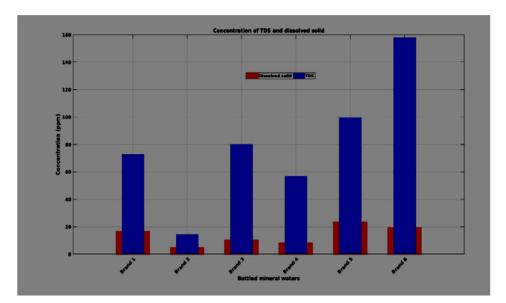


Figure 3. Comparison of TDS concentration with dissolved solid concentration

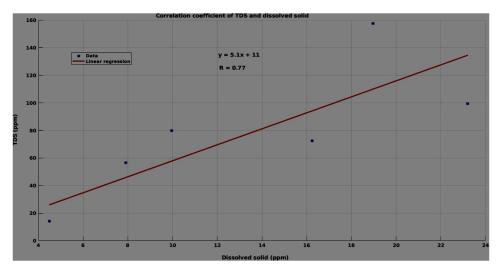


Figure 4. The correlation coefficient of TDS and dissolved solids for six branded bottled mineral waters

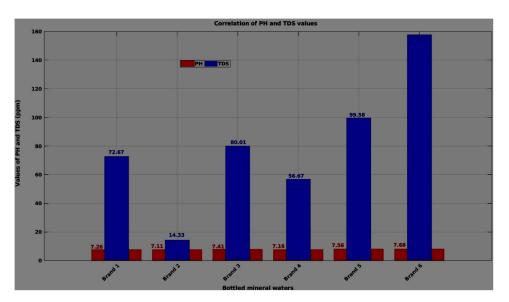


Figure 5. The bar graph of the relationship between TDS and pH value of branded bottled mineral waters.

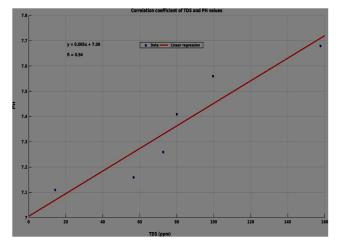


Figure 6. The correlation coefficient of TDS versus pH for six branded bottled mineral waters.

4. Discussions

The WHO published guidelines for drinking water quality which many countries use as the basis to establish their own national standards (56). To compare the study's results, national and international guidelines developed in accordance with WHO and ESA guidelines were used in the current study (see Tables 3 and 4). According to these standard guidelines, the results satisfied the given international and national standards. As a result, all the water samples are safe to drink. All bottled mineral water concentrations are slightly higher than all soil samples' metal concentrations (Fig. 1).

The higher concentration of Mg, Ca, K, Na, Fe and Zn in the soil sample compared to the bottled mineral water could be a result of a higher rate of mineralization in the soil sample (59).

By using Pearson's correlation coefficient, the calculated correlation coefficient between the bottled water and the soil sample was obtained to be a strong positive correlation of value 0.99 (Fig. 2). This there was a strong positive relationship between bottled

water and soil sample parameters. The correlation coefficient (R) between some dissolved solids and the TDS concentration in bottled mineral water was 0.77, and this correlation coefficient was slightly positive (Fig. 3 and 4). This showed that there was a slightly positive match between some dissolved solids and the TDS of water quality parameters. Also, the summation of the main composition concentration is less than the TDS, which is similar to the previous reports (60). The TDS values rise as long as the pH values gradually rise. In the case of alkali and alkaline metals, water from natural springs is referred to as alkaline water, which is rich in alkali, so mineral water has a pH value greater than seven. The TDS and pH values of the branded bottled mineral waters of brands 2 and 6 are lowest and highest, respectively. The correlation coefficient (R) between TDS and pH concentration in bottled mineral waters was 0.94, which is a significant positive association. This demonstrated a significant positive association between the bottled mineral water's TDS and pH levels (Fig. 5 and 6).

When there is a high level of TDS or a low pH in a water source, it is likely that threr are other dangerous chemicals in the water. TDS and pH are both easy to measure, and if something happens to the water, such as pollution, both TDS and pH levels are likely to vary, thus keeping track of thoes change can serve as an early warning signal that something is wrong with the water. As a results, its critical to keep a focus on TDS and pH levels so that if they change, users can react quickly (61).

5. Conclusion

This study gives an insight into the major quality constituents of six bottled mineral water brands currently sold in Ethiopian markets. The important parameters such as pH, total electrical conductivity, total dissolved solids, nitrate, chloride, magnesium, calcium, sodium, potassium, iron and zinc were analyzed. The findings revealed that bottled water brands were safe for human consumption. The metal concentrations in all bottled mineral waters are slightly higher than the metal concentrations in all soil samples. The calculated correlation coefficient between the bottled water and the soil sample and the correlation coefficient we obtained was a strong positive 0.99. The correlation coefficient (R) between some dissolved solids and the TDS concentration in bottled mineral water was 0.77, and this correlation coefficient was slightly positive. The correlation coefficient (R) between TDS and pH concentration in bottled mineral waters was 0.94, and this correlation coefficient was a significant positive correlation. The measured constituents in the brands are within the standard limits set by ESA and WHO for drinking water. However, the physicochemical quality of the brands studied varied, which could be attributed to a variety of factors such as the natural environment, the composition of the source water, and the type of treatment/purification technique(s) used during production. In general, the concentration of analyzed water quality parameters values in this study was compared to the values on the label and showed a slight difference.

The TDS value of bottled mineral water was greater than the summation of the main composition of analyzed dissolved solid materials, and as long as the TDS value increased, the pH values slightly increased.

Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could appear to have influenced the work described in this paper.

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