**ORIGINAL ARTICLE** 



# Physicochemical and heavy metal constituents of the groundwater quality in Haramaya Woreda, Oromia Regional State, Ethiopia

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#### Abstract

In many developing countries, water supply sources are not well protected. However, many people depend on such water sources for their daily consumption. Hence, this study assessed the physicochemical and heavy metal constituents of drinking water and evaluated the quality of the potable water supply in Haramaya Woreda. Water samples were taken from five sampling sites. Physicochemical and heavy metal parameters were analyzed according to the procedures outlined in the APHA (Standard methods for the examination of water and wastewater, 21st edn. Washington DC, 2008). The results showed that the acidity ranged from  $32.67 \pm 1.15$  to  $45.33 \pm 0.58$  mg/L, alkalinity from  $276.67 \pm 1.15$  to  $391.00 \pm 1.73$  mg/L, total hardness from  $271.67 \pm 0.57$  to  $410.67 \pm 0.58$  mg/L, chloride from  $32.90 \pm 1.32$  to  $85.77 \pm 0.25$  mg/L, sulfate from  $194.33 \pm 0.58$  to  $250.67 \pm 0.58$  mg/L, nitrate from  $1.93 \pm 0.15$  to  $13.33 \pm 1.53$  mg/L, phosphate from  $0.015 \pm 0.001$  to  $0.053 \pm 0.002$  mg/L, COD from  $9.33 \pm 0.702$  to  $24 \pm 1.000$  mg/L, Ca from  $61.13 \pm 1.06$  to  $103.17 \pm 1.26$  mg/L, Cd not detected to  $0.069 \pm 0.004$  mg/L, Ca from  $61.13 \pm 1.06$  to  $103.17 \pm 1.26$  mg/L, Cd not detected to  $0.069 \pm 0.004$  mg/L, Ca from  $61.13 \pm 1.06$  to  $103.17 \pm 1.26$  mg/L, Cd not detected to  $0.069 \pm 0.004$  mg/L, Ca from  $61.13 \pm 1.06$  to  $103.17 \pm 1.26$  mg/L, Cd not detected to  $0.069 \pm 0.004$  mg/L, Ca from  $61.13 \pm 1.06$  to  $103.17 \pm 1.26$  mg/L, Cd not detected to  $0.069 \pm 0.004$  mg/L, Ca from  $61.13 \pm 1.06$  to  $103.17 \pm 1.26$  mg/L, Cd not detected to  $0.069 \pm 0.004$  mg/L, Ca from  $61.13 \pm 1.06$  to  $103.17 \pm 1.26$  mg/L, Cd not detected to  $0.069 \pm 0.004$  mg/L, Ca from  $61.13 \pm 1.06$  to  $103.17 \pm 1.26$  mg/L, Cd not detected to  $0.069 \pm 0.004$  mg/L, Ca from  $61.13 \pm 1.06$  to  $103.17 \pm 1.26$  mg/L, Cd not detected to  $0.069 \pm 0.004$  mg/L, Ca from  $61.13 \pm 1.06$  to  $103.17 \pm 1.26$  mg/L, Cd not detected to  $0.069 \pm 0.004$  mg/L, Ca from  $61.13 \pm 1.06$  to  $103.17 \pm 1.26$  mg/L, Cd not detected to  $0.069 \pm 0.004$  mg/L, Ca from  $61.13 \pm 0.004$  mg/L, Ca f Cr not detected to  $0.133 \pm 0.002$  mg/L, Fe from  $0.123 \pm 0.015$  to  $0.530 \pm 0.008$  mg/L, Pb not detected to  $0.217 \pm 0.040$  mg/L, Zn from  $0.135 \pm 0.002$  to  $0.170 \pm 0.003$  mg/L, and Cu from  $0.221 \pm 0.002$  to  $0.288 \pm 0.002$  mg/L. Statistically significant differences (p < 0.05) among the same parameter from different sites were observed. Except Pb, Cr, Cd, and water hardness, the majority of physicochemical and heavy metal values were within the maximum permissible limits of WHO and Ethiopian drinking water quality standards. The constituents outside the limits of the quality standards might cause health problems in the local communities. Therefore, strict monitoring and water treatment is needed to ensure quality sources before the water supply is used for human consumption.

Keywords Water management · Water pollution · Water quality · Water supply · Ethiopia

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# Introduction

Water is a naturally available resource indispensable for the survival of life on the earth and for sustainable socioeconomic development (Getachew et al. 2015). Access to water and sanitation is acknowledged as a fundamental human right in all the nations across the global. Naturally, water covers almost three-fourths of the earth's surface, but accessing clean water for all is a big challenge in developing countries. Furthermore, demand for freshwater is increasing tremendously due to population explosion, rapid urbanization, expansion of mechanized agriculture, economic growth, and rapid industrial advancement (Fito et al. 2017b, 2018a; Sakram and Narsimha 2018; Fito and Alemu 2019). Consequently, both the availability and quality of freshwater are decreasing across the globe, a situation that will result in a severe water shortage for 2.0-2.7 billion people by 2050 (UN-Water 2003; Mekonnen 2011; Fito et al.

2017a). Presently, about 3.6 billion people live in areas that are potentially water scarce at least 1 month per year; this figure is expected to rise to about 4.8–5.7 billion people by 2050 due to an increase in global water demand at the rate of 1% per year (UN-Water 2015). The current estimated global water demand is about 4600 km<sup>3</sup>/year and is projected to be between 5500 and 6000 km<sup>3</sup>/year in 2050, an increase of 20–30%, due to an expected population increase to 9.4–10.2 billion by the same year (UN Water 2018). Even though water quantity and physical availability, water pollution is worsening the progressive deterioration of water quality in many parts of the world and significantly contributing to water scarcity (Mateo-Sagasta et al. 2017).

For many nations across the world, surface water is the major source of water supply for diverse human purposes. However, in some places, surface water availability is insufficient, especially in arid and some semi-arid areas of many nations including Ethiopia. Furthermore, surface water deficiency and pollution are major global problems recently experienced; they are aggravated by environmental crises such as disparities in rainfall, climate change, and global warming. These conditions are currently forcing human being to shift to groundwater as a potential source (Mahaqi et al. 2018). More than 1.5 billion people worldwide rely on groundwater sources for human consumption at this time (Sakram and Narsimha 2018). Globally, climate change and other anthropogenic factors have significantly impacted surface and groundwater quality.

The term "water quality" is frequently used but practically it has no fixed definition; the definition of water quality can be based on many factors such as water sources, purification processes, management practices, and the intended uses of the water (Oluyemi et al. 2010). Generally, water quality is defined as the suitability of water for various uses based on the physical, chemical, and bacteriological properties of the water. Particularly, the physical quality of drinking water is defined with reference to aesthetic considerations such as odor, color, and taste, which may affect its acceptability, whereas the chemical quality of water is defined in terms of the concentrations of the inorganic and organic constituents of water that affect the health of the consumers (Ojo et al. 2012). To obtain a complete profile of water quality, a biological water quality assessment must be made to determine the presence of microorganisms that may have a harmful impact on water consumers. Practically speaking, provision of adequate, safe, accessible drinking water for all is fundamental to human health.

Groundwater is one of the largest freshwater reservoirs of our planet. However, recently, the unsustainable exploitation of aquifer mining has stressed groundwater in terms of both quantity and quality (Denizman 2018). Moreover, huge volume of industrial waste and various agrochemicals from farms are dumped into water courses either intentionally or accidentally, especially in developing counties, resulting in serious water pollution. These pollutants can have fatal effects on human as well as aquatic life (Bhimrao et al. 2018). Groundwater pollution is the direct or indirect alteration of the physical, chemical, and biological properties of a water system that creates a hazard or potential hazard to the health of living organisms. Additionally, the variability of the physicochemical quality of groundwater is highly influenced by geological formations and anthropogenic activities such as landfill leachate (Aduojo et al. 2018). Furthermore, the major factors in the variability of groundwater physicochemical characteristics are the composition of the initial pore water, the composition and physical properties of the soil and rock, the chemical interactions between the rock and infiltrating water, and microbiological processes (UNESCO 2002). The contribution of improperly managed wastewater to water pollution is also significant because little attention is given to wastewater treatment management in many places (UN Water 2018). All these conditions have led researchers to investigate the hydrogeochemistry of groundwater characteristics.

Ethiopia is endowed with naturally abundant water resources; it is considered an East African water tower with large freshwater resources, particularly from rivers, that help to meet domestic requirements and provide for irrigation and hydro-power generation. However, rivers are highly vulnerable to pollution because they serve as dumping sites for agrochemical runoff and industrial and domestic wastewater in many developing countries (Eliku and Leta 2018). Surface water pollution coupled with the rapid growth of population is causing a serious depletion in drinking water supply and a resultant sharp increase in drilling of groundwater for consumption in communities in Ethiopia (Reimann et al. 2003).

The availability and distribution of surface water is not uniform across Ethiopia. In arid and semi-arid areas of Ethiopia especially, river waters are rarely available. Thus in Haramaya District, communities are completely dependent on groundwater for daily use since there is no river crossing the area. The water supply for this region comes mainly from boreholes and hand-dug wells that are open and exposed to pollution. Additionally, the area is surrounded by extensively mechanized small-scale agricultural farms. The presence of farms suggests a high probability of groundwater pollution from agrochemicals such as pesticides, herbicides, and fertilizers (diammonium phosphate and urea) and other wastes that are dumped into the environment. Even though groundwater is less likely to be contaminated with diseasecausing microorganism, it is highly susceptible to pollution from heavy metals and other physicochemical constituents depending on the geology of the area.

The problem of water pollution is aggravated by Ethiopia's backward socioeconomic development, which has resulted in a low living standard, poor environmental conditions, and a low level of social services. Besides this, the health status of Ethiopia is poor, partly because of the deterioration in water quality. Analysis of the physicochemical properties and metal content of potable water is very relevant for public health protection and environmental remediation in the country. Therefore, this study assessed the physicochemical and heavy metal constituents of potable water and evaluated potable water quality of Haramaya Woreda.

## Materials and methods

#### **Description of study area**

This research was conducted in Haramaya District, which is located in east Hararghe administrative zone in Oromia regional state in eastern Ethiopia. The area lies at a latitude of  $9^{\circ}09'-9^{\circ}32'$  north, longitude of  $41^{\circ}50'$  to  $42^{\circ}05'$  east, and at an altitude between 1600 and 2100 m above sea level. The region sits in the moderate and partially semiarid climatic zones. The maximum and minimum mean annual temperatures are 24.0 and 9.4 °C, respectively. The annual minimum and maximum mean rainfalls of the area are 118 and 866 mm, respectively. Wind speed is, on average, 1.6 m/s from October to December and 1.7 m/s from June to September; the average relative humidity is 65%.

#### Water sampling and analyses

Water samples were taken from five sample sites of groundwater at Haramaya Woreda (Meda Belina, Addale Waltaha, Tinike, Haro Adi, and Derartu Mechetu) and the data interpretations were done at the end of the 2018. Water sampling was carried out on a monthly time interval throughout the study period of 2 months with replications using composite sampling techniques. Pre-cleaned plastic bottles were used for sample containers and transported to a laboratory where they were stored in a refrigerator at 4 °C until used for analyses per standard methods (APHA 2008). The specific analysis of each parameter and the corresponding method are shown in Table 1. Finally, descriptive statistical analyses and one-way analysis of variance (ANOVA) were used to compare mean concentrations of each parameter of the five sites at a 95% confidence level using SAS software.

| S. no | Parameter                       | Test method/apparatus  |
|-------|---------------------------------|--|
| 1     | pH                              | Hach HQD field case, Model 58258-00                          |
| 2     | EC                              | Hach photometer HQD field case, Model 58258-00               |
| 3     | Temperature                     | Hach photometer HQD field case, Model 58258-00               |
| 4     | TSS                             | APHA 2540 D, total suspended solids dried at 103-105 °C      |
| 5     | Ca                              | APHA 3500B, atomic absorption spectrometric method           |
| 6     | COD                             | APHA 5220 B, open reflux method                              |
| 7     | NO <sub>3</sub> <sup>-</sup> -N | APHA 4500 B, ultraviolet spectrophotometric screening method |
| 8     | NH <sub>3</sub> –N              | APHA 4500 B,C, distillation followed titration method        |
| 9     | TKN                             | APHA 4500b, macro-Kjeldahl method                            |
| 10    | TP                              | Persulfate digestion method and APHA 4500-P,C                |
| 11    | $PO_4^{3-}-P$                   | APHA 4500-P C, vanadomolybdophosphoric acid                  |
| 12    | Cl-                             | APHA 4500-Cl- B, argentometric                               |
| 13    | $SO_4^{2-}$                     | APHA 3030E, turbidmetric method                              |
| 14    | Acidity                         | APHA 2310 B, titration method                                |
| 15    | Alkalinity                      | APHA 2320 B, titration method                                |
| 16    | Total hardness                  | APHA 2340 C, EDTA titrimetric method                         |
| 17    | Cr                              | APHA 3120 B  |
| 18    | Fe                              | APHA 3120 B  |
| 19    | Cu                              | APHA 3120 B  |
| 20    | Zn                              | APHA 3120 B  |
| 21    | Pb                              | APHA 3120 B  |
| 22    | Cd                              | APHA 3120 B  |
| 23    | Turbidity                       | APHA 2130 B, nephelometric method                            |
| 24    | TDS                             | APHA 2540 C, total dissolved solids dried at 180 °C          |

 Table 1
 Water quality

 physicochemical parameters of
 the five study sites and the test

 methods used
 the five study sites

### **Results and discussion**

#### Physical properties of the potable water

The physicochemical properties of the potable water of the five sites of Haramaya Woreda were analyzed and the results are displayed in Table 2. The results for each parameter were compared with the Ethiopian and WHO water quality guidelines.

*Temperature* The water temperatures for the five sites ranged from 20.0 to 24.5 °C (Table 2). The minimum value  $(20.9 \pm 0.78 \text{ °C})$  was recorded at Derartu Mechitu (DM) whereas the maximum value  $(24.21 \pm 0.28 \text{ °C})$  was recorded at Haro Adi (HA). The water temperatures in the other areas were as follows: Adele Waltaha (AW), Meda Balina (MB), and Tinike (T) were  $21.43 \pm 0.06$  °C,  $23.3 \pm 0.26$  °C, and  $22.7 \pm 0.26$  °C, respectively. A significant difference (p < 0.05) in water sample temperatures among the five sites was observed. However, no significant difference (p > 0.05) in temperature of water was observed in samples from AW and DM or in samples from BM and T. In another study, relatively similar results of temperatures of potable water in the 22-26 °C range were reported (Effendi et al. 2015). Determination of temperature is important because of its effect on other physicochemical phenomena such as rate of chemical and biochemical reactions in water, reduction of solubility of gasses, amplifications of tastes and odors of water, but no health-based prescribed standards have been suggested for temperature of drinking water (WHO 2017).

*pH value* The pH of all the water samples ranged from 7.55 to 7.73 and appeared alkaline in nature (Table 2). The minimum pH (7.59  $\pm$  0.06) was recorded at T whereas the maximum (7.73  $\pm$  0.01) was recorded at HA. The values of pH at sample sites AW, DM, and MB were 7.64  $\pm$  0.01, 7.66  $\pm$  0.01, and 7.67  $\pm$  0.01, respectively. The pH value of every water sample was within the maximum permissible limit of WHO (2017) guidelines for drinking water, which is 6.5–8.5. The pH values of the water samples

showed significant differences (p < 0.05) among samples. The pH of water from sample site HA was significantly different (p < 0.05) from the others. The pH of samples from MB was significantly different (p < 0.05) from DM, HA, and T samples. In general, the results of the study were deemed satisfactory in terms of the pH requirements. The pH values for potable water in Indonesia have been reported at 5.8-6.5 (Effendi et al. 2015). The pH of water is affected not only by its reaction with carbon dioxide, but also by organic and inorganic solutes present in water. Any alteration in water pH is accompanied by changes in other physicochemical parameters, which in turn affect the water quality. The pH maintenance (buffering capacity) is one of the most important attributes of any aquatic system because every biochemical activity depends on the pH of the surrounding water. Generally, the pH of water works within a narrow range and any variations beyond an acceptable limit could be fatal to living organism in water bodies (Fito et al. 2018b; Palamuleni and Akoth 2015).

Electrical conductivity The electrical conductivity of the water samples ranged from 970 to 1240  $\mu$ S/cm (Table 2). The lowest value (972.00  $\pm$  0.65  $\mu$ S/cm) was obtained at T whereas the highest (1237.67  $\pm$  2.08  $\mu$ S/cm) value was obtained at MB. Conductivity values of 1127.33  $\pm$  1.53, 1190.00  $\pm$  2.00, and 1172.67  $\pm$  1.53  $\mu$ S/cm were registered at sites AW, DM, and HA, respectively. Analysis revealed a significant difference (p < 0.05) in electrical conductivity values among water samples. Ewaid and Abed (2017) reported electrical conductivity in the range of 1020–1270  $\mu$ S/cm/L for potable water; the water samples in the present study were within this range. The high variation in electrical conductivity might be due to different anthropogenic and other human factors that increase ionic inorganic and organic pollutants in water bodies.

*Turbidity* Turbidity of the water samples varied from the 0.02 to 6 NTU (Table 2). Turbidity is a measure of the cloudiness of water. In the present study, the maximum turbidity  $(5.9 \pm 0.10 \text{ NTU})$  was recorded at AW whereas the minimum  $(0.27 \pm 0.06 \text{ NTU})$  was recorded at HA. Turbidities of  $4.04 \pm 0.06 \text{ NTU}$ ,  $0.53 \pm 0.06 \text{ NTU}$ , and  $2.07 \pm 0.06$ 

Table 2 Physicochemical parameters of potable water at five sample sites in Haramaya Woreda (mean  $\pm$  SD)

| Parameter            | AW                       | DM                      | НА                         | MB                      | Т                       | Min. | Max.  |
|----------------------|--------------------------|-------------------------|----------------------------|-------------------------|-------------------------|------|-------|
| Temperature (°C)     | $21.43 \pm 0.06^{\circ}$ | $20.9 \pm 0.78^{\circ}$ | $24.21 \pm 0.28^{a}$       | $23.3 \pm 0.26^{b}$     | $22.7 \pm 0.26^{b}$     | 20   | 24.52 |
| pH                   | $7.64 \pm 0.01^{bc}$     | $7.61 \pm 0.01^{\circ}$ | $7.73 \pm 0.01^{a}$        | $7.67 \pm 0.01^{b}$     | $7.59 \pm 0.06^{\circ}$ | 7.55 | 7.73  |
| Conductivity (µS/cm) | $1127.33 \pm 1.53^{d}$   | $1190.00 \pm 2.00^{b}$  | $1172.67 \pm 1.53^{\circ}$ | $1237.67 \pm 2.08^{a}$  | $972.00 \pm .65^{e}$    | 970  | 1240  |
| Turbidity (NTU)      | $5.90 \pm 0.10^{a}$      | $4.04\pm0.06^{\rm b}$   | $0.27 \pm 0.06^{e}$        | $0.53\pm0.06^d$         | $2.07 \pm 0.06^{\circ}$ | 0.02 | 6     |
| TSS (mg/L)           | $14.67 \pm 0.76^{b}$     | $23.07 \pm 0.06^{a}$    | $2.5 \pm 0.50^{\rm e}$     | $8.83 \pm 0.29^{\circ}$ | $4.50 \pm 0.5^{d}$      | 2    | 24.9  |
| TDS (mg/L)           | $581.33 \pm 1.53^{d}$    | $833.67 \pm 0.58^{a}$   | $647.67 \pm 1.16^{\circ}$  | $682 \pm 1.00^{b}$      | $490 \pm 0.00^{e}$      | 490  | 834   |
|                      |                          |                         |                            |                         |                         |      |       |

AW Addale Waltaha, DM Derartu Mechetu, HA Haro Adi, MB Meda Belina, T Tinike

<sup>a–e</sup>Means with different superscripts in a row are significantly different at (p < 0.05)

NTU were measured at DM, MB, and *T*, respectively. There was a significant difference (p < 0.05) in the turbidity measurements among all the samples. Similar assessments of groundwater quality in typical rural settlements in southwest Nigeria reported comparable results of turbidity (1.5–3.7 NTU) in drinking water (Effendi et al. 2015). Turbidities of all the water samples were within the limits recommended by WHO guidelines for drinking water with the exception of the sample from AW. Although turbidity may vary with local circumstances, WHO set 5 NTU as the maximum level of turbidity for drinking water but noted that the healthiest level for drinking water was NTU less than 1 (WHO 2017).

Total suspended solids (TSS) and total dissolved solids (TDS): TSS of water samples ranged from 2.0 to 24.9 mg/L (Table 2). The maximum TSS value  $(23.07 \pm 0.06 \text{ mg/L})$  was recorded at DM and the minimum  $(2.5 \pm 0.5 \text{ mg/L})$  was at HA. TSS values of  $14.67 \pm 0.76$ ,  $8.83 \pm 0.29$ , and  $4.5 \pm 0.5 \text{ mg/L}$  were measured at AW, MB, and *T*, respectively. The analysis showed significant differences (p < 0.05) in TSS values among the water samples. In a similar study assessing groundwater quality in typical rural settlements in southwest Indonesia, lower TSS values (1.00-5.00 mg/L) in drinking water were reported (Effendi et al. 2015). The TSS results strictly matched with the turbidity values. WHO has not set maximum permissible limits on the concentration of TSS in drinking water (WHO 2017).

In the present water analyses, TDS ranged from 490 to 834 mg/L (Table 2). The maximum TDS value (833.67  $\pm$  0.58 mg/L) was obtained at DM whereas the minimum value (490  $\pm$  0.00 mg/L) was at *T*. TDS values of 581.33  $\pm$  1.53, 647.67  $\pm$  1.16, and 682  $\pm$  1.00 mg/L were recorded at AW, HA, and MB, respectively. There is a large significant difference (p < 0.05) in TDS concentrations among the water samples. Another study conducted on potable water showed TDS in the range of 610–87 mg/L (Ewaid and Abed 2017). Total dissolved solids comprised of

inorganic salts (principally calcium, magnesium, potassium, and sodium bicarbonates; chlorides; and sulfates) and small amounts of organic matter that are dissolved in water. The considerable variability of TDS concentrations in water in different geological regions might be due to differences in the availability of minerals in soils. The values of TDS in the water samples from the five sites in the study were below the maximum permissible limits of the WHO drinking water quality standards of 1000 mg/L (WHO 2017). Hence, with respect to this parameter, the water is suitable for human consumption. Generally, agricultural practices often have negative impacts on groundwater quality (Saleh et al. 2017).

#### Chemical properties of the potable water

Some chemical properties of the potable water at the five sites of Haramaya Woreda were analyzed and the results are displayed in Table 3. As with the other physicochemical parameters discussed in the previous section, the results for each parameter were compared with the Ethiopian and WHO water quality guidelines.

Acidity and alkalinity The acidities of water samples ranged from 32 to 46 mg/L (Table 3). The maximum acidity  $(45.33 \pm 0.58 \text{ mg/L})$  was recorded at MB and the minimum  $(32.67 \pm 1.15 \text{ mg/L})$  at AW. Acidities of  $37.33 \pm 0.58$ ,  $39.33 \pm 1.15$ , and  $34.67 \pm 0.58$  mg/L were recorded at DM, HA, and T, respectively. The analysis shows significant differences (p < 0.05) in acidity among the water samples. WHO makes no specific recommendations for some parameters, including acidity, because they do not directly affect health and acceptability is dependent on local conditions. Similarly, the alkalinities of the potable water samples ranged from 276 to 393 mg/L. The maximum alkalinity  $(391 \pm 1.73 \text{ mg/L})$  was obtained at HA and the minimum alkalinity  $(276.67 \pm 1.15 \text{ mg/L})$  was recorded at T. At other sites, alkalinities of  $280.33 \pm 2.52$ ,  $366 \pm 1.00$ , and  $382.33 \pm 0.58$  mg/L at AW, DM, and T, respectively, were

Table 3Chemical parameters of potable water at five sample sites in Haramaya Woreda (mean  $\pm$  SD)

| Parameter (mg/L) | AW                        | DM                        | НА                    | MB                    | Т                        | Min.  | Max.  |
|------------------|---------------------------|---------------------------|-----------------------|-----------------------|--------------------------|-------|-------|
| Acidity          | $32.67 \pm 1.15^{e}$      | $37.33 \pm 0.58^{\circ}$  | $39.33 \pm 1.15^{b}$  | $45.33 \pm 0.58^{a}$  | $34.67 \pm 0.58^{d}$     | 32    | 46    |
| Alkalinity       | $280.33 \pm 2.52^{d}$     | $366.00 \pm 1.00^{\circ}$ | $391.00 \pm 1.73^{a}$ | $382.33 \pm 0.58^{b}$ | $276.67 \pm 1.15^{e}$    | 276   | 393   |
| Total hardness   | $353.93 \pm 0.12^{b}$     | $332.67 \pm 0.58^{\circ}$ | $271.67 \pm 0.57^{e}$ | $410.67 \pm 0.58^{a}$ | $283.33 \pm 0.58^{d}$    | 271   | 411   |
| Chloride         | $54.33 \pm 0.31^{\circ}$  | $85.77 \pm 0.25^{a}$      | $32.90 \pm 1.32^{e}$  | $75.90 \pm 0.50^{b}$  | $46.13 \pm 0.67^{d}$     | 31.9  | 86.0  |
| Sulfate          | $220 \pm 0.00^{\circ}$    | $245.67 \pm 0.58^{b}$     | $194.33 \pm 0.58^{e}$ | $250.67 \pm 0.58^{a}$ | $214.33 \pm 0.58^{d}$    | 194   | 251   |
| Nitrate          | $11.80 \pm 0.10^{b}$      | $13.33 \pm 1.53^{a}$      | $3.40 \pm 0.17^{d}$   | $1.93 \pm 0.15^{e}$   | $10.07 \pm 0.31^{\circ}$ | 1.8   | 15.0  |
| Phosphate        | $0.041 \pm 0.002^{\circ}$ | $0.053 \pm 0.002^{a}$     | $0.015 \pm 0.001^{e}$ | $0.022\pm0.002^d$     | $0.046 \pm 0.002^{b}$    | 0.014 | 0.054 |
| COD              | $9.33 \pm 0.702^{e}$      | $16.57 \pm 0.929^{\circ}$ | $12.6 \pm 1.054^{d}$  | $24 \pm 1.000^{a}$    | $19.47 \pm 0.702^{b}$    | 8.6   | 25    |
| Ca               | $61.13 \pm 1.06^{d}$      | $67.33 \pm 2.08^{\circ}$  | $85.73 \pm 0.15^{b}$  | $103.17 \pm 1.26^{a}$ | $62.63 \pm 0.38^{d}$     | 60.0  | 104.5 |

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<sup>a–e</sup>Means with different superscripts in a row are significantly different at (p < 0.05)

recorded. Statistical analysis showed significant differences (p < 0.05) in alkalinity among the water samples. WHO does not set any maximum permissible limit for alkalinity of water with respect to human health. In a study of drinking water quality in the Ethiopian section of the East African Rift Valley, a comparable result with respect to alkalinity (15–1070 mg/L) was reported (Reimann et al. 2003).

Total hardness and calcium Total water hardness and calcium are highly interconnected; the presence of calcium ions contributes significantly to water hardness. The total hardness of the water samples ranged from 271.0 to 411.0 mg/L (Table 3). The maximum total water hardness  $(410.67 \pm 0.58 \text{ mg/L})$  was recorded at MB whereas the minimum  $(271.67 \pm 0.57 \text{ mg/L})$  was recorded at HA. At the other sampling sites, hardness values of  $353.93 \pm 0.12$ ,  $332.67 \pm 0.58$ , and  $283.33 \pm 0.58$  mg/L were recorded for AW, DM, and T, respectively. The result showed significant differences (p < 0.05) in total water hardness among the water samples. All the water samples fell in the very hard water category even though they were within the WHO maximum permissible limits (500 mg/L) for drinking water (Bernard and Ayeni 2012). In a similar physiochemical analysis of ground water, total hardness of 75-1110 mg/L was reported for drinking water in selected areas of Kaithal City (Haryana) in India (Gupta et al. 2009).

The calcium concentrations for the five sites ranged between 60.0 and 104.5 mg/L (Table 3). The maximum concentration of calcium  $(103.17 \pm 1.26 \text{ mg/L})$  was recorded at MB and minimum concentrations  $(61.13 \pm 1.06 \text{ and}$  $62.63 \pm 0.38$  mg/L) were obtained at AW and T, respectively. The calcium concentrations of  $67.33 \pm 2.08$  mg/L and  $85.73 \pm 0.15$  mg/L obtained at DM and HA, respectively, were lower than the value recorded at MB  $(103.17 \pm 1.26 \text{ mg/L})$  and higher than the values observed at AW  $(61.13 \pm 1.06 \text{ mg/L})$  and T  $(62.63 \pm 0.38 \text{ mg/L})$ . There was a significant difference (p < 0.05) in calcium concentration among the water samples. However, no significant difference (p > 0.05) in calcium concentration was observed between samples from AW and T. Calcium and magnesium are the principal components of hard water and are the most common in groundwater, especially when derived from limestone, dolomite, or chalk aquifers (WHO 2017). This might be the reason for high concentrations of calcium in water. Similar results of calcium concentration in the range of 2.4-196.5 mg/L were documented in a study assessing potable water quality in the Ethiopian section of the East African Rift Valley (Reimann et al. 2003). Calcium concentrations in the water samples analyzed were below the WHO maximum allowable limit, which is 200 mg/L.

Chloride and sulfate The concentration of chloride ions in the potable water samples ranged from 31.9 to 86.0 mg/L (Table 3). The chloride concentration in the present study was highest  $(85.77 \pm 0.25 \text{ mg/L})$  at DM and lowest  $(32.90 \pm 1.32 \text{ mg/L})$  at HA. Chloride concentrations of  $75.90 \pm 0.50$  mg/L,  $46.13 \pm 0.67$  mg/L, and  $54.33 \pm 0.31$  mg/L were observed at MB, T, and AW, respectively. The results showed significant differences (p < 0.05) in chloride concentrations among the water samples. Chloride is naturally distributed in the earth in salt form; therefore, the high concentration of chloride ions in ground water in this study was not surprising. A study conducted in India obtained similar results for chloride concentrations in drinking water (1.00-1240 mg/L) (Reimann et al. 2003). However, no health-based standard for chloride ions in potable water has been defined. At the five sites sampled, sulfate concentrations ranged from 194 to 251 mg/L (Table 3). The maximum sulfate concentration  $(250.67 \pm 0.58 \text{ mg/L})$ was measured at MB whereas the minimum concentration  $(194.33 \pm 0.58 \text{ mg/L})$  was obtained at HA. Similarly,  $220 \pm 0.00$ ,  $245.67 \pm 0.58$ , and  $214.33 \pm 0.58$  mg/L concentrations of sulfate were registered at AW, DM, and T, respectively. The analysis showed significant differences (p < 0.05) among sulfate concentrations of the different water samples. In other research conducted in Ethiopia on potable water quality, sulfate concentrations in drinking ranging from 0.05 to 692 mg/L were reported (Reimann et al. 2003).

Nitrate and phosphate The nitrate concentrations in the water samples were found to be in the range of 1.8–15.0 mg/L (Table 3). The maximum concentration of nitrate  $(13.33 \pm 1.53 \text{ mg/L})$  was recorded at DM whereas the minimum concentration  $(1.93 \pm 0.15 \text{ mg/L})$  was obtained at MB. At the other sites,  $11.8 \pm 0.10$ ,  $3.4 \pm 0.17$ , and  $10.07 \pm 0.31$  mg/L nitrate concentrations were registered at AW, HA, and T, respectively. Statistical analysis showed significant differences (p < 0.05) in nitrate concentrations among the water samples. In a similar study assessing groundwater quality in typical rural settlements in southwest Nigeria, nitrate concentrations ranging from 3.73 to 19.70 mg/L in drinking water were reported (Adekunle et al. 2007). The maximum nitrate concentration in drinking water recommended by WHO is 50 mg/L; nitrate concentrations in the study area were within the safe range.

Concentrations of phosphate ranged from 0.014 to 0.054 mg/L (Table 3). The minimum concentration of phosphate (0.015  $\pm$  0.001 mg/L) was recorded at HA whereas the maximum (0.053  $\pm$  0.002 mg/L) was obtained at DM. Phosphate concentrations of 0.041  $\pm$  0.002, 0.022  $\pm$  0.002, and 0.046  $\pm$  0.002 mg/L were measured at AW, MB, and *T*, respectively. There were significant differences (p < 0.05) in phosphate concentrations among the studied water samples. The phosphate concentrations of all the water samples were within the 5 mg/L recommended limit set by WHO and the Ethiopian government, indicating the water is safe for drinking in terms of this parameter. In similar studies conducted on potable water in Ethiopia, higher nitrate concentrations (1.9–42.40 mg/L) (Yasin et al. 2015) and lower

concentrations of phosphate (0.11–0.15 mg/L) were reported (Effendi et al. 2015).

Chemical oxygen demand (COD) The COD range in the present study was from 8.6 to 25 mg/L (Table 3). The maximum COD value  $(24 \pm 1.000 \text{ mg/L})$  was registered at MB, indicating a higher degree of pollution compared to AW, where the minimum COD value  $(9.33 \pm 0.702 \text{ mg/L})$ was recorded. COD values of  $16.57 \pm 0.929$  mg/L,  $12.6 \pm 1.054$  mg/L, and  $19.47 \pm 0.702$  mg/L were obtained at DM, HA, and T, respectively. There were significant differences (p < 0.05) in COD among the water samples. An elevated level of COD was found at MB, which might be the result of waste disposal in water sources. Similar results of COD concentration (5.8-25 mg/L) in drinking water quality assessment and pollution profiles have been reported (Effendi et al. 2015). Generally, high COD concentration is a physicochemical parameter that is a reliable indicator of water pollution by any oxidizable organic or inorganic pollutant.

### Some selected heavy metal constituents of potable water

As with the chemical properties of the potable water from the five sites of Haramaya Woreda, heavy metals constituents were analyzed; the results are displayed in Table 4. The results for each parameter were compared with the Ethiopian and WHO water quality guidelines.

*Iron* Concentrations of iron ranged from 0.11 to 0.539 mg/L (Table 4). The maximum iron concentration of  $0.530 \pm 0.008$  mg/L was recorded at MB and the minimum value of  $0.123 \pm 0.015$  mg/L at HA. At AW, DM, and *T*, the concentrations of iron were  $0.233 \pm 0.015$ ,  $0.333 \pm 0.016$ , and  $0.124 \pm 0.004$  mg/L, respectively. The analysis showed significant differences (p < 0.05) in iron concentrations among the water samples. However, no significant difference (p > 0.05) in iron concentrations was observed between water samples collected from HA and *T*. The concentrations of iron in the water samples were within the maximum

permissible limits of WHO and Ethiopian water quality guidelines (0.30 mg/L) for drinking water except for samples from AW and MB, which were slightly beyond the standards. Comparable results for iron concentration in drinking water ranging from 0.001 to 18.8 mg/L were reported by Reimann et al. (2003). Normally, groundwater contains high concentration of iron, requiring decolorization of the water before it is supplied for drinking (Bernard and Ayeni 2012).

Cadmium and copper Concentrations of cadmium in the water samples ranged from none detected (ND) to 0.07 mg/L (Table 4). The maximum concentration of cadmium  $(0.069 \pm 0.004 \text{ mg/L})$  was recorded at T whereas minimum concentrations (ND) were documented at AW, DM, and HA. Cadmium concentrations of  $0.034 \pm 0.006$  mg/L were obtained at MB. The analysis showed significant differences (p < 0.05) in cadmium concentrations among the studied water samples. In every water sample except those from MB and T, cadmium concentrations were within the maximum permissible limit of 0.003 mg/L for drinking water set by WHO and Ethiopian water quality guidelines. Awokunmi and Adefemi (2010) conducted a study of physicochemical quality and a trace metal analysis of water in Nigeria and reported similar cadmium concentrations in the range from ND to 0.4 mg/L. The elevation of cadmium concentrations might be associated with cadmium in soils and bedrock; the cadmium content in soils/sediments can reach up to 0.35 ppm (Muwanga and Barifaijo 2006).

Copper concentration in the five water samples analyzed ranged from 0.22 to 0.29 mg/L (Table 4). The maximum concentration of  $0.288 \pm 0.002$  mg/L was measured at MB whereas the minimum concentration of  $0.221 \pm 0.002$  mg/L was at AW. At the other sites,  $0.236 \pm 0.001$ ,  $0.231 \pm 0.002$ , and  $0.230 \pm 0.001$  mg/L copper concentrations were recorded at DM, HA, and *T*, respectively. The results showed significant differences (p < 0.05) in copper concentrations among the different water samples. The concentration of copper in each water sample was within the internationally recommended standard of 2 mg/L for drinking water set by WHO (2017). In a similar water quality analysis, comparable

| Table 4  | Some h    | neavy me  | etal    |
|----------|-----------|-----------|---------|
| constitu | tes of po | otable wa | ater at |
| five sam | ple sites | s in Hara | imaya   |
| Woreda   | (Mean     | ±SD)      |         |

| Param-<br>eter<br>(mg/L) | AW                        | DM                        | НА                        | MB                        | Т                         | Min.  | Max.  |
|--------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|-------|-------|
| Cd                       | ND                        | ND                        | ND                        | $0.034 \pm 0.006^{b}$     | $0.069 \pm 0.004^{a}$     | 0.0   | 0.07  |
| Cr                       | $0.100 \pm 0.001^{b}$     | $0.047 \pm 0.001^{\circ}$ | $0.133\pm0.002^{a}$       | $0.047 \pm 0.003^{\circ}$ | ND                        | ND    | 0.134 |
| Fe                       | $0.233 \pm 0.015^{\circ}$ | $0.333 \pm 0.016^{b}$     | $0.123\pm0.015^d$         | $0.530 \pm 0.008^{a}$     | $0.124 \pm 0.004^{d}$     | 0.110 | 0.539 |
| Pb                       | ND                        | $0.174 \pm 0.015^{b}$     | $0.217 \pm 0.012^{a}$     | $0.217 \pm 0.040^{a}$     | $0.087 \pm 0.010^{\circ}$ | ND    | 0.221 |
| Zn                       | $0.157 \pm 0.002^{\circ}$ | $0.141\pm0.002^d$         | $0.163\pm0.002^{\rm b}$   | $0.135 \pm 0.002^{e}$     | $0.170 \pm 0.003^{a}$     | 0.134 | 0.174 |
| Cu                       | $0.221 \pm 0.002^{d}$     | $0.236 \pm 0.001^{b}$     | $0.231 \pm 0.002^{\circ}$ | $0.288 \pm 0.002^{a}$     | $0.230 \pm 0.001^{\circ}$ | 0.220 | 0.290 |

AW Addale Waltaha, DM Derartu Mechetu, HA Haro Adi, MB Meda Belina, T Tinike

<sup>a–e</sup>Means with different superscripts in a row are significantly different at (p < 0.05)

concentrations of copper (ND to 0.4 mg/L) were reported in Nigeria (Awokunmi and Adefemi 2010). In another study, concentration of Cu in groundwater samples below the maximum permissible limit of WHO was reported (Ogoko 2017).

Chromium Chromium concentrations in water samples ranged from ND to 0.134 mg/L (Table 4). The maximum concentration of chromium  $(0.133 \pm 0.002 \text{ mg/L})$  was recorded at DM whereas the minimum concentration (ND) was found at T. At the other sites, chromium concentrations of  $0.100 \pm 0.001$ ,  $0.047 \pm 0.001$ , and  $0.047 \pm 0.003$  mg/L were obtained at AW, DM, and MB, respectively. Statistical analysis showed large significant differences (p < 0.05) in chromium concentration levels among the water samples. However, no significant difference (p > 0.05) in chromium concentration was observed between samples from DM and MB. The levels of chromium recorded in water samples at AW and HA were slightly higher than the 0.05 mg/L recommended by WHO for drinking water. Similar results for chromium concentration (0.01-0.9 mg/L) were reported (Alhibshi et al. 2014). The high concentration of chromium might be due to anthropogenic activities and other human interferences. This possibility is supported by the fact that the main sources of heavy metals in water are chemical weathering of minerals and soil leaching whereas the anthropogenic sources are associated mainly with domestic effluents, water runoff, and landfill leachate and inputs in rural areas (Madhav et al. 2018). High chromium concentrations in water might also be attributed to the concentration of chromium in the soils; chromium concentration in soil has been reported as high as 40-50 ppm (Muwanga and Barifaijo 2006).

Lead and zinc The concentrations of lead in the drinking water samples ranged from ND to 0.221 mg/L (Table 4). The maximum concentration of lead  $(0.217 \pm 0.012 \text{ mg/L})$ and  $0.217 \pm 0.040$  mg/L) was recorded at HA and MB and the minimum value of ND was observed at AW. Lead concentrations of  $0.174 \pm 0.015$  and  $0.087 \pm 0.010$  mg/L were recorded at DM and T, respectively. Significant differences (p < 0.05) of lead concentrations among the water samples were observed. However, no significant difference (p > 0.05)in lead concentration was observed between the samples from HA and MB. In another water quality study conducted in Ethiopia, lead concentrations of 0.02-0.03 mg/L in drinking water sources were reported (Yasin et al. 2015). In general, the concentration of lead in the potable water sampled is beyond the maximum permissible limits of Ethiopian and WHO water quality guidelines (0.01 mg/L). This indicates that long-term exposure to such water sources can cause bioaccumulation and biomagnification, which can result ultimately in negative impacts on human health. In another study, it was reported that about 26% of the groundwater samples contained lead concentrations above the WHO limits (Boateng et al. 2015).

The concentration of zinc in the water samples ranged from 0.134 to 0.174 mg/L (Table 3). The maximum concentration of zinc  $(0.170 \pm 0.003 \text{ mg/L})$  was recorded at T whereas the minimum value  $(0.135 \pm 0.002 \text{ mg/L})$ was obtained at MB. Concentrations of  $0.157 \pm 0.002$ ,  $0.141 \pm 0.002$ , and  $0.163 \pm 0.002$  mg/L were measured at AW, DM, and HA, respectively. There were significant differences (p < 0.05) of zinc concentrations among the water samples. Zinc is an essential trace element found virtually in all the foods and potable water in the form of salts or organic complexes. The concentration of zinc in every water sample analyzed was below the maximum acceptable limit (5 mg/L) for drinking water of WHO and Ethiopian water quality guidelines. At every water sampling site, zinc concentration was far lower than the standard maximum limit set by WHO and Ethiopian guidelines, which indicates that the water is suitable for drinking with regard to this parameter. Comparable results for zinc concentrations (0.001-5.14 mg/L) in drinking water have been reported by others (Reimann et al. 2003; Yasin et al. 2015).

### Conclusion

This study analyzed water samples taken from five groundwater sites in Haramaya Woreda for their physicochemical properties and heavy metal constituents. The result for each water quality parameter was compared to the Ethiopian and WHO water quality guidelines. The results indicate that the majority of physicochemical parameters considered in this investigation and a few of the heavy metals were within the maximum permissible limits of quality standards. This indicates that the water sources are of marginally tolerable quality and in the safe zone with respect to the aforementioned parameters. However, water samples taken from some water source sites failed to meet the current Ethiopian and WHO drinking water guidelines for a few parameters, namely lead  $(0.217 \pm 0.040 \text{ mg/L})$ , cadmium  $(0.069 \pm 0.004 \text{ mg/L})$ , chromium  $(0.133 \pm 0.002 \text{ mg/L})$ , and total water hardness, which ranged from  $271.67 \pm 0.57$  to  $410.67 \pm 0.58$  mg/L. Hence, exposing local communities to such water sources for long periods of time without intervention could cause severe health problems. The excess concentrations of the heavy metals lead, cadmium, and chromium in potable water are especially troubling as they can cause chronic problems of bioaccumulation and biomagnification, which can have irreversible human health impacts. Therefore, proper water treatment and protection of water sources from anthropogenic activities are essential steps towards the public health protection of the local communities.

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