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Assessment of Physio-Chemical Parameters and Selected Heavy Metals in Hand Pump Water Samples of Yebejeyche, Ageta, and Yewache Keble Muher Aklil Woreda, Gurage Zone, Snnpr, Ethiopia

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Abstract

In the globe the most important natural resource is water, and in the world the contamination of water resources is the major environmental issue. In this regard, monitoring the quality of drinking water at a regular time interval is crucial. Therefore, this study was designed to evaluate hand pump water quality of Yebejeyche (Ye), Ageta (Ag) and Yewache (Yw) in MuherAklilworeda, Gurage Zone, Southern Ethiopia. Specifically, this study was conducted by studying selected physico-chemical parameters such as Temperature (T), Potential hydrogen (pH), Electrical conductivity (EC), Total Hardness(TH), and Total Dissolved Solids(TDS). In addition to these, the concentration of elements like Na, Ca, Cr, Fe, Zn, Cd, and Pb were quantified in three samples. The Temp, pH, and EC were measured at the sampling sites. TH was analyzed by EDTA titration using ammonium buffer at pH 10 and E-Blank T indicator. The concentration of Na and Ca was analyzed using a Flame photometer. Target analytes were extracted from water samples using a wet acidic digestion method followed by the concentration of heavy metals determined using flame atomic absorption spectroscopy (FAAS). The mean range values of T, pH, EC, and TH in the studied area were in the range of 22.89 °C to 22.90 °C, 6.77 to 7.01,394 μ S/cm to 410 μ S/cm, 131 mg/L to 146 mg/L, 4.36 mg/L to 6.3 mg/L were obtained, respectively. The analyzed mean values of Na, Ca, Cr, Fe, Zn, Cd, and Pb were in the range of 30 mg/L to 33.8 mg/L, 24.9 mg/L to 28.2 mg/L, 0.0019 mg/L to 0.0035 mg/L, 0.04 mg/L to 0.05 mg/L, 0.115 mg/L to 0.223 mg/L, 0.003 mg/L to 0.005 mg/L and 0.018 mg/L to 0.0306 mg/L, respectively. All analyzed parameters were within the standards of the world health organization (WHO) guidelines for drinking water quality. Based on this standard, the three hand pump water sources are suitable for drinking purpose

Keywords: Hand pump water, physicochemical parameter, heavy metals, wet digestion and FAAS

1. Introduction

Water is the most important and decisive compound in the globe, all living things such as human beings, animals and plants require water for their survival and growth [1]. Groundwater is an indispensable source of water supply for different kinds of purposes. Currently, the population is booming globally and nationally and their improper consumption has led to the deterioration of surface and groundwater [2]. Generally, the status of groundwater becomes in danger due to anthropogenic activity, fast industrialization, unplanned urbanization, and too much use of fertilizers and pesticides unscientifically in agriculture fields [3]. Fundamentally any activity whereby chemicals or wastes may be released to the environment, either purposefully or unintentionally, has the potential to pollute groundwater. When groundwater becomes polluted, it is challenging and costly to clean up.

Metals are introduced into water bodies through a number of means including, weathering of rocks, leaching of soils, dissolution of aerosol particles from the atmosphere and from several human activities, including mining, processing and the use of metal based materials [4]. The physicochemical properties of groundwater including temperature(Temp), potential hydrogen (pH), electrical Conductivity (EC), total hardness (TH), total dissolved solids (TDS), and investigating the concentration of elements (Na, Ca, Cr, Fe, Zn, Cd and Pb) is very important for public health studies. Therefore, monitoring the level of contaminated substances in groundwater is crucial. The probability of getting adequate safe water is questionable in many developing countries [5]. Specifically, the main causes of water pollution in Ethiopian context are industrial effluents. sewage, urban and rural wastewater.

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agricultural activities, garages, institution, etc. The in drinking water has negative consequences on the health of human beings. Only a very small percentage (2.5%) of earth's total water coverage is clean and suitable for human consumption [6]. Heavy metals are the primary toxic pollutants which affects the quality and safety of drinking water [7]. Due to the accumulation of heavy metals, drinking water pollution is becoming a big problem in many countries.

The main source of drinking water, in Yebejeyche, Ageta and Yewache Kebeles, is underground water . In addition, the people also employ the groundwater for various purposes such as irrigation, sanitation and washing. In these areas, the physicochemical parameters and the concentration levels of selected elements was not yet studied. Accordingly, the present study was focused on the investigation of the status of the groundwater at different sampling sites by studying selected physicochemical parameters and concentration of target analytes.

- 2. Materials and Methods
- 2.1 Description of the Study Area

Muher Aklil woreda is found in Gurage zone, Southern Nations, Nationalities, and People's Region (SNNPR), Ethiopia. It is located at a distance of 200 Km, from the capital city of Ethiopia, Addis Ababa, and 52 Km from Wolkite town. The hand pump drinking water samples were collected from three sampling sites namely Yebejeyche, Ageta and Yewache and then transported to Wolkite university chemistry Laboratory in order to measure EC, Temp, TDS, TH, and pH of the water samples. However, the concentration of the metals was analyzed by FAAS at Amhara Design and Supervision Works Enterprise Laboratory Service, Bahr Dar (ADSWE).



Figure 1. Map of the study areas

2.2. Cleaning Apparatus, Sample Collection, and Preservation

Apparatus were washed with detergents and tap water, rinsed with distilled water, soaked in (1:1) nitric acid for 48 hrs, rinsed with deionized water, dried in oven and kept in dust free place until analysis. The water samples were collected from *Eth. J. Indig. Know. Appl. Sci.* presence of high levels of heavy metals three selected hand pump water sites namely Yebjeyeche(Yb), Ageta(Ag) and Yewach(Yw). From each sampling sites three bottles of water sample was taken. Then, the water samples were stored in refrigerator at approximately a temperature of 4°C.The three collected samples were transported to the Bahir Dar, Amhara Design and supervision works Enterprise laboratory service for further analysis.

2.3. Instruments

For the analysis of the underground water sample, different instruments were used. pH and conductivity meter were utilized to measure concentration of hydrogen ion and the presence of cations and anions in water samples, respectively. Flame atomic absorption spectrophotometer was used for determination of metals in samples.

2.4 Chemicals and Reagents

All the chemicals used in this study were of analytical grade reagents. The stock standard solutions, 1000 mg/L of Pb, Cd, Cr, Zn, Na, Ca, and Fe were used. Disodium salt of EDTA, Ammonium Chloride-Ammonium Hydroxide, (Buffer Solution, pH 10.0), Na2CO3 anhydrous, and CaCO3 were used for the analysis of total hardness. AgNO3 and K2Cr2O7 were used for argentometric titration for the determination of chloride. Distilled water was used for the preparation of stock and working standard solution.

2.5. Procedure

2.5.1. Physicochemical Analysis of Water Samples

Temperature, Electrical Conductivity and pH were measured using in situ sampling (at the sampling site) while the remaining parameters total dissolved solids (TDS) and total hardness (TH) were determined in the Wolkite university chemistry Laboratory [8].

2.5.1.1. Temperature, pH and Electrical Conductivity

The temperature of water sample was recorded by immersing a digital thermometer in each of three sampling sites. The sensing electrode of the pH meter was placed into the sample. The pH of each sample was recorded by the electrode was rinsed with distilled water in the next sample to be determined. At each level of analysis, the probes were thoroughly rinsed de-ionized water before and after each reading [9]. The 100 ml water samples were transferred in to 500 ml of beakers and the readings were taken by immersing the electrode in the water sample.



2.5.1.2. Total Dissolved Solids (TDS)

The TDS of water was measured by Gravimetric method. 100 ml of water sample was first filtered through a standard glass-fiber filter that blocks anything bigger than 2 microns (2 micrometers). This ensures the test measures dissolved solids not solids suspended in the water. The filtrate portion was evaporated to dryness at 180 °C and the amount of total dissolved solids was determined using equation 2.1. The reason for higher temperature was used to remove all mechanically occluded water [10].

TDS in (mg/l)=
$$\frac{Xb-Xa}{Volume(ml)of sample}$$

Equation 2.1, Where: X_b = weight of porcelain dish +weight of the residue (filtrate) after cooling Xa = weight of clean and dried porcelain dish.

2.5.1.3 Total Hardness (TH)

Total hardness was determined by EDTA method. 100 ml of water sample were measured and introduced into a beaker containing a stirrer bar and then three drops of Eriochrome Black T indicator was added. Next, the water sample was titrated with 0.01 M EDTA solution until the sample turns blue color. Total hardness is expressed as equivalent of calcium carbonate concentration [10] and calculated by equation 2.2.

Total hardness as CaCO₃(mg/l)

= Volume of EDTA X M of EDTA X MW of CaCO3 X1000 ml of sample

2.5.1.4. Heavy metal analysis of water samples

Flame atomic absorption spectroscopy was applied for the determination of metals in water sample using a calibration curve method. Appropriate amounts of each target analyte were weight and put into a 1000 ml volumetric flask to prepare the stock standard solution. To determine metals of hand pump water sample, standard solutions of seven points, including calibration blanks were prepared for each metal. Calibration curves were prepared for each metal. Calibration curves were prepared for each of the metals using proper dilution of stock solutions for each metal in a solvent. The calibration standard solution was used to calibrate the instruments response with respect to analyte concentration. Standard mixture solution consists of the metal at the same concentrations were prepared by taking of the same volume of each metal stock standard solution. In wet digestion of water samples, 20 ml con HNO₃, 5 ml HClO₄, and10 ml of H₂O₂ peroxide were added to 100 ml water samples, respectively. The samples were placed on a hot plate and heated at 100°C for 3 hours. The samples were removed from the hot plate soon as a clear solution was observed. The digested solution was cooled at room temperature and filtered into 50 ml volumetric flasks using Whitman filter paper No.541 (125 mm). Then, it was washed thoroughly using warm distilled water and topped up to the mark. Finally, the samples were ready to be Flame Atomic aspirated by Absorption Spectrophotometer (spectra AA-10). То get acceptable results the average values of the three replicates were calculated for each determination. Distilled water was used as a blank sample and it was analyzed in a similar procedure to the preceding one.

3. Results and Discussions

3.1. Physicochemical Analysis

Some physicochemical parameters which determine the underground hand pump water quality were measured at each sampling sites and the data is presented in Table 1.

Table 1. The results of the physicochem	nica	al
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Sample sites				
Paramet	Yebejeyche(Ageta(Ag)	Yewache(Y	WHO
ers	Yb)	Mean ±SD	w)	Standa
	Mean ±SD		Mean ±SD	rd
Temp.°C	22.63 ±0.200	22.93±0.51	22.83±0.32	
		3	1	
pH(0-14	6.77±0.030	7.01±0.030	6.86 ± 0.085	6.5-8.5
)				
$EC(\mu S/$	394.66±5.03	410.33±1.5	405.66±2.5	≤1500
cm)	3	27	16	
TDS(mg	254.73±1.49	263.90±1.5	259.30±1.0	<1000
/1)	7	52	53	
TH(mg/l	146.33±1.52	131.66±1.5	135.66±2.0	500
)	7	27	82	
Ca(mg/l)	28.1 ± 0.458	25.33±	26.25 ± 0.11	≤100
		0.145		
Na(mg/l)	33.8± 1.058	30±0.700	31.8± 0.5	≤20

parameters of hand pump water samples (n=3).

3.1.1. Temperature

Temperature is a measure of hotness and coldness of water and affects the rate of chemical reaction. Cold water is generally more potable than warm water, and temperature has impact on the acceptability of a number of other inorganic constituents and chemical contaminates that may affect taste. Temperature

enhances the growth of microorganisms and impacts the taste, odor, and color of water [11]. In this study, temperature was found in the range of 22.63°C - 22.93 °C (Table 1).Therefore, the entire selected samples were permissible to drinking, because the samples analyses were found below the WHO guidelines [12]. The higher value of water temperature observed in the present study was attributed to the environmental factor of the kola region [13].

3.1.2. pH

pH is a measure of hydrogen ion concentration in water sample and used to judge the water sample either it is acid or alkaline. The current investigation ranges were 6.77–7.01 which are in the range of WHO standards. The average pH value of Yb and Yw were slightly acidic, but exists within the guidelines of drinking water (Table 1).The lower average value of pH of hand pump water may be resulted due to dissolution of sulphate, phosphate and carbonate rocks in a long period of time.

3.1.3. Electrical conductivity (µS/cm)

Conductivity is the ability of a water sample to carry an electrical current and varies with the number and types of ions present in the solution. The most desirable limit of EC in drinking water is prescribed as 1500 μ S/cm [14]. The current investigation ranges were 394.66 to 405.66 μ S/cm which are below WHO standards (Table 1). The high conductivity of the groundwater is occurred due to the elongated contact of it with the rock.

3.1.4. Total Hardness

Hardness is the property of water that prevents the lather formation with soap and increases the boiling points of water. WHO has specified the total hardness of water to be a maximum of 500 mg/l of CaCO₃. In this study, the mean values of TH were between 131.66 mg/l - 146.33 mg/l; it was within the allowable limit.

3.1.5. Total Dissolved Solids (TDS)

The total dissolved solids consist of calcium, chlorides, nitrate, phosphate, iron, sulfur, and other ions [15]. The average TDS values of water samples were obtained as 254.73 mg/l (Yb), 263.90 mg/l (Ag), and 259.3 mg/l (Yw). According to WHO specification TDS up to 500 mg/l is the highest desirable and up to 1,500 mg/l is maximum permissible. In the study area the TDS value varies between a minimum of 254.73 mg/l and a maximum of 263.90 mg/l, indicating that most of the groundwater samples lie within the highest

permissible limit (Table 1). All sample values were within permissible limit of WHO standards. 3.1.6. Calcium, Sodium

Calcium is an indispensable element in the human body for cell construction and bone building. The mean values of calcium concentration were found 25.33 mg/l (Yb), 28.10 mg/l (Ag) and 26.43 mg/l (Yw) (Fig 2). According to quality water standards the upper limit of concentration of calcium in drinking water is 100 mg/l. Therefore, all the samples mean values of Ca^{2+} were observed within the guidelines, so the water samples are suitable for drinking purpose.

Sodium is an essential element and present in natural waters. Although, concentrations of sodium in potable water are typically less than 20 mg/l, they exceed this in some countries. The average values of the sodium concentration in all water samples were between 30 mg/l to 33.8 mg/l, but the concentrations of sodium in these samples exceed 20 mg/l, it might be due to the dissolved salts on the underground water from natural rocks.



Figure 2. Concentration of parameters in various water samples

3.2. FAAS Analysis of heavy metals

The levels of selected heavy metals were analyzed by validated analytical method. The mean with standard deviation values of all metals determined in the water samples collected from the three sampling sites were shown in Table 2.

Table 2. Summary of the mean concentration (X \pm SD, n=3) of heavy metals in the water sample

Sampling sites				
Heavy	Yebejeyche	Ageta	Yewach	
metals	Mean±SD	Mean±SD	Mean±SD	
Cr	0.0022±0.00	0.0035±0.0	0.0019	
(mg/l)	05	005	±0.0046	

Fe (mg/l)	0.04±0.010	0.05±0.010	0.03±0.020
Zn	0.115±0.000	0.223±0.00	0.149±0.00
(mg/l)	2	01	46
Cd	0.005±0.000	0.004±0.00	0.003±0.00
(mg/l)	8	1	02
Pb	0.0306±0.00	0.018±0.00	0.028±0.00
(mg/l)	15	1	1

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3.2.1. Iron (Fe), Zinc (Zn), Chromium (Cr), Cadmium (Cd) Lead (Pb)

In the present study, the average values of iron concentration in water samples of Yb (0.04 mg/l), Ag (0.05 mg/l) and Yw (0.03 mg/l) were obtained. All the samples were under the guideline that stated by WHO standards. The average values of Zn in the water samples were Yb (0.115 mg/l), Ag (0.223 mg/l), and Yw (0.149 mg/l). In all three water sample sites, the Zn concentration was within the permissible limit of WHO.

Cr exists in trivalent and hexavalent states. Hexavalent Cr enters to water from industrial waste water which mainly discharges from paints and tanning factory. The chromium mean concentrations values of the studied samples were found between 0.0019 mg/l to 0.0035 mg/l (Table 2). All three sample sites were within the permissible limit.

The cadmium may occur in groundwater naturally or as a contaminant from sewage sludge, fertilizers, and polluted groundwater of mining and industrial effluents [13]. In the present study, the average values of cadmium concentration in the water samples were Yb (0.005 mg/l), Ag(0.004 mg/l), and Yw (0.003 mg/l). All three water samples were within the permissible limit of WHO standards.

Lead can poison humans even in low concentrations. It is used in many products found in and around homes. But, the concentration of Pb may be increased due to human activities and it enters into the environment through the exhaust of cars. In this study, the average values of lead in three samples were Yb (0.0306 mg/l), Ag (0.018 mg/l), and Yw (0.028 mg/l). The concentration of the water samples exceeded the maximum concentration stated by USEPA and ESS, but within the limit of the guideline of WHO. The high concentration of lead might be the corrosion of pipes, due to the slightly acidic nature of the water in the welded part.

3.3 Comparison of heavy metals in hand pump water Samples

The comparison of the concentration of heavy metals in the three samples is shown in the following graph.



Figure 3. The graphs of heavy metals concentrations of hand pump water samples.

3.4 Method Validation and Quality Control Results

3.4.1 Calibration Curve and Linearity of Instrumental Responses

The calibration equation of each analyzed metal is revealed in Table 3. As observed from calibration curves, the correlation coefficient (regression, r^2) value of each metal varied in the range of 0.997-0.999.

Ana	Calibration	IDL	LOD	LOQ	r ²
ly.	equation	(mg/l)	(mg/l)	(mg/l)	
Na	Y=0.9886x+0.1299	0.050	0.120	0.360	0.999
Ca	Y=0.1376+0.0015	0.020	0.060	0.180	0.999
Fe	Y=0.0299x+0.0067	0.002	0.005	0.015	0.997
Cr	Y=0.0411+0.0009	0.003	0.050	0.200	0.999
Zn	Y=0.1707+0.0025	0.0025	0.046	0.138	0.999
Cd	Y=0.1475+0.0017	0.001	0.003	0.012	0.999
Pb	Y=0.158x+0.0013	0.001	0.0015	0.004	0.999
				5	

Table 3. The result of IDL, LOD, LOQ, r^2 values of metals in hand pump water samples (n=3)

These values were greater than the minimum linear correlation coefficients of accepted value of 0.995 set by [10]. Therefore, there was a linear relationship between instrumental response and standard concentration of each analytes. These indicated that, the method was suitable for the determination of unknown concentration in the individual water 5

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samples. Instrumental detection limit (IDL), limit of detection (LOD), and limit of quantification (LOQ) of the target analytes are shown in Table 3.

3.4.2. Method Accuracy and Precision

In the present study, for evaluating analytical methods accuracy and precision were made on triplicate of laboratory-fortified matrix (n=3) spiked with a mid-range of calibration concentration. The calculated recoveries of all metals in water sample were in the range of 86.56% - 104.77%. Therefore, the results obtained from this analytical method were in the required level of accuracy. For evaluating precision of these analytical methods, relative standard deviation was calculated from replicates of measurements. Percent relative standard deviations of all metal were in range of 0.040% - 3.90%. Therefore, the analytical method was in good precision.

3.4.3. Comparison of the Current Results with Standards

The water quality parameter of the three representative hand pump water samples of the present study was compared with WHO drinking water quality standards. Based on the output of the study, three hand pump water samples were recommended for drinking purposes because the level of water quality parameters (Temp, pH, EC, TH, TDS, Na, Ca, Fe, Cr, Cd, Zn, and Pb) were below the maximum permissible limits of WHO, 2017 sets for drinking water.

Sampling Sites				
Anal. (mg/g)	Yebejeyche Mean*±SD	Ageta Mean* ±SD	Yewach Mean*±S D	[12]
Cr	0.0022±0.00 05	$0.0035 \pm 0.000 5$	0.0019±0 .0046	0.000 -0.1
Fe	0.04 ± 0.01	$\begin{array}{c} 0.05 \pm \\ 0.01 \end{array}$	0.03± 0.02	0.300
Zn	0.115± 0.0002	0.223± 0.0001	0.149± 0.0046	5.000
Cd	0.005± 0.0008	0.004± 0.001	0.003±0. 0002	0.005 - 0.010
Pb	0.0306± 0.0015	0.018± 0.001	0.0218± 0.001	0.100
Na	28.1±0.0020	25.3±0. 0005	24.± 0.0005	1.0- 200
Ca	0.671± 0.0005	1.192± 0.001	1.054± 0.0011	75- 100

Conclusion

Groundwater is an important source of drinking water for many people around the world and its contamination results in poor drinking water quality. Selected physiochemical parameters of three ground water samples were analyzed viz Temp, pH, EC, TH, and TDS. In addition to these, two major chemicals (Na and Ca) and five heavy metals (Cr, Fe, Zn, Cd, and Pb) of target analytes were determined . The results of the current study were compared with various guidelines for quality drinking water and found within the standards of WHO guideline for drinking water quality.

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