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Water Quality Assessments as Implication to Human Health: A Case Study in Awash Sebat and Its Surrounding Areas, Afar, Ethiopia

HINDEYA GEBRU AND JEMAL AHMED

Department of Earth science, Collage of Natural and Computational sciences, Samara University, PO Box: 132, Samara, Ethiopia

Email: *hindualem@gmail.com, jema99@yahoo.com*

Abstract: Present paper reports the results of surface and sub-surface water on quality from Afar National State, Eastern Ethiopia. The area forms part of the main Ethiopian rift valley system and has long history of fluorosis problems. The geological setting of the area consisted of vesicular basalt, ignimbrite, alluvial and out wash sediments. Water sampling (11 surface and 13 sub-surface water samples) was carried out in January 2012 and analyzed for major and trace element contents using Atomic Absorption Spectrometer and titration methods. The major cations and anions in groundwater are present in the order of Na>>Ca>Mg>K and HCO_3>>Cl>SO_4 >NO_3->CO_2, but in surface water Na>>Ca>K>Mg and HCO_3>> SO_4 >Cl>> NO_3-, respectively. Among the cations, sodium concentration exceeds the maximum acceptable limit in about 25% of the water samples. The bromine and fluorine values in both waters are exceeding the maximum acceptable limit for drinking purpose. Bromine is ranging from 0.8 to 11 mg/l show higher values in all samples and fluorine ranging from 0.6 to 11.5 mg/l show higher values in 54.2% of the samples. High amounts of fluorine, visible in the area in the form of dental fluorosis, observed mainly in surface water samples, is contributed by Lake Beseka which is partly fed by Awash River. Data indicate that the surface water is suitable for irrigation and groundwater for both drinking and irrigation purposes. If surface waters are to be used for drinking, the excess fluorine contents needs to be removed using chemical coagulation treatment mechanisms.

Keywords: *Drinking water quality, Fluorosis, Bromine, Awash Sebat Kilo, Lake Beseka, Afar, Ethiopia*

1. Introduction

The Ethiopian rift valley is part of East African rift valley which runs from Syria through Afar triple junction to Mozambique. This rift valley is characterized by active tectonic set up, volcanic eruption, and volcanic lakes. The surface and groundwater are show high fluorine and saline. The high fluoride concentrations in water are linked to the geology of the MER; which is composed of young volcanic materials and fluvial-lacustrine sediments that release several toxic elements into the environment including fluoride. Previous studies have also provided evidence of high prevalence of dental and skeletal fluorosis in the region (Gossa, 2006; Kloos and Tekle-Haimanot, 1999; TekleHaimanot et al., 1987; and Rango, 2012).

According to the Rnago (2012) finding, the highest fluoride levels in main Ethiopian rift valley were found in highly-alkaline (pH of 7 to 8.9) groundwater characterized by high salinity; high concentrations of sodium (Na+), bicarbonate (HCO3−), and silica (SiO2); and low concentrations of calcium (Ca2+). Gizaw (1996) quoted the thermal waters in the MER are characterized by high Na, HCO3, F and by a near neutral to alkaline pH. Lake Beseka is one of the rift valley lakes that laterally expands and increases its elevation from time to time at a very fast rate (Ayalew, 2009). The Lake water is saline (EC<6.3 dS/m), sodic (SAR~300) or alkaline (pH<9.6), not usable for irrigation and drinking or consumption (Olumana 2010).

Anthropogenically, Awash River is mixed with Lake Beseka through drainage system (open canal) and it may be naturally mixed through geological structures at Methara area. This mixing condition might affect the quality of Awash River water. There were medical observations of incidences of dental and crippling fluorosis in the rift valley (Teklehaimanot et al., 1987). There are a number of diseases proved to be connected to geochemical characteristics of the environment (Fergusson, 1990). For example, the endemic degenerative heart disease in china- known as Keshan Disease- was attributed due to selenium deficiency (Yang, 2000); kidney disease in Sri Lanka where as high fluoride content in drinking water was considered as possible risk factors (Dissanayake, 1991), and concern over the health of residents of eastern Ethiopia- Awash area- has been known for the occurrences of dental and skeletal flourosis and Kidney related diseases (Teklehaimanot et al., 1987), which attracts the researcher. For the protection and conservation of water resource in the study area, it is found to be important to characterize the quality of water. Groundwater contamination with arsenic, fluoride and nitrate recently possesses serious health hazards to large sector of communities all over the world. Trace element concentrations in the natural water widely vary depending on the geochemistry of rocks in the immediate environment and interaction of different water bodies. So, knowledge of rock types in a particular area can help to find out potential health problems with interaction of water bodies and concentration of particular elements. Therefore, this research is proposed to investigate the impact of Lake Beseka to the Awash River used for water supply of the Awash Sebat kilo community and for the pastoral communities of Afar region, and to provide some answers to surface and sub-surface water quality aspects of the area in relation to public health. The aim of this study was to conduct a scientific assessment of surface and sub-surface water quality; to determine the level of major, minor and trace element concentrations and distributions in water of the area, and to identify the possible sources in relation to human health.

2. Description of the Study Area

The area of the study is located in Eastern Ethiopia within the main Ethiopian rift valley system at about 350 km south western of Samara, Afar National State. Geographically, the study area is bounded between 603500 to 635000m E and 991500 to 1024500m N. The Kebena, Kesem and Fulwuha intermittent streams intern drain to the perennial Awash River towards northeast of the study area. Generally, the drainage pattern is dendritic. The area is covered by flat topography, slightly steep hill and deep river gorges. The elevation ranges from 820m to 1120m above sea level. With a monthly temperature (ranging from 22.6^{O}C to 30.06 ^{O}C), the climate of the study area is characterized by semi-arid to arid climatic zone, and the area attains mean annual rainfall of about 606.6mm.

3. Methodology

The surface and sub-surface water samples were collected from Awash Sebat Kilo and its surrounding areas. Previous published literatures in the area were mainly focused on geology, geological structures, hydrogeology and environmental. At 1:50,000 scale, topographic map was used to illustrate the drainage and the physiography of the area. Before conducting field work, base map was also prepared with 1:50,000 scale from topographic sheet. The geological map has been produced with dominant geological structures.

Twenty four water samples; thirteen groundwater, and eleven surface waters were collected. Eleven of the surface water samples were taken from Awash River and at different locations of Awash Sebat killo water treatment process for community supply; lake Beseka and Awash River at Methara and national park fall, and groundwater from hand dug wells and boreholes (Fig. 1). Each sample was collected in one liter properly numbered and washed polyethylene bottle. After sampling, the bottles were tightly covered with caps, and they were sealed with tap so as to minimize oxygen contamination and to reduce the escape of dissolved gases. The samples were kept in cool place to minimize chance of chemical reaction, which can result in precipitation of dissolved elements.

The chemical analysis of the water samples were carried out in the Laboratory of Geological Survey of Ethiopia, Addis Ababa. The concentration anions and trace elements, like chlorine (Cl^-), fluoride (F^-), bromine (Br^-), bicarbonates, carbonates (CO_3^{2-}), $NO3^-$, and SO_4^{-2} were analyzed using titration methods. Major cations (Ca^{+2}, Mg^{+2}, Na^+ and K^+) and some trace elements (Cd, Pb, Cr, Mn and Be) were analyzed using Atomic Absorption Spectrometer (AAS) to know the general composition of the water bodies of the area and the interaction between surface waters. The detection limit of atomic absorption spectrometer (AA-6800, Shimadzu model) is 0.1 for cations. Besides, the physico-chemical parameters (i.e. TDS, pH and EC) were recorded in the field. Analytical treatment of data was made using Excel, Aquachem and ArcGIS. Data obtained from water samples were compared with the national and international standards such as WHO (1984) to see whether or not the water samples are in line with the recommended range, and they are safe to human health in general and to the society in particular. Electrical conductivity (EC); Total Dissolved Solid (TDS); hardness (Th as CaCO3); pH, and alkalinity were also recorded. Sodium and salinity hazard of the water samples were calculated and interpreted. The water type of each sample was determined, and the concentrations of surface and groundwater samples were also compared.

4. Geology and Hydrogeological Settings

Geology of the area consists of vesicular basalt, ignimbrite, outwash sediments and alluvial deposits. The vesicular basalt is found in the northwest, southwest and central part of the study area. It covers large part of the area. This basalt contains different size vesicles ranging from 1mm to 10cm in diameter. At places it overlain by the alluvial deposit. This unit is characterized by columnar joints and shows blocky nature. Most of the groundwater wells were drilled in this lithology due to its water bearing nature and due to presence of joints and fractures.

Around the southern part of the study area, ignimbrite rocks are exposed mainly by river, hill and quarry exposures. It is associated with vesicular basalt, and covers the Awash Sebat Kilo town. Ignimbrites have economic importance for the community as dimension stone and construction material. The ignimbrite rock has elongated or welded fragments which range in size from very fine to 4cm with variegated colors; the rock is massive with green color. In some parts of the ignimbrite rock the welded fragments are removed and replace with open spaces; the horizontal bedding, and the vertical and horizontal joints that help the communities in making dimension stone for construction purpose. Hydro geologically, ignimbrite rocks in this area are not productive layers. The eastern part of the study area (around Awash Arba) is covered by thick out wash sediments. The out wash sediment contains clay, silt and gravels. The river exposure of this formation has pinkish, grey and black colors. It indicates the bottom part's fine materials; it makes tilted laminated layers, grain size increasing up-ward, gravels (coarse grain, weak sorted loose materials) overlain the fine loose materials. This is water bearing sediment next to the vesicular basalts due to the presence of sand and gravel grains.

Alluvial deposits are found mainly in the north and northwest of the study area, and covers larger area next to vesicular basalt rock. It is overlain and bounded by vesicular basalt rocks. It contains clay, silt and sand grains. Gravels are bedded present in the streams that drain to Awash River. Major part of the area is covered by agricultural lands and naturally vegetated forests.

The lithology of the area is affected by different structures such as faults, joints and fractures. The major structural features in the area are faults. There are a number of minor and major fault escarpments, producing horst and graben structures and almost parallel to NNE-SSW direction producing “en echelon” features. These faults are observed mainly in the southwestern parts of the area affecting the vesicular basaltic unit. The grabens are filled by the alluvial deposits and common around Sabure village. Joints and Fractures are exposed within ignimbrite rock in southern and southwestern parts of the area. They also affect the vesicular basaltic unit with an orientation mainly of NE-SW parallel to the fault. Opening of joints varies from tight up-to few centimeters and they continue for tens of meters in a discontinuous manner. Some of the joints and fractures are filled by stringers.

Basaltic lava flows and ignimbrites constitute the main aquifers in the whole area which forms part of the Main Ethiopian Rift system. Due to the high intensity fracturing, the secondary permeability and porosity is well developed (Tesfay, 1982; Tamiru, 1993; Gizaw, 1996; Tamiru and Vernier, 1997; Tamiru, 2000).

From the hydrogeological point of view, the most groundwater points are concentrated in the alluvial deposits (sand, gravel and boulders layers), outwash sediments, and vesicular and fractured basalt rocks. There are groundwater hot springs that drain following the fractured and fissural cracks of the volcanic rock exposers in the northeastern part of the area. These hot springs locally called Fulwuha and the community believe that it has medicinal value for skin diseases.

Lake Beseka and the surrounding areas located in the volcanically active place are most productive basaltic rock aquifers and small crater fill with water dominated place. According to Kebede etal (2007) aquifers in Beseka are mainly alluvial/lacustrine sediments, ignimbrites and basalts which occur in a complex interfingering; the region is characterized by the junction of several faults systems: NNE rift faults, EW faults and NS faults of the Afar depression; depth to water table ranges between 50 and 120 m and highly fractured terrain with new fissures in the processes of opening.

5. Results

5.1. Physico-chemical parameters

The pH value for all the water samples are ranges from 7.13 to 8.4 except for one sample taken from Lake Beseka, having 9.48. Except for Lake Beseka, which has 5111 µS/cm, Electrical Conductance (EC) of the surface and subsurface waters of the area varies from 351 to 3950 µS/cm at 25^oC with a mean of 982 µS/cm. Except Lake Beseka water, which contains 3067mg/l, the Total Dissolved Solid (TDS), the water samples range in TDS from 211-2370 mg/l with a mean of 589 mg/l. Hardness level for the surface and groundwater in the area ranges from 22.34 to 630.30 mg/l $CaCO_{3,}$ except Lake Beseka water sample which showed lower value 9.96 mg/l $CaCO_3$. The alkalinity of the water of the area varies from 104 to 980 mg/l $CaCO_{3,}$ but Lake Beseka has maximum value of 1867.14 mg/l $CaCO_3$.

5.2. Major Ions

The collected surface and sub-surface water samples were analyzed for major cations (Ca^{+2}, Mg^{+2}, Na^+ and K^+) and anions (HCO_3, NO_3^- and $SO4^{-2}$). The Na concentration in the samples varies from 31 to 925 with a mean of 167.4 mg/l shows higher values than the other cations. Ca ranges from 4 to 95 mg/l, with a mean of 39.3 mg/l but one sample shows 226 mg/l. Mg ranges from 2 to 31 mg/l with mean of 9.8 mg/l, and K ranges from 4 to 19 mg/l with a mean of 8.2 mg/l except one sample with 0.8 mg/l. The concentration of Lake Beseka water showed 1307mg/l for Na, 57mg/l K, 3mg/l Ca and 0.6 mg/l Mg.

Except one sample, which contains 1129mg/l and has an average of 398.5mg/l, the HCO3 concentration shows high values, as compared to the other major anions which vary from 127 to 878 mg/l. Except two samples, which are AHW-13 (36mg/l) and ASW-15 (12 mg/l), the CO_3 is below detection limit. The value of Cl in the samples of surface and subsurface waters varies from 9 to 638 mg/l and an average of 86.4mg/l; SO_4 varies from 8 to 195 mg/l and an average of 61.6 mg/l; NO_3 varies from 0.4 to 31 mg/l and contains an average of 6.5 mg/l. The lake Beseka water sample has 1459 mg/l HCO_3, 402 mg/l CO_3, 425mg/l Cl and 434mg/l SO_4 concentrations.

5.3. Trace Elements

Out of 7 trace element analysis, the bromine and fluorine elements show significant concentration value but the other five trace elements (Be, Cd, Cr, Pb and Mn) are below detection limits. With a mean value of 2.5 mg/l, the results of bromine range from 0.8 to 8.9 mg/l. In the study area, in the Lake Besaka water at Metahara town, 8.9 mg/l is maximum bromine value, whereas 0.8 mg/l has to be in the treated Awash River water for the Awash Sebat Kilo community. The surface and sub-surface water collected from various sites of Awash Sebat Kilo and the surrounding areas contained fluorine of 0.6 – 11.5 mg/l with an average value of 2.3 mg/l. The maximum value of 11.5 mg/l was recorded in sample (ASW-22) collected from Lake Besaka water at Metahara town in south west of Awash Sebat Kilo town, while the minimum value of 0.6 mg/l was recorded from both bore hole and hand dug wells around Kebena and Kesem villages.

Table 1: *Major ions and water type of groundwater samples*

Sample name	Major cations and anions (mg/l) and water type										
	Na^+	K^+	Ca^{2+}	Mg^{2+}	HCO_3^-	CO_3^{2-}	Cl^-	F^-	SO_4^{2-}	NO_3^-	Water type
AHW-6	254	9	23	2	451	_	125	1.5	80	31	$NaHCO_3Cl$
AHW-7	223	7	20	4	551	_	71	1.7	43	0.7	$NaHCO_3$
AHW-8	61	0.8	24	18	329	_	9	1	8	4.4	$NaMgCaHCO_3$
AHW-9	31	5	39	12	249	_	10	0.6	10	14.6	$CaNaMgHCO_3$
AHW-10	140	8	17	11	388	_	48	1.6	38	4	$NaHCO_3$
AHW-11	40	5	95	27	464	_	37	0.6	27	6.6	$CaMgHCO_3$
AHW-13	925	6	5	3	1129	36	638	8.7	195	8	$NaHCO_3Cl$
AHW-14	292	4	5	4	659	_	74	1.7	75	22.6	$NaHCO_3$
AHW-16	102	11	61	15	366	_	96	1.5	41	11.5	$NaCaHCO_3Cl$
AHW-17	189	19	57	22	266	_	223	1.6	188	23	$NaCaHCO_3SO_4$
AHW-18	61	8	226	16	317	_	50	0.7	43	6.6	$CaNaHCO_3$
AHW-19	85	8	45	10	350	_	29	0.9	17	4	$NaCaHCO_3$
AHW-20	93	6	41	31	371	_	43	0.9	27	4.4	$NaMgCaHCO_3$

Table 2: *Major ions and water types of surface water samples*

Sample name	Major cations and anions (mg/l) and water samples										
	Na^+	K^+	Ca^{2+}	Mg^{2+}	HCO_3^-	CO_3^{2-}	Cl^-	F^-	SO_4^{2-}	NO_3^-	Water type
ASW-1	133	9	26	5	358	_	48	2.4	56	0.9	$NaHCO_3$
ASW-2	130	9	35	5	361	_	47	2.5	62	0.4	$NaCaHCO_3$
ASW-3	127	9	21	5	362	_	45	2.3	60	0.4	$NaHCO_3$
ASW-4	117	9	38	5	281	_	43	1.8	11	1.3	$NaCaHCO_3$
ASW-5	117	9	24	5	307	_	42	2.1	102	0.9	$NaHCO_3SO_4$
ASW-12	95	7	21	10	127	_	53	0.6	112	0.4	$NaSO_4HCO_3Cl$
ASW-15	480	17	4	3	878	12	193	4.8	105	1.3	$NaHCO_3Cl$
ASW-21	36	7	25	4	183	_	17	1.1	21	1.8	$NaCaHCO_3$
ASW-22	1307	52	3	0.6	1459	402	425	11.5	434	0.4	$NaHCO_3$
ASW-23	83	9	25	4	256	_	30	1.8	50	0.4	$NaCaHCO_3$
ASW-24	37	6	26	4	162	_	17	1.1	45	0.4	$NaCaHCO_3SO_4$

Table 3: *Trace elements and physico-chemimical parameters of groundwater samples*

Sample name	Easting	Northing	Trace elements (mg/l)						Physico-chemical parameters		
			Be	Cd	Cr	Pb	Mn	Br^-	pH	EC (µS/cm)	TDS (mg/l)
AHW-6	626326	1022726	<1	<0.1	<1	<0.5	<0.1	2.8	7.88	1270	760
AHW-7	616080	1023419	<1	<0.1	<1	<0.5	<0.1	2.9	7.9	1110	666
AHW-8	611771	1021032	<1	<0.1	<1	<0.5	<0.1	0.8	7.87	515	309
AHW-9	610274	1018143	<1	<0.1	<1	<0.5	<0.1	0.8	7.72	448	264
AHW-10	606055	1014165	<1	<0.1	<1	<0.5	<0.1	1.7	7.43	796	478
AHW-11	605979	1011514	<1	<0.1	<1	<0.5	<0.1	1.2	7.77	834	500
AHW-13	604491	1008886	<1	<0.1	<1	<0.5	<0.1	11	8.6	3950	2370
AHW-14	608799	1011244	<1	<0.1	<1	<0.5	<0.1	2.3	8.22	1335	801
ASW-15	618760	1013714	<1	<0.1	<1	<0.5	<0.1	4	8.4	2060	1236
AHW-16	625790	1007927	<1	<0.1	<1	<0.5	<0.1	2.6	7.48	964	578
AHW-17	626361	999667	<1	<0.1	<1	<0.5	<0.1	5	7.97	1440	864

AHW-18	628700	1008928	<1	<0.1	<1	<0.5	<0.1	1.8	7.86	711	427
AHW-19	632039	999419	<1	<0.1	<1	<0.5	<0.1	1.2	7.59	647	388
AHW-20	633631	995262	<1	<0.1	<1	<0.5	<0.1	1.6	7.8	734	440

Table 4: *Trace elements and physico-chemimical parameters of surface water samples*

Sample name	Easting	Northing	Trace elements/ mg/l						Physico-chemical parameters		
			Be	Cd	Cr	Pb	Mn	Br^-	pH	EC (µS/cm)	TDS (mg/l)
ASW-1	629438	993912	<1	<0.1	<1	<0.5	<0.1	1.1	8.09	779	467
ASW-2	629230	993994	<1	<0.1	<1	<0.5	<0.1	1	8.05	769	461
ASW-3	629243	993990	<1	<0.1	<1	<0.5	<0.1	0.9	7.83	762	457
ASW-4	629277	993976	<1	<0.1	<1	<0.5	<0.1	1	7.24	769	461
ASW-5	629277	993976	<1	<0.1	<1	<0.5	<0.1	0.8	7.56	734	440
ASW-12	605044	1009904	<1	<0.1	<1	<0.5	<0.1	1.4	7.13	692	415
ASW-21	601147	978045	<1	<0.1	<1	<0.5	<0.1	2.1	7.43	384	230
ASW-22	598925	980480	<1	<0.1	<1	<0.5	<0.1	8.9	9.48	5111	3067
ASW-23	611184	977472	<1	<0.1	<1	<0.5	<0.1	1.2	7.99	538	323
ASW-24			<1	<0.1	<1	<0.5	<0.1	0.9	7.87	351	211

6. Discussion

6.1. Physico-chemical parameters

pH values of both surface and sub-surface waters indicate that slightly basic to highly alkaline in nature. About 90% of the water samples are within the range of WHO (2004) standard limits (6.5 to 8.5), greater than 7 and indicate HCO_3 more dissolved than CO_3. The water samples that were collected from hand dug wells, boreholes, hot spring and Lake Beseka have high value of electrical conductance. They are not good for drinking purpose because they exceed the standard limit of WHO (1984). According to the standards set by WHO (2004), the TDS maximum tolerance limit of the surface and subsurface waters of the area are suitable for drinking purpose and considered as fresh water. However, the sample collected from one borehole in Sabure village, hot spring and Lake Beseka waters have been found greater than the maximum tolerance limit, 1000 mg/l. According to TDS classification of WHO 12.5% of the total water samples are categorized as excellent (<300), 58.33%; good (300-600), 16.66%; fair (600-900) and 12.5% un-acceptance (>1200). Water supply with hardness greater than 200 mg/l are considered poor but tolerated by consumers: those in access of 500 mg/l are unacceptable for most domestic purposes (Guideline for Canadian drinking water, 1996). Based on the hardness classification (Sawyer, 1960), 29.16%, 45.83%, 16.66%, and 8.33% of the water samples are classified as soft, medium hard, hard, and very hard waters respectively. Totally, both hard and very hard, the 25 % of the water samples give unpleasant taste. Excessively hard water can affect the function and lifetime of plumbing systems and appliances. Surprisingly, due to the presence of low calcium and magnesium concentrations, the lake Beseka water is categorized under the soft water. Except the water samples collected from borehole in Sabure village, hot spring and Lake Beseka, which have high content of bicarbonate and carbonates, the alkalinity of the area is within the tolerance limit because it is not beyond 500 mg/l.

6.2. Major Ions (Cations and anions)

The major cations of the groundwater compositions are present in the order as Na>>Ca>Mg>K but of the surface water are order as Na>>Ca>K >Mg (Table 1and 2). The finding shows the Na concentration is much more than K that indicates that ability to decompose and weathering of the sodium rich minerals and rocks in the area. The sodium concentration of Awash River, downstream of Lake Beseka, has relatively higher than upstream of the lake Beseka which indicates that there is an input mineral concentration from the lake. Ca2+ is the second cations which abundant in the study area but much more less than Na+. In all source of the water, the composition has low calcium concentration because the rate of decomposition of most igneous-rock minerals like anorthite is slow (Hem, 1985). The concentrations of sodium in the waters are within the maximum tolerance limits. Due to the water, rock and soil interactions, the 25% of the samples including Fulwuha hot springs, hand dug welsl from Sabure village and Lake Beseka, are showing higher values than the recommended for drinking water (200 mg/l) (WHO, 1984). Low concentrations of Na+ have little or no effect, but high concentrations increase the corrosive effect, unpleasant taste, reduce water softness and suffer pregnant.

The major anions of groundwater are present in the order as HCO_3>>Cl>SO_4 >NO_3> CO_2 but in surface water as HCO_3>>SO_4>Cl>>NO_3>CO_2 (Table 1 and 2). Bicarbonates are the dominant anion in both surface water and groundwater because of the presence of carbonate mineral in the volcanic rocks and dissociation of carbonic acids. A little amount of bicarbonate does not have an adverse effect on human health unless in large amount by combining with calcium and magnesium can cause carbonate hardness, affect the taste and corrosiveness of the water. In general the source of bicarbonate is the interaction of rainfall through atmospheric CO_2 with soil and carbonate minerals rich rock (Gupta and Sighal, 1999). According to the WHO (1984), chlorine and sulfate contents in the surface and sub-surface waters are below the maximum permissible limit (for Cl, 250 and SO_4, 400 mg/l).

6.3. Trace Elements

6.3.1. Bromine

In all the samples, the values are higher than the WHO maximum allowable value, 0.01mg/l. The values of bromine in the study area could probably be related to intrusive bodies or underground brine deposits; as bromine value with volcanic rocks and brine deposit is relatively higher (Hem, 1992). In addition to this, the value of bromine is high around the irrigated area of Sabure village due to the agricultural activities where fertilizer is used for sugar cane (Fig. 1). The water samples from groundwater have relatively more concentration of bromine than surface water, which indicates that the sources might be the intrusive bodies or underground fluid brine or formations. Some of the health effects that can be caused by excess bromine value in water are malfunction of nervous system; gastrointestinal and disturbances in genetic material, and damage to organs such as liver, kidneys, lungs, and thyroid glands. Some forms of organic bromine, such as ethylene bromine, can even cause cancer (US EPA, 2001).

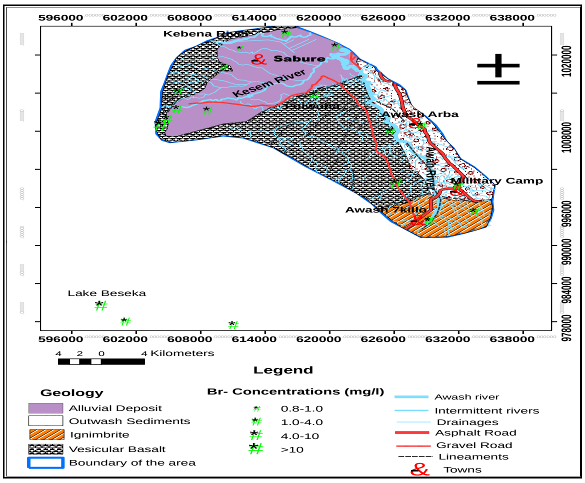

Fig. 1: *Spatial distribution of Br concentration*

6.3.2. Fluorine

As the other part of the Main Ethiopian and East African Rift Valleys, the surface and sub-surface waters in the study area is highly affected by fluorine concentrations (eg. in central Ethiopia by Rango etal., 2012; Nairobi in Kenya by Marleen etal., 2008; Arumeru District in Northern Tanzania by Ghiglieri etal., 2010). Hem (1985) noted that fluoride levels generally do not exceed 1 mg/L in most natural waters with TDS levels below 1000 mg/L. But in the rift valley and specifically in this area, out of the twenty four samples, thirteen of them indicate values higher than maximum allowable limit (1.5mg/l) of WHO (2004) drinking water guideline. Some other researchers have suggested 0.7 mg/l as an action level for tropical countries with high daily intake of water (Evan and Stamm, 1991). Warnakulasuria et al. (1992) have also noted that the WHO (2008) recommended levels of 1.5mg/l fluorine in drinking waters are not acceptable for hot and dry climates. It emphasized that in setting of national standards for fluoride, it is particularly important to consider climatic conditions, volume of water intake and intake of fluoride from other sources (WHO, 2008).

According to Rango et al. (2012), in the Ziway–Shala basin in particular, wells had high fluoride levels (mean 9.4 ±10.5 mg/L; range: 1.1 to 68 mg/L), with 48 of 50 exceeding the WHO (2008) drinking water guideline limit. Bedrock aquifers in alkaline magmatic rocks and metamorphic rocks are particularly associated with fluoride-contaminated groundwater. The minerals directly responsible for its release are fluorspar, fluorapatite, amphiboles (e.g. horneblende, tremolite) and certain micas.

Weathering and leaching of fluorine bearing rocks and minerals could consider as important factors in the concentration of fluoride in the surface and ground water. Excessive intake of fluoride-rich water can cause dental fluorosis (mottling of teeth), skeletal fluorosis (depilating disease, which affects bones) and can harm nerves and muscles. The high fluoride is not only possible risk factor but it is possible that there is some relationship with the disease or it could even increase the severity of the disease (Dissanayake, 1991). Many animal experiments reported that the kidney damage can occur even at low levels of fluoride exposure over large period of time (Liu et al., 2005). A high concentration of fluorides in drinking water is link with cancer (Smedley, 1992). The permissible limit of fluoride depends on temperature; higher intake fluoride can be permissible in colder climate area (Hamill and Bell, 1986).

The spatial distribution of fluoride concentration in the area is classified according the impact of fluoride on health (Fig. 2). The first classification of water samples is fluoride value from 0.5 to 1.5 mg/l, which promotes dental health. The second categorization is water sample with 1.5 to 4 mg/l of fluoride concentration that causes dental fluorosis (mottling of teeth). The third classification is water sample having fluoride concentration from 4.0 to 10.0 mg/l, which causes dental and skeletal fluorosis (pain in back and neck bones). The last one is water sample having greater than 10.0 mg/l of concentration of fluoride, which cause crippling fluorosis (Dissanayake, 1991; Gupta and Singhal, 1999). The treated awash Sebat kilo water supply tank has fluoride concentration with ranged value from 1.8 to 2.5 mg/l, which is above the maximum acceptance limit in drinking water. The community intake this amount of concentration; as a result, they can be affected by mottling of teeth.

Two water samples from Fulwuha hot spring and Sabura borehole have been classified within the range from 4.0 to 10.0 mg/l of fluoride concentration. The water sample from Lake Beseka has greater than 10.0 mg/l, which can affect Awash River because they are connected each other at the dawn stream of the lake (Fig.2).

6.4. Water Type, Salinity and Sodium Hazards

The major ion composition of surface and sub-surface waters is used to classify water into various types based on the dominant cations and anions. The water type of the area is dominated by Na-HCO_3 due to high concentration of sodium from cations and bicarbonate from anions.

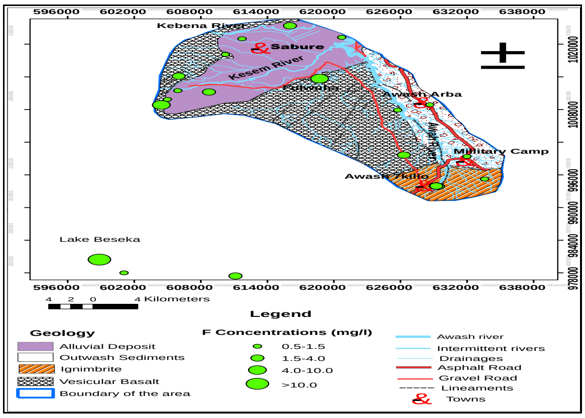

Fig. 2: *Spatial distribution of F concentration*

From the Piper diagram (Fig. 3), it is possible to conclude that bicarbonate contents are higher than chloride and sulphate contents in the water samples; sodium plus potassium contents are higher than the concentrations of calcium and magnesium; sodium plus potassium contents of surface waters are higher than subsurface water samples; bicarbonate plus carbonate contents of subsurface water are higher than surface water samples. Most of the surface and sub-surface water types are combined from the sodium types of cations and bicarbonate type of anions which give Na-HCO^{-}_3, and the alkalis exceed alkaline earths due to the presence of high content of sodium in the surface and subsurface waters, but Lake Beseka is highly alkaline water.

Sodium hazard is known by determining SAR (Table 5) using the three major cations of Na, Ca and Mg and classified groundwater as excellent (0-10); good (10-18); fair (18-26), and poor (>26) (Richards, 1954). According to this, most of the samples fall within the excellent category having a range of SAR from 0.21 to 8.435, but three samples from Sabure village and one sample from Lake Beseka fall under poor category.

Salinity hazard is measured based on EC values. This means conductivity measurements give a strong indication of overall salinity and water with high EC value, which is highly saline water. EC of water for irrigation suitability was classified by Wilcox (1955) as excellent (<250); good (250-750); permissible (750-2250); doubtful (2250-5000), and unsuitable (>5000). According to this classification, about 41.66% water samples of the area are classified under good; 50% within the permissible; one sample or 4.16% within doubtful. The water samples of Lake Beseka were also unsuitable for irrigation. Generally, the samples were set on the S1C2>S2C3>S3C3>S4C3 of the Wilcox classification (Fig. 4), but the water samples from the Fulwuha spring and Lake Beseka are out of the classification due to the presence of high amount of EC and as they cannot be used for drinking and irrigation purposes.

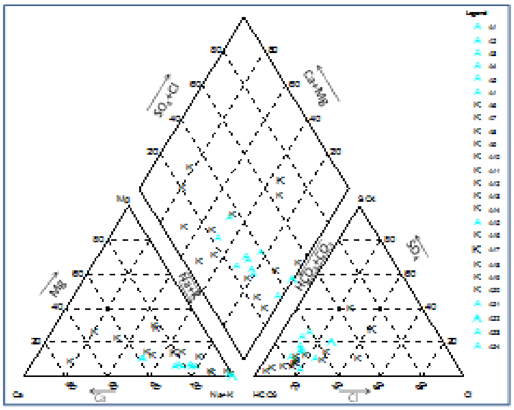

Fig. 3: *Piper diagram of groundwater and surface water*

Most of the groundwater and surface water samples are categorized under safe and suitable for irrigation purpose except the one sample taken from Lake Beseka which characterized by highly saline, sodicity, toxic and unsuitable based on the parameter(Table 5).

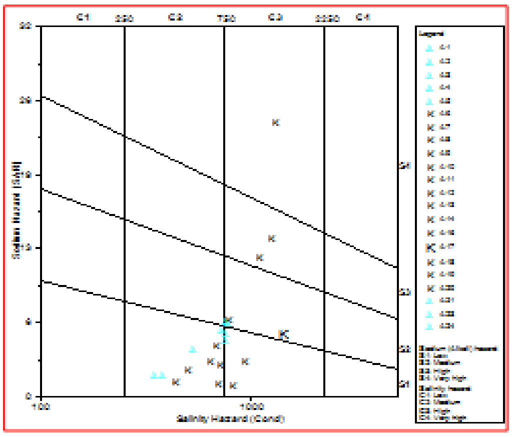

Fig. 4: *Wilcox Diagram of the groundwater and surface water*

***Table 5:** Irrigation waters*

Classification of Groundwater quality for irrigation use

Classification Items (Concentrations in meqL^{-1})	**Categories**	**Ranges**	**Min**	**Max**	**Average**	**St. dv.**	**Samples (%)**
Salinity Hazards: classified based on the electrical conductivity (Richard, 1954)	Low-C1	<250	448	3950	1134.9	901.2	0
	Medium-C2	250-750					38.46
	High-C3	750-2250					53.85
	Very High-C4	2250-5000					7.69
Sodium Adsorption Ratio: $SAR = \frac{Na^+}{\sqrt{\frac{Ca^{2+}+Mg^{2+}}{2}}}$ (USSL, 1954)	Excellent-S1	0-10	0.93	80.8	11.98	21.69	69.2
	Good-S2	10-18					15.4
	Fair-S3	18-26					7.7
	Poor-S4	>26					7.7
Residual Sodium Carbonate: $RSC = (CO_3^{-2} + HCO_3) - (Ca^{2+} + Mg^{2+})$ (Eaton, 1950)	Safe	<1.25	0	19.1	4.2	5.4	30.8
	Marginal	1.25-2.5					23.1
	Unsuitable	>2.5					46.1
Permeability Index: $PI = \frac{Na^+ + \sqrt{HCO_3^-}}{Ca^{2+}+Mg^{2+}+Na^+}$*100% (Doneen, 1964)	Class-I	>75%	32.34	120.4	88.2	24.9	84.6
	Class-II	25-75%					15.4
	Class-III	<25%					0
Kerry's Ratio or Exchangeable Sodium Ratio: $KR = \frac{Na^+}{Ca^{2+} + Mg^{2+}}$	Safe	<1	0.21	81.06	9.92	22.2	38.46
	Unsuitable	>1					61.54
Sodium Percentage: $SP = \frac{Na^+}{Ca^{2+}+Mg^{2+}+Na^++K^+}$*100%	Excellent	<20%	17.17	98.41	59.24	26.6	15.4
	Good	20-40%					7.6
	Permissible	40-60%					30.7
	Doubtful	60-80%					15.4
	Unsuitable	>80%					30.7
Magnesium Hazard: $MH = \frac{Mg^{2+}}{Ca^{2+} + Mg^{2+}} * 100\%$ (Szabolcs and Darab, 1964)	Safe and Suitable	<50%	10.5	56.9	36.67	11.09	69
	Harmful and unsuitable	>50%					31

Classification of surface water quality for irrigation use

Classification Items	**Catagories**	**Ranges**	**Min**	**Max**	**Average**	**St.dv**	**Samples (%)**
Salinity Hazards:	Low-C1	<250	351	5111	1177	1316	0
	Medium-C2	250-750					45.5
	High-C3	750-2250					45.5
	Very High-C4	2250-5000					9
Sodium Adsorption Ratio:	Excellent-S1	0-10	1.76	180	24	50.6	82
	Good-S2	10-18					0
	Fair-S3	18-26					0
	Poor-S4	>26					18
Residual Sodium Carbonate:	Safe	<1.25	0	36.6	6.6	10.2	27.3
	Marginal	1.25-2.5					9.1
	Unsuitable	>2.5					63.6
Permeability Index:	Class-I	>75%	92.8	115.7	105.9	6.59	100
	Class-II	25-75%					0
	Class-III	<25%					0
Kerry's Ratio or Exchangeable Sodium Ratio:	Safe	<1	0.98	285.5	32.2	81	18.2
	Unsuitable	>1					81.8
Sodium Percentage:	Excellent	<20%	47.1	97.4	71.2	15.2	0
	Good	20-40%					0
	Permissible	40-60%					18.2
	Doubtful	60-80%					63.6
	Unsuitable	>80%					18.2

Magnesium Hazard:	Safe and Suitable	<50%	17.8	55.3	27.35	11.17	90.9
	Harmful and Unsuitable	>50%					9.1

7. Conclusions

This study indicates that pH value of the sampled waters ranged from 7.13 to 8.4, which are under permissible for drinking water. Water from Lake Beseka is highly alkaline. The water type of the area is dominated by Na-HCO_3 due to high concentration of sodium from cations and bicarbonate from anions. Generally, the samples have been set on the S1C2>S2C3>S3C3>S4C3 of the Wilcox Diagram classification, but the water samples from the Fulwuha spring and Lake Beseka are out of the classification due to the presence of high amount of EC; so they cannot be used for drinking and irrigation purposes. The concentration of sodium, which is the only major cation in the waters, is within the maximum tolerance limits. The surface and subsurface water in the study area have values of Br and F exceeding MAC guideline standards for water. Awash Sebat Kilo water supply is contaminated from the continuously expand of Lake Beseka.

Further, detailed studies including isotope studies are necessary to see if there is underground mixing of Lake Basaka water to Awash River water. Sediments might be mixed into sand filtration, one of the treatment processes during rainy season or run off, so it is better to build a protecting wall as controlling measures. It is recommendable to make extension of the kidney, cancer, and crippling flourosis diseases caused by the presence of more doses of bromine and fluorine that may affect the communities of the area. Finally, it is advisable to provide groundwater supply for the community of Awash Sebat kilo town that can be found in the nearby villages.

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