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 B – data collection
 C – statistical analysis
 D – data interpretation
 E – manuscript preparation
 F – literature search

Groundwater property and composition variability under long-term irrigated area of Wonji Plain, Ethiopia

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Abstract

Wonji Shoa Sugar Estate (WSSE), located in the flood plain of the Awash River (Ethiopia), has been under long-term (>60 years) irrigation, industrial activities and agro-chemical usage. In this study, the hydrochemical properties of groundwater bodies available at WSSE have been characterized for quality compositions. Water samples were collected from groundwater monitoring piezometers distributed in the sugarcane plantation and then analysed for physico-chemical quality parameters (pH, EC, major cations and anions) following standard procedures. Other chemical indices (e.g., total dissolved solids (TDS), total hardness (TH), magnesium absorption ratio (MAR), base exchange (r_1), meteoric genesis (r_2)) were derived from the measured water quality parameters. The compositional variability and groundwater classification has been presented using the Box and Piper plots. The potential sources of minerals were suggested for each of the considered water sources based on their quality characteristics. Both trilinear Piper plot and meteoric genesis index revealed that groundwater of the area is shallow meteoric water percolation type with a changing of hydrochemical facies and mixing trend. Groundwater of the area, is group 1 (Ca-Mg-HCO₃) type, with no dominant cations and HCO₃ are the dominant anions. Overall, the study result elucidates that the chemical composition of GW of the area showed spatial variability depending upon the variations in hydrochemical inputs from natural processes and/or anthropogenic activities within the region. The local anthropogenic processes could be discharges from sugar factory, domestic sewage and agricultural activities.

Key words: chemical composition, groundwater, physico-chemical, quality parameters, quality variability

INTRODUCTION

Groundwater (GW) quality (composition and property) is one of the most sensitive issues worldwide, potentially influenced by several natural and anthropogenic factors [DINKA *et al.* 2015; FOSTER 2006; SRINIVASAMOORTHY *et al.* 2012; TODD, MAYS 2005]. Some of the natural factors include catchment lithology and geology, residence time of groundwater in the rock, pH and ambient temperature, chemical composition of the aquifer, climatic conditions prevailing during formation, quantity of water available in the aquifer and its rate of circulation and the velocity and direction of water movement [FREEZE, CHERRY 1979; TODD, MAYS 2005]. The anthropogenic factors mainly include effluents from agricultural, industrial and domestic

activities [SRINIVASAMOORTHY *et al.* 2012]. Agro-chemicals, in particular, are the major source of GW pollution in irrigated agricultural areas. Compounding the concern about GW quality degradation is the fact that GW, once polluted, could remain for decades or centuries, owing to its slow movement and reaction in the vadose zone. Moreover, the remediation of contaminated groundwater is very difficult as the result of its large storage zone, long residence time for recharge and physical inaccessibility [FOSTER 2006].

In Wonji-Shoa Sugar Estate (WSSE) (Ethiopia), there has been a continuous supply of irrigation water and agro-chemicals since its establishment in the 1950s. Such intensive agricultural activities can introduce a number of potential contaminants into groundwater system of the area.

In such very shallow groundwater table (GWT) areas [DINKA *et al.* 2013, 2014; DINKA, NDAMBUKI 2014], the opportunity time for infiltrated water is expected to increase causing fast downward mobility of possible pollutants into the shallow GWT and contaminating them quickly. The leaching of agro-chemicals to groundwater system in such agricultural area is of great concern to human health and sustainability of agriculture and environment of the region. More than 50,000 people live in Wonji plain generating their livelihood from the sugar estate, directly or indirectly [DINKA *et al.* 2013].

Groundwater quality evaluation in such long-term irrigated area (WSSE) is very important to protect the public health and other purposes (agriculture, industry, fishing, recreation, tourism and protection of aquatic ecosystems). Groundwater monitoring will help to better understand the effect of irrigation on groundwater so that future trends of groundwater quality can be predicted. Groundwater quality evaluation plays a great supportive role in various water management programs such as planning and management of groundwater resources, water supply, environmental impact assessment, modelling groundwater systems, and/or mapping groundwater vulnerability. It is gaining significant importance due to intense urbanization, industrialization and agricultural activities that are putting the soil and water to greater risk of contamination [TIWARI, SINGH 2014].

A detailed hydrochemical characterization of groundwater of Wonji Plain has not been reported so far, except the report made by DECHASA [1999]. He studied the groundwater quality of the Ethiopian Rift Valley, including Wonji area, from very few boreholes and hand-dug shallow wells and gave a general highlight about the water quality of the area. Very little information is available on the processes, chemical composition and evolution of the groundwater resources of the area. Due to the changing hydrological conditions and anthropogenic activities in the region in particular and the regional Rift Valley influences

in general, the hydrochemistry of groundwater is expected to change over time. Hence, the characterization of the groundwater hydrochemistry has paramount importance. This study presents the hydrochemical characteristics of groundwater in Wonji Plain and its compositional variability. The potential hydrochemical sources of each of the considered parameters are suggested.

MATERIALS AND METHODS

THE STUDY AREA

The study area was located in the Wonji Plain, East Shoa-Zone of Oromia regional state, Central Rift Valley of Ethiopia (Fig. 1), specifically at Wonji-Shoa Sugar Estate (WSSE). Wonji plain is located in the flood plain of Awash river at about 110 km South-East of Addis Ababa, capital city of Ethiopia. The plain area is topographically viewed as a topographic depression surrounded by various ranges of mountain chains. Sugarcane is the most crop grown in the plantation area. The study area has an average rainfall of about 832 mm. The average minimum temperature of the area is 12.6°C and average maximum temperature is 28.5°C. The yearly average precipitation and wind speed is 768 mm and 2.81 m·s⁻¹, respectively. The climate of the area is generally classified to be semi-arid. The soils of WSSE area are described as loams, silty loams and clay loams, generally classified as light (30%) and heavy (70%) textured soils. The soils are formed from volcanic derived colluviums and alluvium on plains and terraces, developed under hot tropical conditions. Detailed information about the study area can be obtained from recent publications [DINKA *et al.* 2013; DINKA, NDAMBUKI 2014]. Especially, DINKA and NDAMBUKI [2014] described the study area very well including location, topography, climate, soils, geology and vegetation cover and irrigation water management.

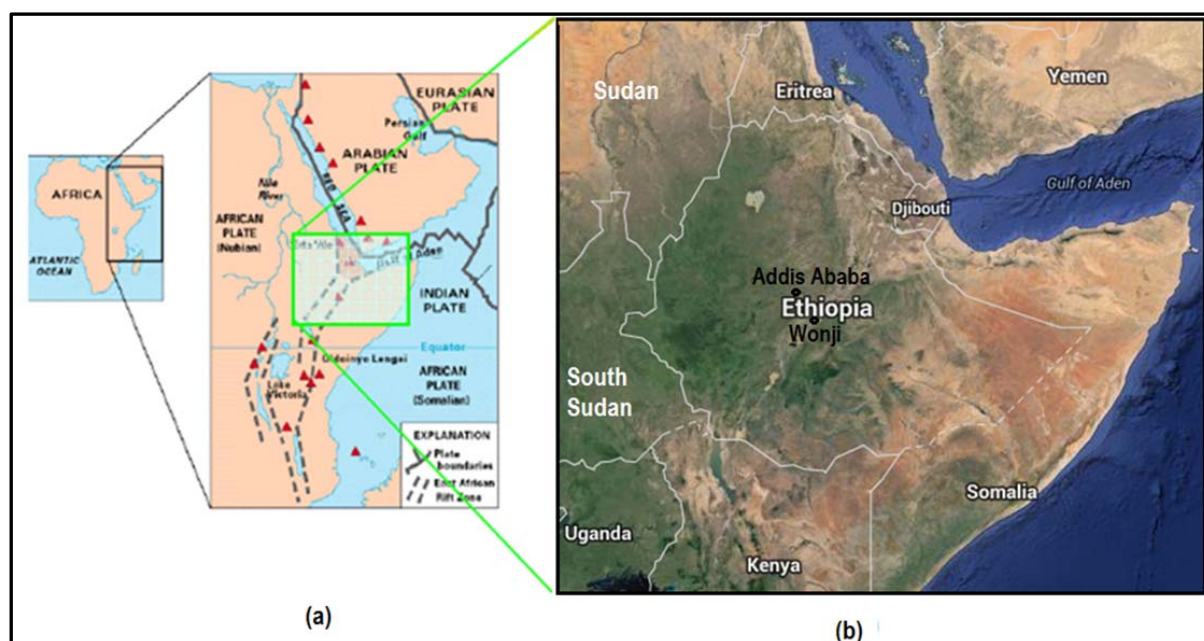


Fig. 1. Study area: a) Great East Africa Rift Valley, b) location of Wonji in Ethiopia; source: own elaboration

GROUNDWATER SAMPLING, ANALYSIS AND INTERPRETATION

The study comprises of measuring the groundwater quality from piezometers (PVC tubes) installed in different parts of plantation fields for the purpose of monitoring GWT depth (Fig. 2). Note that the GWT depth in the study area is very shallow (<2 m) (see DINKA *et al.* [2013; DINKA, NDAMBUKI 2014]). A total of 60 representative water samples were collected (30 samples each year) in 2009 and 2010. Two samples were collected from each piezometer. Sampling period is almost at the end of the irrigation season (May). The water sampling was done using clean polyethylene bottles to avoid potential leaching.

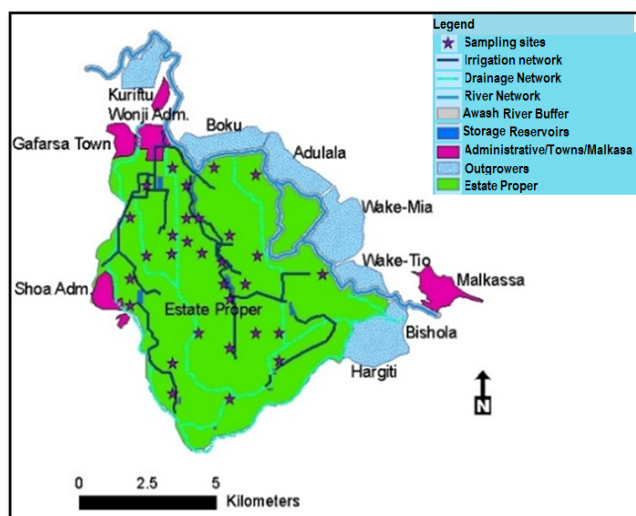


Fig. 2. Wonji-Shoa sugar plantation (estate proper and outgrowers) showing GW sampling sites, the Awash River, administrative areas, and villages/towns; source: own study

All groundwater samples were collected and analysed on the same day at Wonji Central Laboratory, for important physico-chemical parameters (pH, *EC*, soluble cations and anions) following standard test procedures [APHA 2012; WHO 2011]. Electrical conductivity (*EC*) and pH values were measured using conductivity and pH meters, respectively. Calcium (Ca) and magnesium (Mg) ions were determined by EDTA titration; sodium (Na) and potassium (K) by flame photometre; carbonate (CO₃) and bicarbonate (HCO₃) by acid (H₂SO₄) titration; chloride (Cl) by titration with 0.05 N AgNO₃; sulphate (SO₄) by spectrophotometer; and fluoride (F) and boron (B) by potentiometric methods. Other parameters (*TH*, *TDS* and *MAR*) were derived from measured physico-chemical parameters. Total hardness (*TH*) was determined from Ca and Mg shown in Eq. 1 [DINKA *et al.* 2015; REDDY, KUMAR 2010; SARKAR, HASSAN 2006]. The value of total dissolved solid (*TDS*) was determined from *EC* by the empirical formula (Eq. 2) [DINKA *et al.* 2015; PRADHAN, PIRASTEH 2011] since *EC* value is less than 5 dS·m⁻¹. Magnesium ratio (*MAR*) was determined using Eq. 3 [DINKA *et al.* 2015].

$$TH = 2.497 Ca^{2+} + 4.11 Mg^{2+} \quad (1)$$

$$TDS = 640 EC \quad (2)$$

$$MAR = \frac{Mg^{2+}}{Ca^{2+} + Mg^{2+}} 100 \quad (3)$$

Where: *TH* = total hardness, *TDS* = total dissolved solids (mg·dm⁻³), *EC* = electrical conductivity (dS·m⁻¹), *MAR* = magnesium absorption ratio; Ca and Mg values are in mg·dm⁻³.

PRASAD *et al.* [2009] indicated that graphical presentation of chemical analysis data makes understanding of complex groundwater systems simpler and quicker. Therefore, hydrochemical data of the study area were presented graphically in the form of Piper and Box plots. Trilinear Piper diagrams [PIPER 1944] were plotted based on dominant ions (cations and anions) in order to identify the hydrochemical facies and hence the water type. The computer program (GW chart) was used for plotting the Piper diagrams. The Piper plot reflects the effects of chemical reactions occurring between the minerals within the lithologic framework and anthropogenic inputs [DINKA 2017]. The water type was also classified based on the values of base exchange index (*r*₁) and meteoric genesis index (*r*₂) proposed by SOLTAN [1999] and used by others [HARITASH *et al.* 2008; REDDY, KUMAR 2010; SINGH *et al.* 2014].

$$r_1 = \frac{Na^+ - Cl^-}{SO_4^{2-}} \quad (4)$$

$$r_2 = \frac{(Na^+ + K^+) - Cl^-}{SO_4^{2-}} \quad (5)$$

Na⁺, Cl⁻, K⁺, SO₄²⁻ are in meq·dm⁻³.

Finally, the characteristics of each of the considered physico-chemical constituents are described briefly. The potential chemical origins of major ions for the different water types were suggested based on this study result and literature recommendation

RESULTS AND DISCUSSION

COMPOSITIONAL VARIABILITY

The analytical analysis results of physicochemical parameters are presented in Figures 3–4. Figure 3 presents the box plot for the considered parameters, including the minimum, percentile (25% and 75%), median and maximum values. The spatial variation and distribution pattern for the selected physico-chemical quality variables are illustrated in Figure 4.

An interesting feature which can be observed from the results, especially from the values of the range and CoV, is that water quality of the study area showed large compositional variability (except pH) from location to location. From the measured values, K and B ions are the highly variable parameters (CoV = 140%) and followed by Cl, Mg, *EC*, HCO₃, Na, Ca, etc. The least variable parameter is the pH, with CoV of 3.2% only. The spatial variability has implications for the causes of groundwater quality in the area. The large compositional variability could mainly be attributed to anthropogenic activities and geochemical processes prevailing in the region. Interestingly, plantation

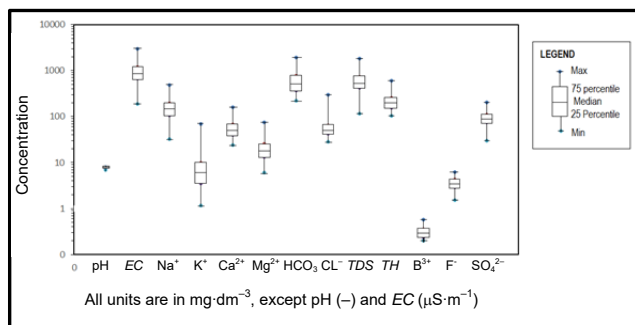


Fig. 3. Box plot for major quality parameters (average values); EC = electrical conductivity, TDS = total dissolved solids, TH = total hardness; source: own study

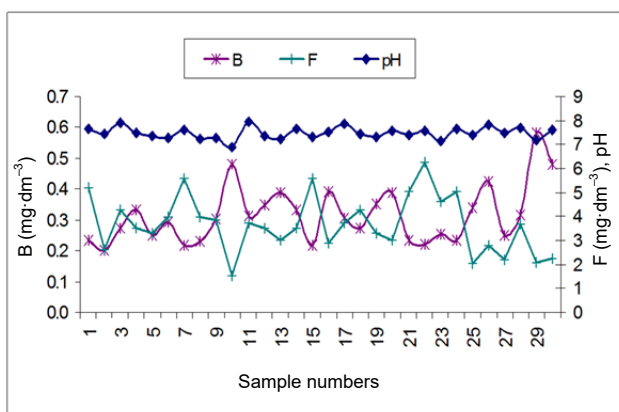
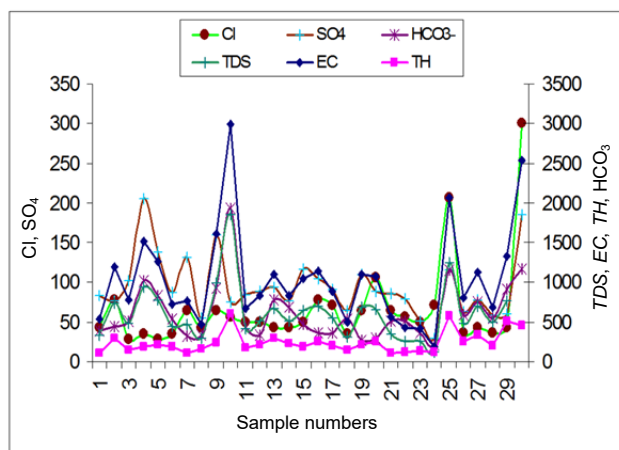
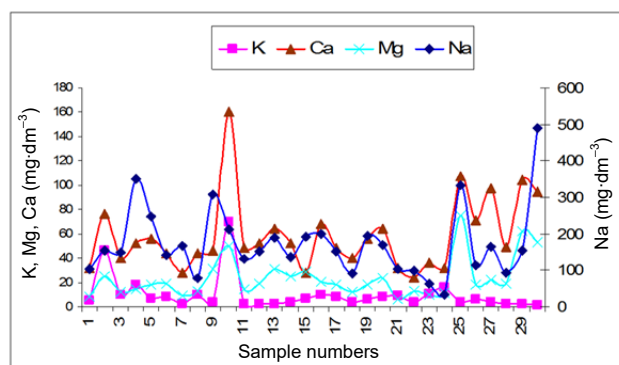


Fig. 4. The variation and distribution pattern of the water quality parameters (average values); EC, TDS, TH as in Fig. 3; source: own study

fields with relatively high content of cations have showed relatively high values of anions, and vice versa (Fig. 4). Moreover, plantation fields with relatively high concentration of soluble salts ($EC:TDS$) have relatively high values of other parameters (Na, Ca, K, HCO_3^- , Cl and TH), and vice versa. This means that the latter ones are the main responsible for the quality status of water in the study area.

The groundwater of the area is generally classified as slightly alkaline/basic ($pH > 7.0$). An alkaline pH is usually a measure of CO_3 and HCO_3^- ions. However, the CO_3 ion in the study area is almost nil, and hence HCO_3^- ion is the dominant anion. HCO_3^- ions are usually dominant in groundwaters with low to medium mineralization [DINKA *et al.* 2015]. Thus, it is possible to suggest, based on dominant pattern, that groundwater of the area is undergoing medium levels of mineralization process. In general, the soluble cations and anions can be arranged according to their dominance as $Na > Ca > Mg > K$ and $HCO_3^- > SO_4 > Cl > CO_3$, respectively. But, the cationic and anionic dominance patterns are changing from location to location. For example, the cationic dominance pattern is $Na > Ca > K > Mg$ in sample 4 (field 48), $Ca > K > Na > Mg$ in sample 10 (field 63), etc. Similarly, the anionic dominance pattern in field 4 is $SO_4 > HCO_3^- > Cl > CO_3$.

DESCRIPTION OF INDIVIDUAL QUALITY VARIABLES

In the subsequent sub-sections, the characteristics of each of the considered physico-chemical constituents and their potential sources of chemicals are described briefly.

The pH value. The pH values obtained (6.90–7.94) are within the range of neutral to slightly alkaline/basic. The potential sources of alkaline pH in the study area can be the levels of hard-water minerals (bicarbonate, borates, silicates and phosphates), nutrient recycling and release of basic industrial (paper and sugar factory) effluents and agricultural chemicals (use of fertilizer like urea). Water pH has a significant effects on many chemical reactions during water treatments [PRADHAN, PIRASTEH 2011]. It also affects the taste of water and increases the scale formation in pipe systems [JAMSHIDZADEH, MIRBAGHERI 2011]. The spatial variation of pH is not too high (Fig. 3), with CV of 3% only. The highest and lowest values of pH were recorded for samples 11 (field 18) and 10 (field 63). Interestingly, field 63 has relatively higher concentrations of other ions and field 18 has relatively the lowest concentration of other ions. That means pH is negatively correlated with most of the other parameters (except Cl, F and SO_4), which can also be visualized from Figure 4.

Total salts: EC and TDS. The EC values are within the ranges of 0.118–2.299 $dS \cdot m^{-1}$, with average value of 1.038 $dS \cdot m^{-1}$. As opposed to the pH, the highest EC value was recorded for sample 10 (field 63) and the lowest EC value was recorded for sample 24 (field 11). About 83.3% of the samples have $EC < 1500 \mu S \cdot cm^{-1}$ (0.187–1.50 $dS \cdot m^{-1}$) and the remaining proportion has EC in the range of 1.50–3.00 $dS \cdot m^{-1}$. High value of EC denotes the proportionally high value of dissolved ions, especially major cations. As clearly observed from Figure 4, fields with higher EC values has higher values of major cations, especially HCO_3^- ,

TH , Ca^{2+} , Na^+ and Mg^{2+} ions. That means EC values are highly correlated with HCO_3^- , and followed by TH , Ca , Na , Mg , etc. The EC value also reveals the mineralization of water types. Based on EC value [KABBOUR, ZOUHRI 2005], about 30% and 47% of the water samples showed a significant and high mineralization, respectively. More than 75% of the groundwater of the area are undergoing medium to high rate of mineralization. EC is used to measure the ability of water to carry an electric current. Absolutely pure water is a poor conductor of electricity. It measures the salinity level – the presence and concentration of dissolved salts in water [DAVIS 2010].

Water with soluble dissolved salts has relatively higher EC , which is proportional to the amount of salts dissolved in water [GODGHATE *et al.* 2013]. This argument is also true for the study area. Groundwater samples with relatively high EC values also have relatively high TDS values (Fig. 4). The TDS values are varying from 115–1847 $mg\cdot dm^{-3}$, with average value of 641 $mg\cdot dm^{-3}$. About 90% of the samples have $TDS < 1000\ mg\cdot dm^{-3}$ and categorized as fresh water and the remaining samples (10%) are classified to be brackish ($TDS > 1000\ mg\cdot dm^{-3}$). High values of TDS ($TDS > 500\ mg\cdot dm^{-3}$) indicates the presence of slightly elevated concentrations of salts and is related to the problem of water hardness [HEROJEET *et al.* 2013]. Higher TDS ($>500\ mg\cdot dm^{-3}$) can cause excessive scaling in water pipes, water heaters, boilers and household appliances [GODGHATE *et al.* 2013]. The principal constituents of high TDS values are usually major dissolved ions: cations (Na , Ca , Mg , K) and anions (Cl , CO_3 , HCO_3 , SO_4 , NO_3). That means a high concentration of salts of Na , Ca , and Mg are usually responsible for high amounts of TDS . In the study area, however, the concentration of Ca and Mg salts are not high (Fig. 4), and hence the major source contributing to TDS in the groundwater of the area is the Na salts. The higher values of EC and TDS for some groundwater samples is indicator of higher ionic concentrations, probably due to the anthropogenic activities in the region and geological weathering conditions acquiring high concentrations of the dissolved minerals. The local anthropogenic activities could be discharges from intensive and prolonged agricultural activities (fertilization, chemigation, etc.) and discharges from industrial and domestic wastes. Agricultural activities (use of fertilizers and other chemicals) can introduce ions and metals into the groundwater [DINKA *et al.* 2015; HARITASH *et al.* 2008; LAAR *et al.* 2011]. Apart from agricultural practices, TDS in groundwater can also originate from the weathering of rocks or soils, sewage systems, urban runoff and industrial wastes [ASADI *et al.* 2007; DINKA *et al.* 2015]. The area is under long term (>60 years) irrigation, industrial activities and agro-chemical usage. Thus, the contribution of agro-chemicals for dissolved solids are significant. The dissolved solids of the area are expected to increase in the future due to the intensive usage of agro-chemicals and their subsequent residual and downward mobility effects.

Major cations. The average values of soluble cations and anions are relatively low in concentration in groundwater of the area. However, the concentrations of Na and HCO_3^- ions in some fields (48, 66, 101, 153, 63, 169, 131,

105, 195, and 189) are very high compared to the others (Fig. 3). Na ion concentration is found to be in the range of 32–489, with average value of 172 $mg\cdot dm^{-3}$. Most salts of Na are not active in chemical reactions even though they are readily soluble in water [PRADHAN, PIRASTEH 2011]. The dominance of Na concentration in some of the groundwater samples of the study area could be due to natural activities such as the weathering of Na bearing minerals/rocks (such as halite, limestone, feldspar and montmorillonite), and/or cation exchange process (i.e. precipitation of Ca and Mg ions or cation exchange between rock and water). The source of Na ion could also be due to deposition of rock salts, its displacement from absorbed complex of rocks and soils by Ca and Mg , and/or halite ($NaCl$) dissolution [DINKA *et al.* 2015]. Na^+ is about 3-fold higher than Ca and Cl , indicating that the groundwaters of the area are likely to be gaining Na^+ from anthropogenic sources, such as industrial effluent (use of lime/soda ash ($NaCO_3$) in sugar processing), domestic sewages, and/or agricultural activities (use of agro-chemicals).

The measured K ion concentration is in the range of 1–69, with average value of 10 $mg\cdot dm^{-3}$. As expected, the concentration of $K \ll Na$ (K nearly one-tenth that of Na) in the water samples of the area. This is actually due to the fact that K minerals have a weak migratory ability and are resistant to decomposition by weathering processes [DINKA *et al.* 2015; NIKANOROV, BRAZHNIKOV 2012; PRADHAN, PIRASTEH 2011]. The concentration of K in groundwater of the area is expected to increase in the future due to the use of fertilizers (urea) and other industrial activities in the region.

The concentration range of Ca is between 24 and 160 $mg\cdot dm^{-3}$, with average value of 58 $mg\cdot dm^{-3}$. While high concentration of Ca has scaling problems and impaired lathering of soaps; low concentration of Ca ($<16\ mg\cdot dm^{-3}$) can cause possible corrosive effects. However, Ca is important for the health of natural water bodies since it is known to reduce the toxicity of many chemical compounds (e.g. NO_2) [WILLIAM *et al.* 1986]. The MAR value of about 60 indicates that there is Ca removal by either ion/cation exchange or calcite ($CaCO_3$) precipitation. The measured Mg ion concentration is in the ranges of 6–75, with average value of 23 $mg\cdot dm^{-3}$. The natural sources of Mg ions are chemical weathering and dissolution of dolomite, marls, and other rocks. Discharges from industries and agriculture are the anthropogenic sources of Mg ion. The Mg^{2+} content is relatively low in the groundwater of the area. The Mg ion is seldom dominant in natural waters due to the fact that Mg has weak biological activity and the highest solubility [DINKA *et al.* 2015]. Moreover, the dissolution of Mg rich minerals is usually a slow process [RAMESH, JAGADEESWARI 2012].

Major anions. The measured HCO_3^- content is between 220 and 1928, with average value of 617 $mg\cdot dm^{-3}$. The highest HCO_3^- contents were observed on fields 63, 201, 52 and 48. As expected based on the value of the slightly alkaline pH, the CO_3^{2-} content in the groundwater of the area is very low (0–42 $mg\cdot dm^{-3}$). Both CO_3 and HCO_3^- ions occur in the form of carbonate system of chemical equilibrium, usually associated with the high pH (alka-

linity) and hardness of water, which gives an unpleasant taste to water. Dissolution of carbonate rocks (eg. limestone, dolomite, magnesites) and carbonic acid (H_2CO_3) are the sources of CO_3 and HCO_3 ions [DINKA *et al.* 2015; NIKANOROV, BRAZHNIKOV 2012; RAMESH, JAGADEESWARI 2012].

The SO_4 concentration found in the water samples is in the ranges of 32 to 205, with mean value of $95 \text{ mg}\cdot\text{dm}^{-3}$. Higher values of SO_4^{2-} ($>150 \text{ mg}\cdot\text{dm}^{-3}$) was recorded in samples 4 (field 48), 30 (field 201) and 9 (field 153). The sources of SO_4 ion in these fields could be natural and/or anthropogenic activities [DINKA *et al.* 2015; NIKANOROV, BRAZHNIKOV 2012]. The human economic activities affecting the concentration of SO_4 ion in groundwater of the area could be agricultural (phosphatic fertilizers) and industrial activities (use of soda ash in sugar clarification process). The principle natural sources are lithology (weathering of rocks), volcanic activities, and biochemical process [HEROJEET *et al.* 2013]. Other natural sources of SO_4 ions include the decomposition and oxidation of substances containing sulfur (fossil fuels and dissolution of sulfur bearing minerals such as pyrite and gypsum) [DINKA 2017; DINKA *et al.* 2015], the leaching of natural deposits of MgSO_4 (Epsom salts) or NaSO_4 (Glauber's salt), and the sulphides of heavy metals (iron, nickel, copper and lead) [DWAFF 2004].

The concentration of Cl obtained in the study area varies between 28 and 300, with a mean value of $66 \text{ mg}\cdot\text{dm}^{-3}$. All groundwater samples have normal Cl content ($<15 \text{ meq}\cdot\text{dm}^{-3}$). High Cl content was recorded for fields 52 and 201. The high Cl content in some fields could be due to pollution by agriculture (fertilizers or chemicals), domestic sewage, animal wastes (organic) and/or industrial origin. Chloride originates from NaCl_2 which gets dissolved in water from rocks and soil. Cl may be accumulated in groundwater from chloride-rich minerals or rocks, domestic sewage and agricultural activities [SELVAKUMAR *et al.* 2014]. High Cl content is an indicator of the presence of large amount of organic matter [GODGHATE *et al.* 2013; YADAV 2002].

The B ion concentration obtained was in the range between 0.2 and 0.58, with average value of $0.31 \text{ mg}\cdot\text{dm}^{-3}$. About 70% of the samples exceeded $0.3 \text{ mg}\cdot\text{dm}^{-3}$. B usually exists as dissociated boric acid and borax [WHO 2011].

Its concentration is not high in the groundwater samples. Groundwater samples of the study area have F content varying between 1.51 and 6.3, with average value of $3.7 \text{ mg}\cdot\text{dm}^{-3}$, which is very high. This could be due to agricultural and industrial area and the weathering of fluorine bearing minerals like fluoride and apatite. Almost 35% of the groundwater samples have $\text{F} > 4 \text{ mg}\cdot\text{dm}^{-3}$. The use of water containing F content as high as $4 \text{ mg}\cdot\text{dm}^{-3}$ may cause usually cause dental and skeletal fluorosis [HARTISHA *et al.* 2008; KARRO, UPPIN 2013; WHO 2011]. High F content in groundwater is due to the bedrock containing F minerals. Groundwater usually contains F dissolved by geological formations [ASADI *et al.* 2007]. Groundwater of the Ethiopian rift valley regions are usually characterized by high F content due to the fact that the area is geologically not stable. Fluorine is the most electronegative and reacts with most of the other elements [KARRO, UPPIN 2013]. This characteristics makes F content relatively high in water obtained from groundwater. The pH-F relation is presented as in Figure 5a. As opposed to the result obtained by DECHASA [1999], the highest F content is not associated with the highest pH value. There is no distinct relationship between pH and F content. But it is important to note that the alkaline nature of groundwater of the area is indicator for the elevated concentration of F in GW of the area. This is due to the fact that the OH ion replaces the F concentration of clay minerals and increases the concentration of F in groundwater. It is evident from Figure 5b that there is exponential/power relationship between Ca and F content in GW of the study area. Higher F content of the area is associated with lower Ca content. Higher F content in GW is often associated with low Ca content, which is controlled by controlled by fluorite (CaF_2). In general, in addition to anthropogenic activities, the alkaline nature ($\text{pH} > 7$), low Ca content, high temperature and the semi-arid climatic conditions of the study area increases the solubility of CaF_2 and hence responsible for the high F content. High F content is actually the characteristics of Ethiopian Rift valley regions due to its unstable geologic weathering condition.

High F content in GW is usually associated with the dissolution of calcite, weathering and leaching of amphiboles, fluorite, apatite and mica [SINGH *et al.* 2011]. A relationship between Na and Cl was plotted (Fig. 6a) in order to check whether Na and Cl ions are due to halite dissolu-

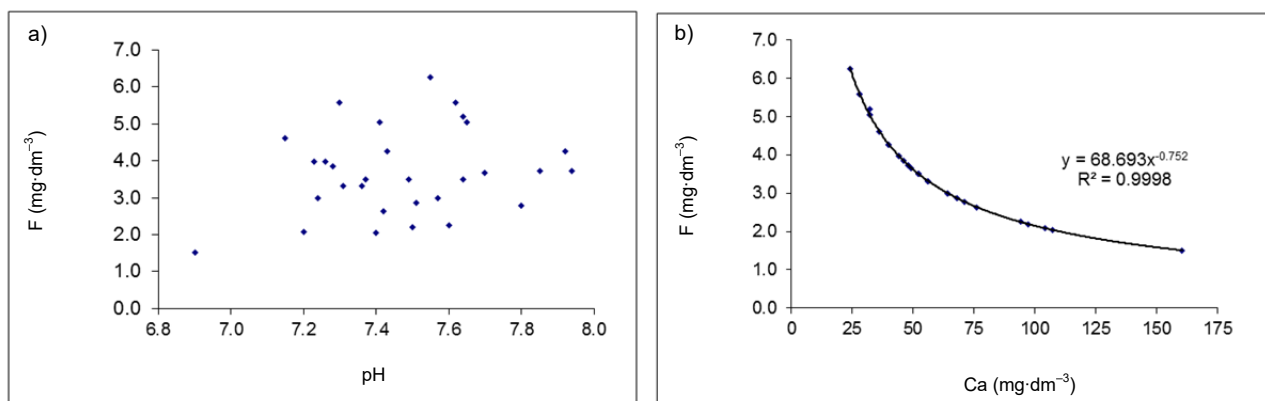


Fig. 5. Relation between fluoride with: a) pH, b) calcium; source: own study

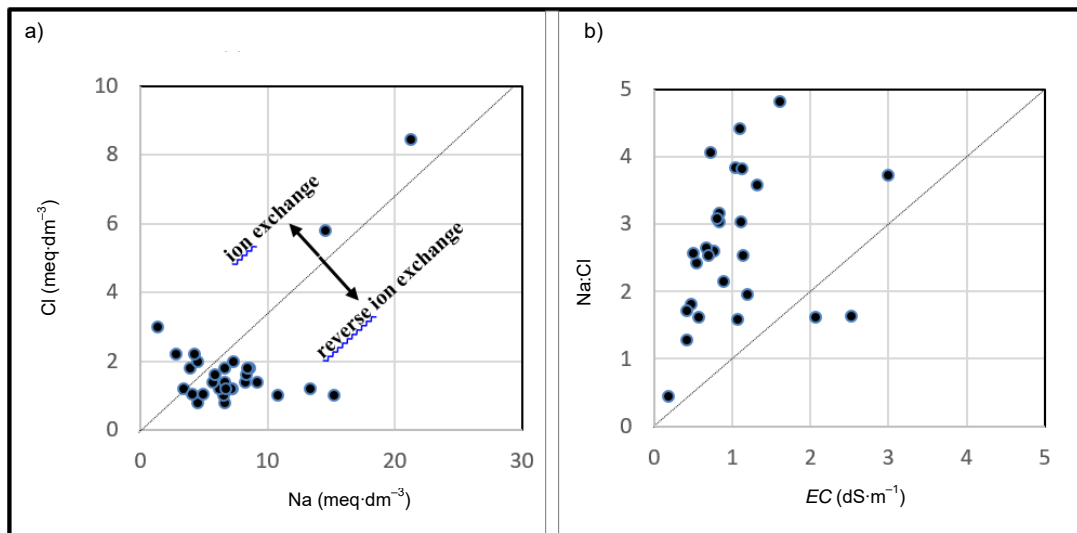


Fig. 6. Relation between: a) Na vs. Cl (meq·dm⁻³), b) Na:Cl vs. EC (dS·m⁻¹); source: own study

tion or other processes (e.g., ion exchange). As shown in Figure 6a, there is no linear relationship between Na⁺ and Cl⁻ in the groundwaters of the area. This suggests that the concentration of Na and Cl ions in these water sources is heavily influenced by factors other than the dissolution of halite [OSTOVARI *et al.* 2013]. Only few samples are along the 1:1 slope line, indicating halite dissolution could be the sources for Na and Cl ions. Most of the samples are below the 1:1 slope line, indicating that the sources of Na and Cl ions are mostly due to reverse ion exchange rather than ion exchange. However, at very high value of Cl⁻, the plot is above the 1:1 slope, indicating the sources are mostly due to ion exchange.

Figure 6b illustrates the plot of Na:Cl vs. EC in order to check whether the weathering of silicate rocks or evaporation/evapotranspiration in the region is one of the important processes responsible for the higher concentration of Na in groundwater of this area. If the evaporation/evapotranspiration process is the dominant one, the Na:Cl ratio would be unchanged, assuming that no mineral species are precipitated, and the plot of Na:Cl versus EC would give a horizontal line [RAJMOHAN *et al.* 2000]. Interestingly, the plot (Fig. 5) shows that Na:Cl increases with an increase in EC value, which is also true for the Na vs. Cl plot. Furthermore, the plot (Fig. 6b) also indicates that most of the water samples are above the fresh water evaporation line, further indicating evaporation/evapotranspiration may not be the major process controlling groundwater chemistry. Hence, Na in the groundwater of the study area might have been derived from some other processes. All groundwater samples (except 1 sample) have Na:Cl > 1 (Fig. 6b), indicating ion (cation) exchange is the major process, which is replaced by silicate weathering. In general, it is possible to suggest that ion exchange, reverse ion exchange processes and halite dissolution are the possible for Na and Cl in the study area.

Hardness. The average value of TH obtained in this study was 214.2, varying from 85 to 604 mg·dm⁻³. TH values obtained indicates that 50% of the samples are moderately hard (TH > 200 mg·dm⁻³), 33% are hard (TH = 200–

500), and 17% very hard (TH > 500 mg·dm⁻³). Water hardness indicates the water quality, mainly in terms of Ca and Mg ions (Ca or Mg carbonates). The scum deposits on enamelled surfaces of baths and hand basins are related to the effects of Mg and Ca hardness. Water hardness is responsible for scale developments in water heating appliances (caused by deposits of carbonates) and plumbing (which transports hot water). The low suds production inhibiting the leathering of soap and resulting in scum formation is also the effect of hard water [DWA 2004].

GROUNDWATER TYPE CLASSIFICATION

Piper diagrams. The water types were classified using trilinear Hill–Piper plots for the major cations and anions (Fig. 7). The piper plot also allows mixing effects between waters, if two projected lines cross each other. As clearly revealed by the piper plots, most of the various water sources of the area have distinct hydrochemical facies. As described by MARGHADE *et al.* [2012], hydrochemical facies reflect the effects of chemical reactions occurring between the minerals within the lithologic framework and any other anthropogenic inputs [DINKA 2017]. The central diamond (Fig. 7) indicates that all groundwater of the area are categorized under group 1 (Ca-Mg-HCO₃) water type. Group 1 water types are usually due to water-rock interaction and recharge from rainfall and/or irrigation. Its origin is the dissolution of carbonate rocks in the aquifer through the action of percolating waters enriched in CO₂ after being in contact with the atmosphere [MARGHADE *et al.* 2012]. Groundwater of the area might receive solutes from the chemical weathering of aluminum silicates, dissolved CO₂, volcanic glass and limestone dissolution, and industrial emissions. Additionally, dissolution of evaporites (e.g., halite or gypsum) may contribute due to semiarid climatic conditions of the area.

In general, the following points can also be identified from the Piper diagram: (i) Ca-Mg-HCO₃ water type; (ii) no dominant cations; (iii) bicarbonates are the dominant

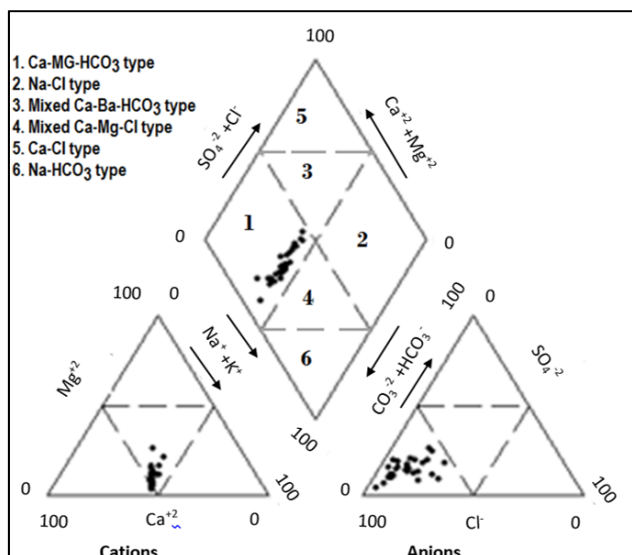


Fig. 7. Trilinear Piper diagram (epm) of the groundwater samples at Wonji; source: own study

anions; (iv) alkaline water ($\text{Ca}+\text{Mg}-(\text{CO}_2+\text{HCO}_3)$) is dominant; (v) saline water ($\text{Na}+\text{K}-\text{Cl}$) is not dominant. All the water samples are clustered together and there is a mixing trend towards Na, K, and Cl/SO_4 rich waters. The mixing trend is more likely the effect of agro-chemicals. The dominance of alkaline water may be due to the sand dunes in the area. Furthermore, Na and K are less than 50%. The result obtained in this study is different from the report made by DECHASA [1999], which states that groundwater of the area is Na-K- HCO_3 type and there are no dominant cations and anions. This condition explains the changing hydrochemical facies for the groundwater of the area over-time due to the changes in its hydrochemical composition. Type of water with dominant ions represents surface waters and shallow volcanic aquifers. The dominance of bicarbonate ion is also in agreement with the discussion made earlier under pH.

Meteoric genesis index. The groundwater type is also governed by the value of meteoric genesis [HARITASH *et al.* 2008]. Based on the value of meteoric genesis (Fig. 8), about 70% of the samples have met gen >1, indicating that the groundwater is shallow meteoric water percolation type. Meteoric groundwaters are waters that have recently been involved in atmospheric circulation, whose isotopic composition is similar to that of surface waters [BOKHARI, KHAN 1992]. This condition confirms that the chemical constituents are not occurring naturally only, but due to the intensive use of agricultural chemicals for long period of time, factory waste water, domestic waste, runoff, etc. The effect of the use of agro-chemicals on the physico-chemical characteristics of the groundwater of the area is evident from the groundwater type. In such very shallow groundwater areas [DINKA, NDAMBUKI 2014], the downward mobility of agrochemicals is fast (i.e. low residence time); and thus the changing of hydrochemical composition of the groundwater is expected. This idea further strengthens the mixing trend and changing hydrochemical facies suggested earlier based on the Piper plot (section Piper diagrams).

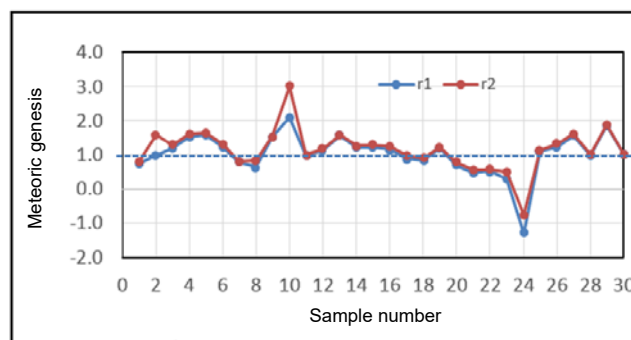


Fig. 8. Base exchange index and meteoric genesis index for each groundwater sample; source: own study

CONCLUSIONS AND RECOMMENDATIONS

In the present study, the hydrochemical quality composition of groundwater under long-term irrigation was investigated and characterized. The study result indicated that groundwater of the study area is slightly alkaline/basic in nature and showed compositional variations from one location to another location. The spatial variation could be the result of the respective groundwaters being in contact with different aquifer materials or minerals for significantly different periods of time as well as the anthropogenic inputs from industrial, domestic and agricultural effluents. The result also showed that groundwaters of the area is undergoing low to high level of mineralization. Both trilinear Piper plot and meteoric genesis index revealed that groundwater of the area is shallow meteoric water percolation type with a changing of hydrochemical facies and mixing trend. In general, groundwater of the area is Ca-Mg- HCO_3 type, with no dominant cations and HCO_3 are the dominant anions. Group 1 waters (Ca-Mg- HCO_3 type) are due to water-rock interaction and recharge from rainfall.

There are indicators for some of the quality variables that there are natural and anthropogenic sources. The anthropogenic processes could include discharges from factory effluents, domestic sewage, and agricultural activities. The result also suggested that ion exchange, reverse ion exchange, evaporation, silicate weathering, halite dissolution, etc. are the possible sources for most of the major ions (Na, Cl, HCO_3 , etc.) in the study area. Moreover, the groundwater of the area were formed by the mixing of a deep-seated magmatic CO_2 -rich groundwater with the shallow groundwater resulted in changing and mixing trend of geohydrochemical facies and compositions.

This study was done for two years only and presents the property of physico-chemical quality parameters only. Long-years detailed study, which includes both dry (pre-monsoon) and wet (post-monsoon) season data sampling, is recommended in order to verify this study results and clarify uncertainties associated with few years' data. Therefore, the author of this article would like to suggest the following further investigations:

- delineating the hydro-chemical sources and evolution of the groundwater of the study area. this plays a significant role for effective management of the available water resources, and hence, sustainable socio-economic development of the region;

- detailed investigation on multivariate, geospatial and trend analysis. this study helps to understand the impact of anthropogenic activities on groundwater of the area, which requires long-term groundwater quality monitoring data;
- analysing the impacts of organic pollutants (filtercake, mud, bagasse, etc.) and agro-chemicals (nitrate, phosphate, pesticides, herbicides, etc.) on groundwater of the area. more emphasis should be paid specific to the organic pollutants and agro-chemicals available in the study area;
- analysing the GW quality status for different uses (irrigation, domestic, industry, etc.); specially, evaluation of the possibility for conjunctive use of groundwater for irrigation plays the crucial role for the controlling the groundwater rise and contamination in such shallow water table areas, and hence extremely important for sustainability of the sugarcane plantation and environment of the region;
- quantification of the flow pattern, solute transport and specific yield using physical based models. This requires characterization of the bed-rock and delineating the quaternary (sub-surface) aquifers and GW through-flow of the region.

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Megersa Olumana DINKA

Właściwości wód gruntowych i zmienność ich składu na długotrwałe nawadnianym obszarze Równiny Wonji w Etiopii

STRESZCZENIE

Plantacja trzciny cukrowej Wonji Shoa usytuowana na równinie zalewowej rzeki Awash (Etiopia) była nawadniana ponad 60 lat i stanowiła obiekt działalności przemysłowej i rolniczej. W przedstawionych badaniach scharakteryzowano właściwości i jakość wód podziemnych na plantacji. Próbkę wody pobierano z piezometrów rozmieszczonych na plantacji i analizowano w nich parametry fizyczne i chemiczne (pH, przewodnictwo elektrolityczne, główne kationy i aniony) zgodnie z obowiązującymi normami. Inne wskaźniki chemiczne (np. całkowite substancje rozpuszczone – *TDS*, całkowita twardość – *TH*, współczynnik absorpcji magnezu – *MAR*, wskaźniki r_1 (base exchange) i r_2 (meteoric genesis)) wyprowadzono z mierzonych parametrów jakości wody. Zmienność składu i klasyfikację wód gruntowych przedstawiono za pomocą wykresów pudełkowych i trójkątno-rombowych wykresów Piper. Na podstawie cech jakościowych wody zaproponowano potencjalne źródła substancji mineralnych dla każdego z badanych zasobów wody. Zarówno wykres Piper, jak i indeks wody opadowej wykazały, że wody gruntowe na badanym obszarze pochodzą z perkolacji wód opadowych o zmiennych właściwościach hydrochemicznych. Wody te należą do typu I (Ca-Mg-HCO₃) bez dominującego kationu i z wodorowęglanami jako dominującym anionem. Wyniki badań dowodzą, że skład chemiczny wód gruntowych badanego obszaru zależy od zmienności dopływu z procesów naturalnych (opadu) i działalności człowieka. Lokalne procesy antropogeniczne to głównie zrzuty ścieków z produkcji cukru, ścieków bytowych i dopływy z rolnictwa.

Słowa kluczowe: *cechy fizyczne i chemiczne, parametry jakościowe, skład chemiczny, wody gruntowe, zmienność jakości*