ADDIS ABABA UNIVERSITY

SCHOOL OF GRADUATE STUDIES

DETERMINATION OF FLUORIDE AND SELECTED METALS IN THE SOILS OF ETHIOPIAN RIFT VALLEY AND IRRIGATION WATER IN THE SURROUNDING AREA

By

ELIAS GIZAW

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LISTS OF ACRONYMS AND ABBREVIATIONS

ISE	Ion Selective Electrode
FAAS	Flame Atomic Absorption Spectrometry
TISAB	Total Ionic Strength Adjusting Buffer
TDS	Total Dissolved Solid
EC	Electrical Conductivity
WHO	World Health Organization
EPA	Environmental Protection Agency
FAO	Food and Agricultural Organization
SD	Standard Deviations
ND	Not Detected
AAAK	Addis Ababa Arat Killo Campus
AK	Akaki
DZ	Debre-Zeyt
MO	Mojo
WO	Wonji
AL	Alem-Tena
ME	Meki
ZU	Zuway
AD	Adami-Tullu
BU	Bulbulla
WSF	Water Soluble Fluoride
TF	Total Fluoride

ABSTRACT

The occurrence of dental and skeletal fluorosis among the population in the Ethiopian Rift Valley provided the motivation to investigate occurrence of fluoride in soil and water. The objective of this study was to determine the levels of fluoride in Ethiopian Rift Valley soils and the nearby irrigation water sources and the correlation of fluoride with metals. Nine soil samples from the surface horizon (0-20 cm) depth and water samples were collected from high fluoride zone of Ethiopian Rift Valley and one controlling group collected from the College of Natural Sciences (Arat Killo Campus), Addis Ababa University. The sample was collected by random sampling technique. The soil samples were air dried, grinded, sieved and weighed, then measured for both fluoride and metals content. The pH, conductivity, salinity and total dissolved solid in water and soil sample were also measured. Fluoride determination was made by fluoride ion selective electrode and metal determination by flame atomic absorption spectrophotometer. The validation of optimized procedure was evaluated using standard addition (spiking) method and an acceptable percentage recovery was obtained. The fluoride concentration in water sample was found in the range of 0.143-8.03 mg/L which are below the WHO limits of fluoride concentration for irrigation (less than 10 mg/L). The water soluble and total fluorides in soil were 2.32-16.2 µg/g and 209-1210 µg/g, respectively. The mean metal concentration (µg/g dry weight basis) range in soil samples and mg/L in water samples respectively were: Na (684-6703, 8.64-67.3), Mg (1608-11229, 22.7-66.7), K (1776-4394, 1.11-20.3), Ca (7547-22998, 16.7-267), Cr (9.79-79.3, 0.071-0.169), Mn (143-700, 0.048-37.2), Co (50.3-112, 0.354-1.48), Ni (446-1288, 0.274-40.9), Fe (12180-32681, 6.04-47.7), Cu (8.85-45.4, 0.088-0.251) and Zn (30.5-89.2, 0.144-0.562). Fluoride was found to have significant correlation with major metals (Fe, Cu and Cr), but the correlation with other trace metals were not significant.

KEYWORDS: Fluoride, Metals, Water, Soil, Ethiopian Rift Valley

1. INTRODUCTION

1.1. SOIL

1.1.1. Definitions of soil

Soil is a natural body comprised of solids (minerals and organic matter), liquid, and gases that occurs on the land surface, occupies space, and is characterized by one or both of the following: horizons, or layers, that are distinguishable from the initial material as a result of additions, losses, transfers, and transformations of energy and matter or the ability to support rooted plants in a natural environment.

The upper limit of soil is the boundary between soil and air, shallow water, live plants, or plant materials that have not begun to decompose. Areas are not considered to have soil if the surface is permanently covered by water too deep (typically more than 2.5 meters) for the growth of rooted plants.

The lower boundary that separates soil from the non-soil underneath is most difficult to define. Soil consists of horizons near the Earth's surface that, in contrast to the underlying parent material, have been altered by the interactions of climate, relief, and living organisms over time. Commonly, soil grades at its lower boundary to hard rock or to earthy materials virtually devoid of animals, roots, or other marks of biological activity. For purposes of classification, the lower boundary of soil is arbitrarily set at 200 cm [1].

1.1.2. Soil formation

The formation of soil happens over a very long period of time. It can take 1000 years or more. Soil is formed from the weathering of rocks and minerals. The surface rocks break down into smaller pieces through a process of weathering and is then mixed with moss and organic matter. Over time, this creates a thin layer of soil. Plants help the development of the soil. The plants attract animals, and when the animals die, their bodies decay. Decaying matter makes the soil thick and rich. This continues until the soil is fully formed. The soil then supports many different plants [2].

Soil formation, or pedogenesis, is also the combined effect of physical, chemical, biological, and anthropogenic processes on soil parent material. Soil genesis involves processes that develop layers or horizons in the soil profile. These processes involve additions, losses, transformations and translocations of material that compose the soil. Minerals derived from weathered rocks undergo changes that cause the formation of secondary minerals and other compounds that are variably soluble in water, these constituents are moved (translocated) from one area of the soil to other areas by water and animal activity. The alteration and movement of materials within soil causes the formation of distinctive soil horizons [3].

1.1.3. Soil compassion

Soils are a mixture of different things; rocks, minerals, and dead, decaying plants and animals. Soil can be very different from one location to another, but generally consists of organic and inorganic materials, water and air. The inorganic materials are the rocks that have been broken down into smaller pieces. The size of the pieces varies. It may appear as pebbles, gravel, or as small as particles of sand or clay. The organic material is decaying living matter. This could be plants or animals that have died and decay until they become part of the soil. The amount of water in the soil is closely linked with the climate and other characteristics of the region. The amount of water in the soil is one thing that can affect the amount of air. Very wet soil in a wetland probably has very little air. The composition of the soil affects the plants and therefore the animals that can live there [4].

1.1.4. Types of soil

Sand, silt, and clay are the basic types of soil. Most soils are made up of a combination of the three. The texture of the soil, how it looks and feels, depends upon the amount of each one in that particular soil. The type of soil varies from place to place on our planet and can even vary from one place to another [4].

Soils differ significantly from place to place because the original parent material differed in chemical composition, depth, and texture (from coarse sand to fine clay), and because each soil shows the effects of environmental factors including climate, vegetation, macro- and microorganisms, the relief of the land, and time since the soil began forming. The result of these factors is a dynamic, living soil with complex structure and multiple layers (horizons). Soils have regional patterns, and differ substantially over short distances. These differences have shaped local and regional land use patterns throughout history. Because of this, historians have studied soil for clues about how people lived and for explanations of historical events and patterns [5].

1.1.5. Uses of soil

Soil is used in agriculture, where it serves as the primary nutrient base for plants; however, as demonstrated by hydroponics, it is not essential to plant growth if the soil-contained nutrients could be dissolved in a solution. The types of soil used in agriculture (among other things, such as the purported level of moisture in the soil) vary with respect to the species of plants that are cultivated.

Soil resources are critical to the environment, as well as to food and fiber production. Soil provides minerals and water to plants. Soil absorbs rainwater and releases it later, thus preventing floods and drought. Soil cleans the water as it percolates. Soil is the habitat for many organisms: the major part of known and unknown biodiversity is in the soil, in the form of invertebrates (earthworms, woodlice, millipedes, centipedes, snails, slugs, mites, springtails, enchytraeids, nematodes, protists), bacteria, archaea, fungi and algae; and most organisms living above ground have part of them (plants) or spend part of their life cycle (insects) belowground. Above-ground and below-ground biodiversities are tightly interconnected [6, 7] making soil protection of paramount importance for any restoration or conservation plan.

The biological component of soil is an extremely important carbon sink since about 57% of the biotic content is carbon. Even on desert crusts, cyanobacteria lichens and mosses capture and sequester a significant amount of carbon by photosynthesis. Poor farming and grazing methods have degraded soils and released much of this sequestered carbon to the atmosphere. Restoring the world's soils could offset some of the huge increase in greenhouse gases causing global warming while improving crop yields and reducing water needs [8-10].

Waste management often has a soil component. Septic drain fields treat septic tank effluent using aerobic soil processes. Landfills use soil for daily cover. Land application of wastewater relies on soil biology to aerobically treat BOD. Organic soils, especially peat, serve as a significant fuel resource; but wide areas of peat production, such as sphagnum bogs, are now protected because of patrimonial interest. Both animals and humans in many cultures occasionally consume soil. It has been shown that some monkeys consume soil, together with their preferred food (tree foliage and fruits), in order to alleviate tannin toxicity [11].

Soils filter and purify water and affect its chemistry. Rain water and pooled water from ponds, lakes and rivers percolate through the soil horizons and the upper rock strata; thus becoming groundwater. Pests (viruses) and pollutants, such as persistent organic pollutants (chlorinated pesticides, polychlorinated biphenyls), oils (hydrocarbons), heavy metals (lead, zinc, cadmium), and excess nutrients (nitrates, sulfates, phosphates) are filtered out by the soil [12]. Soil organisms metabolize them or immobilize them in their biomass and necromass [13], thereby incorporating them into stable humus [14]. The physical integrity of soil is also a prerequisite for avoiding landslides in rugged landscapes [15].

1.1.6. Soil solution

Soils retain water that can dissolve a range of molecules and ions. These solutions exchange gases with the soil atmosphere, contain dissolved sugars, fulvic acids and other organic acids, plant nutrients such as nitrate, ammonium, potassium, phosphate, sulfate and calcium, and micronutrients such as zinc, iron and copper. Some arid soils have sodium solutions that greatly affect plant growth. Soil pH can affect the type and amount of anions and cations that soil solutions contain and that exchange with the soil atmosphere and biological organisms [16].

1.1.7. Soil properties

Soils have many different properties. These properties combine to make soils useful for a wide range of purposes. Soil properties govern what types of plants grow in a soil or what particular crops grow in a region. Here are some of the main soil properties that are important.

1.1.7.1. Soil texture

Soil texture refers to the relative proportion of sand, silt and clay size particles in a sample of soil. Clay size particles are the smallest being less than 0.002 mm in size. Silt is a medium size particle falling between 0.002 and 0.05 mm in size. The largest particle is sand with diameters between 0.05 for fine sand to 2.0 mm for very coarse sand. Soils that are dominated by clay are called fine textured soils while those dominated by larger particles are referred to as coarse textured soils [17].

1.1.7.2. Soil structure

Soil structure is the way soil particles aggregate together into what are called peds. Peds come in a variety of shapes depending on the texture, composition, and environment. *Granular*, or crumb structures, look like cookie crumbs. They tend to form an open structure that allows water and air to penetrate the soil. *Platy structure* looks like stacks of dinner plates overlaying one another. Platy structure tends to impede the downward movement of water and plant roots through the soil. Therefore, open structures tend to be better agricultural soils.

Bulk density of a soil is the mass per unit volume including the pore space. Bulk density increases with clay content and is considered a measure of the compactness of the soil. The greater the bulk density, the more compact the soil. Compact soils have low permeability, inhibiting the movement of water. The use of heavy agricultural equipment can cause compaction of soil, especially in wet clay soil. Soil compaction results in reduced infiltration and increase runoff and erosion [17].

1.1.7.3. Water holding capacity

All soils have the ability to hold water in their pores and on the surfaces of mineral grains and structural aggregates. This ability varies from soil to soil and relates closely to the texture of the soil. Sandy soils, while easy to cultivate, often suffer from the fact that they cannot hold onto much water and have a poor water holding capacity. They are often known as thirsty soils. Clay soils by contrast have lots of small pores in which they can store water. This means that they always have some water for the plants that grow in them and thus have a good water holding capacity [18].

1.1.7.4. Acidity and alkalinity

The term pH is used to indicate the level of acidity or alkalinity of a soil. It is important to try to understand pH because it helps to decide what is the best plant or crop for a particular soil. The range of pH values in soils is usually between 3 and 8 though most world soils are between 5.5 and 7.5. Below pH 7 the soils are termed acid and above pH 7 alkaline. The pH of the soil is important in determining the type of vegetation that will grow in the soil and the type of organisms that will live there. For example some types of earthworm prefer acid conditions (low pH) while others prefer more alkaline conditions (higher pH) [18].

1.1.7.5. Soil color

Color in various types of soils is due primarily to the amount of organic matter and the chemical state of the iron and other compounds in the mineral fraction of the soil. Other minerals such as quartz, granite, and heavy black minerals may also influence soil color. Unweathered parent materials tend to be gray in color or else will have the color of the natural minerals from which they are derived. The color of subsoils can reveal a great deal about the age and drainage conditions in the soil. Iron compounds can exist as oxidized forms, which are red; as hydrated oxides, which are yellow; and as reduced forms, which are gray [19].

1.1.7.6. Soil organisms

The mineral soil harbors a varied population of living organisms that play a prominent and indispensable role in the changes constantly occurring within the soil. Many groups of organisms live in the soil and range in size from microscopic to those that are visible to the naked eye. Some of the microscopic-sized organisms are the bacteria, fungi, actinomycetes, algae and protozoa. Most soil organisms depend on organic matter for food and energy. Consequently, they are generally found in the top twelve inches of soil. One of the most important functions of soil microorganisms is the decomposition of organic matter. One of the products formed when organic matter is decomposed is carbon dioxide. Also, nitrogen and other essential plant nutrients are released and made available to growing crops [19].

1.1.7.7. Soil electrical conductivity (EC)

Soil electrical conductivity, which is known as EC, is the ability of soil to conduct electrical current. EC is expressed in milliSiemens per meter (mS/m). Traditionally, soil scientists used EC to measure soil salinity. However, EC measurements also have the potential for estimating variation in some of the soil physical properties in a field where soil salinity is not a problem [20].

Electrical conductivity (EC) is the most common measure of soil salinity and is indicative of the ability of an aqueous solution to carry an electric current. Plants are detrimentally affected, both physically and chemically, by excess salts in some soils and by high levels of exchangeable sodium in others. Soils with an accumulation of exchangeable sodium are often characterized by poor tilth and low permeability making them unfavorable for plant growth.

By agricultural standards, soils with an EC greater than 4 dS/m are considered saline. In actuality, salt-sensitive plants may be affected by conductivities less than 4 dS/m and salt tolerant species may not be impacted by concentrations of up to twice this maximum agricultural tolerance limit. Thus, the reclamation scientist must exercise care in interpretation of salinity standards. Salinity should be defined in terms of the predisturbance land use potential, the proposed post disturbance land use, and the plant species to be seeded on the site [21].

1.1.7.8. Soil salinity

Salinity is a soil property referring to the amount of soluble salt in the soil. It is generally a problem of arid and semiarid regions. A saline soil is also a soil that has enough soluble salts to impair plant productivity. There are many kinds of salts. Salts are not limited to table salt (sodium chloride). Salts found in the soil could be anything but sodium chloride. Soil salts include calcium, magnesium, potassium, bicarbonate, carbonate, chloride, sulfate, nitrate, and sodium. Many of these salts are plant nutrients. Too much of a good thing can become a problem. A soil with a white crust may not be affected by sodium but may be considered saline [22].

1.1.7.9. Total dissolved solids (TDS)

Total dissolved solids (TDS) are solids in water that can pass through a filter. TDS is a measure of the amount of material dissolved in water. This material can include carbonate, bicarbonate, chloride, fluoride, sulfate, phosphate, nitrate, calcium, magnesium, sodium, organic ions, and other ions. A certain level of these ions in water is necessary for aquatic life. Changes in TDS concentrations can be harmful because the density of the water determines the flow of water into and out of an organism's cells. However, if TDS concentrations are too high or too low, the growth of many aquatic life can be limited, and death may occur. High concentrations of TDS may also reduce water clarity, contribute to a decrease in photosynthesis, combine with toxic compounds and heavy metals, and lead to an increase in water temperature. TDS is used to estimate the quality of drinking water, because it represents the amount of ions in the water. Water with high TDS often has a bad taste and/or high water hardness, and could result in a laxative effect [23].

1.1.8. Micro and macro-nutrients in soil

Plants require both macro-nutrients and micro-nutrients for their growth. The essential micronutrients for plants required are boron, chlorine, sodium, copper, iron, manganese, zinc, vanadium and molybdenum. They are required at trace levels and if present at higher levels, have a toxic effect. Most of these serve as components of essential enzymes. Some of these such as chlorine, manganese, iron, zinc and vanadium are likely to take part in photosynthesis.

The essential macronutrients required for the plants are carbon, hydrogen, oxygen, nitrogen, phosphorous, sulfur, potassium, calcium and magnesium. The atmosphere and water are the sources of carbon, hydrogen and oxygen. Some plants, directly from atmosphere, through nitrogen fixing bacteria, may obtain nitrogen. The other essential macronutrients are obtained from the soil. Nitrogen, phosphorus and potassium (NPK) are commonly added to soil as fertilizers. Calcium deficiency in soil is due to calcium uptake by plants, and leaching by carbonic acid in acidic soils, and competitions with high levels of sodium, potassium and magnesium in alkaline soils. Calcium-deficient soils are generally treated with lime (liming) to provide the required calcium supply for plants.

Magnesium is made available to plants through ion-exchanging organic matter or clays. Magnesium deficiency in soil is caused by high levels of calcium, sodium or potassium, sulfur in the form of assimilable SO_4^{2-} is taken up by the plants. Unlike in the case of K^+, sulfate ions are not bound by ion-exchange binding and it would be available for assimilation by plant roots [24].

1.1.9. Elemental composition

The elemental composition of soil varies over a wide range, permitting only a few general statements to be made. Those soils that contain less than 12–20% organic carbon are termed mineral. All other soils are termed organic. Carbon, oxygen, hydrogen, nitrogen, phosphorus, and sulfur are the most important constituents of organic soils and of soil organic matter in general. Carbon, oxygen, and hydrogen are most abundant; the content of nitrogen is often about one-tenth that of carbon, while the content of phosphorus or sulfur is usually less than one-fifth that of nitrogen.

Besides oxygen, the most abundant elements found in mineral soils are silicon, aluminum, and iron. The distribution of chemical elements will vary considerably from soil to soil and, in general, will be different in a specific soil from the distribution of elements in the crustal rocks of the Earth. The most important micro or trace elements in soil are boron, copper, manganese, molybdenum, and zinc, since these elements are essential in the nutrition of green plants. Also important are cobalt, selenium, cadmium, and nickel. The average distribution of trace elements in soil is not greatly different from that in crustal rocks [25].

1.1.10. Forms of nutrient elements in soils

Elements having an electrical charge are called ions. Positively-charged ions are cations; negatively-charged ones are anions. The most common soil cations (including their chemical symbol and charge) are: calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+), ammonium (NH_4^+), hydrogen (H^+) and sodium (Na^+). Notice that some cations have more than one positive charge. Common soil anions (with their symbol and charge) include fluoride (F^-), chloride (Cl^-), nitrate (NO_3^-), sulfate (SO_4^{2-}) and phosphate (PO_4^{3-}). Note also that anions can have more than one negative charge and may be combinations of elements with oxygen [26].

1.2. FLUORIDE

1.2.1. Properties of fluoride

Fluoride is the anion F^-, the reduced form of fluorine. Both organic and inorganic compounds containing the element fluorine are sometimes called fluorides. Fluoride, like other halides, is a monovalent ion (−1 charge). Its compounds often have properties that are distinct relative to other halides. Structurally, and to some extent chemically, the fluoride ion resembles the hydroxide ion. Fluorine-containing compounds range from potent toxins such as sarin to life-saving pharmaceuticals such as efavirenz, and from inert materials such as calcium fluoride to the highly reactive sulfur tetra fluoride. The range of fluorine-containing compounds is considerable as fluorine is capable of forming compounds with all the elements except helium and neon [27, 28].

1.2.2. Sources of fluoride

Fluorides are released into the environment naturally through the weathering of minerals, in emissions from volcanoes and in marine aerosols [29]. The main natural source of inorganic fluorides in soil is the parent rock [30]. During weathering, some fluoride minerals (e.g., cryolite or Na_3AlF_6) are rapidly broken down, especially under acidic conditions [31]. Other minerals, such as fluorapatite [$Ca_5(PO_4)_3F$] and calcium fluoride, are dissolved more slowly [32]. The mineral fluorophlogopite (mica; [$KMg_3(AlSi_3O_{10})F_2$] is stable in alkaline and calcareous soils [33]. However, its solubility is affected by pH and the activities of silicic acid (H_4SiO_4) and aluminium (Al^{3+}), potassium (K^+) and magnesium (Mg^{2+}) ions.

Anthropogenic sources of fluoride into the environment include the following: the industrial production and use of chemicals such as, hydrogen fluoride (HF), calcium fluoride (CaF_2), sodium fluoride (NaF), fluorosilicic acid (H_2SiF_6), sodium hexafluorosilicate (Na_2SiF_6), sulfur hexafluoride (SF_6), and phosphate fertilizers [34]. Phosphate fertilizers are the major source of fluoride contamination of agricultural soils. They are manufactured from rock phosphates, which generally contain around 3.5% fluorine [33]. However, during the manufacture of phosphate fertilizers, part of the fluoride is lost into the atmosphere during the acidulation process, and the concentration of fluoride in the final fertilizer is lowered further through dilution with sulfur (superphosphates) or ammonium ion (ammoniated phosphates); the final product commonly contains between 1.3 and 3.0% fluorine [35].

1.2.3. Occurrence of fluoride

Many fluoride minerals are known, but paramount in commercial importance are fluorite and fluorapatite. Fluoride is found naturally in low concentration in drinking water and foods. Water with underground sources is more likely to have higher levels of fluoride, whereas the concentration in seawater averages 1.3 mg/L [36]. Fresh water supplies generally contain between 0.01–0.3 mg/L, while the ocean contains between 1.2 and 1.5 mg/L [37].

Solutions of inorganic fluorides in water contain F^{-} and bifluoride HF^{2-} [38]. Few inorganic fluorides are soluble in water without undergoing significant hydrolysis. Examples of inorganic fluorides include hydrofluoric acid (HF), sodium fluoride (NaF), and uranium hexafluoride (UF_6). In terms of its reactivity, fluoride differs significantly from chloride and other halides, and is more strongly solvated due to its smaller radius/charge ratio. Its closest chemical relative is hydroxide. The Si-F linkage is one of the strongest single bonds. In contrast, other silyl halides are easily hydrolyzed.

1.2.4. Health effects of fluoride

Fluoride has beneficial effects at low concentrations (less than about 2 mg daily intakes) in drinking water, and other sources, when teeth are being formed; fluoride safely strengthens the enamel, the hard outer 'shell' of the tooth. This, in turn, stops cavities from forming and teeth from decaying. The fluoride content of tooth tissues reflects the available fluoride at the time of tooth formation. This is why it is important to have sufficient fluoride when teeth are forming. However, taken in quantity (just over 2 mg of fluoride) is extremely toxic and dangerous [39].

Fluoride can be one of the most volatile and active harmful chemicals in the body. Fluoride can attack mercilessly, against any age group, but its effects are especially harmful to developing children and the elderly. The detrimental effects of fluoride are varied. Below is a list of some of the recently documented, harmful effects of drinking fluoridated water:

1) Fluoride is known to cause dental fluorosis, a defect of the tooth enamel caused by fluoride’s interference with developing teeth. Its visible signs are mottled or yellowed teeth. Nearly 30% of children drinking fluoridated water suffer from dental fluorosis on two or more teeth.

2) Fluoride is associated with Alzheimer’s disease and other forms of dementia. Fluoride enters the brain and enables aluminum to cross the blood-brain barrier, resulting in increased risk for these diseases. Fluoride has also been associated with low IQ and mental retardation in children.
3) Fluoride can cause a crippling bone disease called skeletal fluorosis. In more mild forms, symptoms of this disease include chronic joint pain, similar to the symptoms of arthritis. Arthritis has now reached near epidemic levels in the United States, and the connection to fluoridated water should be considered.
4) Fluoride depresses the activity of the human thyroid gland and has been commonly used as an effective treatment for patients with overactive thyroids. Fluoride may depress the activity of the healthy thyroid, as well, resulting in an underactive thyroid, a common cause of obesity. More than 20 million people in the United States receive treatment for thyroid problems.
5) Fluoride disrupts the activity of normally functioning hormones. Fluoride can reduce levels of melatonin, the sleep hormone, in the body, causing chronic insomnia [40].

1.2.5. Effects of fluoride on plants

Plants are exposed to fluoride in the soil, and in the air as a result of volcanic activity, natural fires, wind-blown dusts, pesticides, or as emissions from processes in which fluorine-containing materials are burned, manufactured, handled, or used [41]. The main route of entry of fluoride into animals is by ingestion, so plants are important vectors of the element in all ecosystems.

Fluoride is taken up from the soil by passive diffusion, and then it is carried to the shoot by transpiration. In temperate climates, and in most soils, the amount accumulated in this way is small so the average content of leaves in a non-polluted atmosphere is usually less than 10 mg F/kg dry weight. Where soils are saline or enriched by fluoride-containing minerals or the atmosphere contains elevated fluoride concentrations, the concentration may be much higher. In such areas, there may be sufficient plant uptake of fluoride to contribute significantly to the human or animal diet. This factor should be considered in areas with endemic fluorosis. A number of species accumulate high concentrations, even when grown on low-fluoride soils, perhaps because of complex formation with aluminium [42]. The tea family, Theaceae, is the best known of these accumulators, but there are several others that warrant further investigations [42].

Gaseous and particulate fluorides in the air are deposited on exposed plant surfaces, whilst gaseous fluoride enters leaves through stomatal pores. Fluoride is also constantly lost from plants by a variety of little-understood processes [42]. Superficial deposits may be tenaciously held and may account for over 60% of the total fluoride content of the leaf. Though such deposits are of negligible toxicity to the plant, they may present a hazard for grazing animals. Fluoride that penetrates the internal tissue of leaves or that is deposited on active surfaces such as stigmata may affect a variety of metabolic processes and result in effects on appearance, growth, or reproduction. Recent reviews of the metabolic effects of fluoride have been reported by Bonte [43] and by Weinstein and Alscher-Herman [44].

1.2.6. Fluoride in soil and rock

The mean fluoride content of rocks lies between 0.1 and 1.0 g/kg. The main primary fluoride-containing minerals are fluorspar (CaF_2), cryolite ($3NaF \times AlF_3$), and apatite [$3Ca_3(PO_4)_2 \times Ca(F,OH,Cl)_2$], but in most soils it is associated with micas and other clay minerals [42]. Sodium fluoride and magnesium fluoride are also found as natural minerals.

The mean fluoride content of mineral soils is 0.2-0.3 g/kg [41], whereas that of organic soils is usually lower. However, in soils which have developed from fluoride-containing minerals it may range from 7-38 g/kg [45-47].

The fluoride content of top soil may be increased by the addition of fluoride-containing phosphate fertilizers, pesticides, irrigation water, or by deposition of gaseous and particulate emissions. Davison [42] calculated that phosphate fertilizers typically add between 0.005 and 0.028 mg F/kg per year to soil. A concentration of 1 µg F/m^3 in air similarly adds about 0.004-0.018 g/kg per year. Soils have a capacity to fix fluoride, so depletion by leaching and removal by crops is very slow. In the USA, one estimate of the annual loss was 0.0025 g/kg per year [48]. Much research by MacIntire and his colleagues showed that addition of fluoride did not significantly increase uptake by plants, though there was evidence that this might be the case in saline soils [42].

Factors that influence the mobility of inorganic fluorides in soil are pH and the formation of aluminium and calcium complexes [49]. In more acidic soils, concentrations of inorganic fluoride were considerably higher in the deeper horizons. The low affinity of fluorides for organic material results in leaching from the more acidic surface horizon and increased retention by clay minerals and silts in the more alkaline, deeper horizons [50]. This distribution profile is not observed in either alkaline or saline soils [51]. The fate of inorganic fluorides released to soil also depends on the chemical form, rate of deposition, soil chemistry and climate [50].

Fluoride in soil is mainly bound in complexes. The maximum adsorption of fluoride to soil was reported to occur at pH 5.5 [52]. In acidic soils with pH below 6, most of the fluoride is in complexes with either aluminium or iron (e.g., AlF^{2+}, AlF_2^+, AlF_3^0, AlF_4^-, FeF^{2+}, FeF_2^+, FeF_3^0) [53]. Fluoride in alkaline soils at pH 6.5 and above is almost completely fixed in soils as calcium fluoride, if sufficient calcium carbonate is available [54]. Fluoride binds to clay by displacing hydroxide from the surface of the clay [55]. The adsorption is strongly dependent upon pH and fluoride concentration. It is most significant at pH 3–4, and it decreases above pH 6.5.

Pickering [56] determined changes in free fluoride ions and total fluoride levels following equilibration of either poorly soluble fluoride species, such as calcium fluoride and aluminium fluoride, or wastes from aluminium smelters. The experiments were carried out on materials that had different cation-exchange capacities, such as synthetic resins, clay minerals, manganese oxide and a humic acid. Increased amounts of fluoride were released from fluoride salts and fluoride-rich wastes when solids capable of exchanging cations were present. The effect was greatest when there were more exchange sites available and when the fluoride compound cation had greater affinity for the exchange material. In a few cases, soluble complex ions were formed when the released fluoride attacked the substrate, such as illite or alumina wastes.

MacIntire *et al*. reported that 75.8–99.6% of added fluoride was retained by loam soil for 4 years [57]. Fluoride retention was correlated with the soil aluminium content. The leaching of fluoride occurred simultaneously with the leaching of aluminium, iron and organic material from soil [32]. Soil phosphate may contribute to the mobility of inorganic fluoride [58]. Oelschläger reported that approximately 0.5–6.0% of the annual addition of fluoride (atmospheric pollution and artificial fertilizers) to a forest and agricultural areas was leached from the surface to lower soil horizons [59]. Arnesen and Krogstad found that fluoride (added as sodium fluoride) accumulation was high in the upper 0–10 cm of soil columns, where 50–90% of the accumulated fluoride was found [60]. A study by McLaughlin *et al.* involving long-term application of phosphate fertilizers has shown a large portion of fluoride applied as impurities in the fertilizer to remain in the 0- to 10-cm depth of the soil profile [61].

In sandy acidic soils, fluoride tends to be present in water-soluble forms [62]. Street and Elwali determined the activity of the fluoride ion in acid sandy soils that had been limed [63]. Fluorite was shown to be the solid phase controlling fluoride ion activity in soils between pH 5.5 and 7.0. At pH values below 5.0, the fluoride ion activity indicated super saturation with respect to fluorite. These data indicate that liming of acid soils may precipitate fluorite, with a subsequent reduction in the concentration of fluoride ion in solution.

Murray reported that low amounts of fluoride were leached from a highly disturbed sandy podzol soil of no distinct structure [64]. Even at high fluoride application rates (3.2–80 g per soil column of diameter 0.1 m with a depth of 2 m), only 2.6–4.6% of the fluoride applied was leached in the water-soluble form. The pH of the eluate increased with increasing fluoride application, and this was probably due to adsorption of fluoride, releasing hydroxide ions from the soil metal hydroxides. Over time, the concentration of water-soluble fluoride decreased due to increased adsorption on soil particles.

Mean soil concentrations in Pennsylvania, USA, were 377, 0.38 and 21.7 mg/kg for total fluoride, water-soluble fluoride and resin-exchangeable fluoride, respectively. The authors suggested that fluoride is relatively immobile in soil, since most of the fluoride was not readily soluble or exchangeable [65].

The water-soluble fluoride in sodic surface soil treated with gypsum increased with increasing exchangeable sodium percent [66]. The increase in exchangeable sodium per cent also caused an increase in soil pH, which in turn caused an increase in water-soluble fluoride. Incubation studies revealed that a major portion of the added fluoride was adsorbed to soil within the first 8 days. Adsorption to soil followed Langmuir isotherms up to an equilibrium soluble fluoride concentration (11.4 mg/L), with precipitation at higher concentrations.

Calcium fluoride was formed in soils irrigated with fluoride solutions. Calcium fluoride is formed when the fluoride adsorption capacity is exceeded and the fluoride and calcium ion activities exceed the ion activity product of calcium fluoride [67]. Less than 2% of applied fluoride was measured in the leachate, and between 15 and 20% of added fluoride was precipitated as calcium fluoride. Fluoride was precipitated in the upper profile, although the authors expected that once the adsorption mechanisms were exceeded, soluble fluoride would leach deeper into the soil with continued irrigation. A large fraction of the fluoride in topsoil sampled at a distance of 0.5–1.0 km from an aluminium smelter was reported to be in water-soluble form [32]. The authors concluded that the fluoride was present as calcium fluoride.

Breimer *et al.* determined the vertical distribution of fluoride in the soil profiles sampled near an industrial region [68]. In calcareous soils, fluoride (as extractable with hydrochloric acid) was restricted to the top 40–50 cm, probably due to the precipitation of calcium fluoride in the presence of lime. Water-extractable fluoride showed an increase with depth in the horizons and subsequently decreased to base levels in the lower subsoil.

The adsorption of fluoride from the water phase may be an important transport characteristic in calcareous soils at low flow rates, but this exchange may be rate-limited at high flow rates [69]. Dissolved fluoride concentrations may be high around the root zone in soils with a high fluoride input such as from atmospheric deposition. The high concentrations exist only for a limited time until the fluoride is withdrawn from the solution. The adsorption isotherm was reported to be non-linear between initial concentrations of 10 and 50 mg fluoride/liter. Retention of fluoride in uncontaminated calcareous soil was higher than retention in calcareous soil from areas with fluoride contamination. The adsorption and desorption of fluoride in acidic soil were not related to previous fluoride contamination.

Fluoride-containing solutions increased the mobilization and leaching of aluminium from soils. Leaching of aluminium was reported to be greater from soil contaminated from an aluminium smelter than from uncontaminated soil [70]. In the uncontaminated soil, losses of aluminium from the acid soil were higher than those from the calcareous soil. Arnesen also found that fluoride can solubilize aluminium, iron and organic material and can increase soil pH through exchange with hydroxide ions [71].

Unlike other soluble salts, fluoride was not leached from naturally salinized salt-affected soil. It was redistributed within the soil profile [72]. The adsorption of fluoride to soils increased with decreasing pH within the pH range 8.5–6. Retention of fluoride in the soil was positively correlated with ammonium acetate extractable iron.

1.3. ETHIOPIAN RIFT VALLEY

1.3.1. Description of the region

The Ethiopian Rift system extends from the Kenyan border up to the Red Sea and is divided into four sub-systems: Lake Rudolf, Chew Bahir, the Main Ethiopian Rift (MER) and the Afar. The seismically active MER transects the uplifted Ethiopian plateau for a distance of 1000 km, extending from the Afar Depression southwards across the broad zone of basins and volcanic ranges to the watershed of lake Chamo. This study focuses on the MER.

The climate is sub-humid in the central part of the MER, semi-arid close to the Kenyan border and arid in the Afar region. One of the hottest places on Earth the “Dalol Depression” with average annual temperature of around 50 ^{0}C is found in the Afar. The annual rainfall within the limits of the rift varies from around 100 mm in much of the Afar up to around 900 mm close to lake Abaya. The rainfall is much higher in the adjacent highlands; some times as high as 1500 mm.

The elevation within the rift varies in a wide range from close to 2000 m a.s.l. at lake Abaya and around 120 m below sea level in the Dalol Depression. There are many highly elevated volcanic hills and mountains both within the rift floor and the highlands. The hills, ridges and volcano-tectonic depressions separate the rift lakes. Many of the lakes are located within a closed basin fed by perennial rivers. The major rivers in the region are Awash, Meki-Katar, Dijo and Bilate feeding lakes Abhe, Ziway, Shala and Abaya, respectively. Lakes Abaya and Chamo are seasonally connected by overflow channel, Ziway and Abiyata by the Bulbula river, Langano and Abiyata by the Horakelo river. Awassa, Abiyata, Shala, Bskea and Afrera are terminal lakes. The alkalinity of the lakes increases generally as one goes towards the north. In fact terminal lakes without surface water outlet such as Abiyata and Shala and the lakes in the arid Afar region have very high alkalinity and some of them are used for abstraction of salts.

The largest commercial farms in the country are present downstream of the Koka dam irrigated by the regulated flow of the Awash river which drains through the rift starting from the central highlands through the northern part of the MER and finally ending in lake Abhe at the border with Djibouti. Out of the Awash basin, Meki and Katar rivers and lake Ziway are also used for irrigation.

The geological and geomorphological features of the region are the result of Cenozoic volcano-tectonic and sedimentation processes. Except some patchy Precambrian outcrops to the south and northern edge the rift is covered with Cenozoic volcanics and sediments. The rift formation is associated with extensive volcanism. Several shield volcanoes were developed in large parts of adjacent plateaux. The volcanic products in many places were fissural basaltic lava flows, stacked one over the other, alternating with volcano-clastic deposits derived from tuff, ignimbrite and volcanic ash. The basalt extrusions were interspersed with large accumulations of rhyolite and trachyte, breccias, ignimbrite and related shallow intrusions [73]. Most of the rift valley flat plains around lakes are covered with thick lacustrine deposits and volcanoclastic Quaternary sediments [74].

1.3.2. The soils of Ethiopian Rift Valley

Thirteen major soil mapping units and a further six sub-units based on the FAO/UNESCO soil classification are of importance in the Rift Valley. The major soil units in terms of area covered are: Vertisols (19.2%), Cambisols (17.9%), Fluvisols (16.2%), Regosols (15.8%), Lithosols (9.5%), Andosols (7.1%) and Acrisols (6.1%) [75, 76].

The soils of the Rift Valley are largely derived from recent volcanic rocks and, by comparison with many areas of Africa; their base status is generally good. The main parent materials of the Rift Valley soils are basalt, ignimbrites, lava, gneiss, volcanic ash, alluvium and pumice. Some of the soil problems include, low phosphorus levels, micronutrient imbalances and in some cases poor physical structure [77].

1.3.3. Fluoride in Ethiopian Rift Valley soil

Fluoride is a natural constituent of the biosphere, and, consequently, of clay and soil. The inherent fluoride content, however, varies greatly from one area to another. Geology as well as the local topography [78] and depth of the soil layer [79].

The East African Rift Valley which cuts through Ethiopia is geomorphologically still an active volcanic region. The volcanic rocks particularly in the young basalt contain high concentrations of fluoride and fluorapatite. Large fault systems in the Valley create conditions that allow very deep percolation of infiltrating surface water. The floor of the Rift Valley which is characterized by high hydrothermal activity accelerates the solubility of fluorite. The hot climate and high fluoride water bed of the Rift Valley therefore favour the development of endemic fluorosis [80].

The volcanic base-rock in the African Rift system is predominantly alkaline, and rich in e.g. sodium and fluoride. The soil produced by the weathering of these rocks is similarly rich in fluoride. After precipitation, however, rainwater leaches fluoride from soils as well as from crystalline rocks [81]. The surface waters of East Africa, therefore, usually have high fluoride concentrations [82]. Furthermore, since the hydrochemistry of aquifers is strongly influenced by the surrounding lithology, the fluoride content of ground water of Rift Valley is high, frequently to the extent that the waters are rendered unfit for human consumption [83, 84].

Several studies have been carried out on determination of the levels of fluoride in waters of Ethiopian Rift Valley and different methods of defluoridation techniques. Among the previous studies, fluoride contamination and treatment in the Ethiopian Rift Valley [95], High-fluoride drinking water and a health problem in the Ethiopian Rift Valley and assessment of lateritic soils as defluoridating agents [83], fluoride levels in water and endemic fluorosis in Ethiopian Rift Valley [96] shows the fluoride levels of water samples in the different sites of the Rift Valley, The geographic distribution of fluoride in surface and groundwater in Ethiopia with an emphasis on the Rift Valley [97], the origin of high bicarbonate and fluoride concentration in waters of the main Ethiopian Rift Valley**,** East African Rift system [98].

Different studies also carried out on fluoride binding capacity of different types of Ethiopian Rift Valley soils and search for the soil best fit for fluoride removal in high fluoride waters such as soil adsorption defluoridation of drinking water for an Ethiopian rural community [99] and investigated brick and pot chips as defluoridating media, and reported fluoride binding capacities up to 0.56 mg/g [100]. The sulfur distribution in selected site of Ethiopian Rift Valley soils also determine under humid and semi-arid climate [101]. The status of Mn, Fe, Cu, Zn, B and Mo in Rift Valley Soils of Ethiopia were also determined [102]. Agricultural development in the central Ethiopian Rift valley: A desk-study on water-related issues and knowledge to support a policy dialogue and **s**ome improper water resources utilization practices and environmental problems in the Ethiopian Rift were also studied [103, 104]. However, there is no report in the literature indicates the levels of fluoride in Ethiopian Rift Valley soils and its correlation with the levels of metal. Therefore, this study is planned to generate a database for fluoride levels in soils, its correlation with metals concentration and recommend types of plant grown in the farm of Ethiopian Rift Valley and provide useful information for future studies which will be conducted on capacity of plants to adsorb inorganic fluoride from the soil and its health effect in human.

1.4. Objectives

1.4.1. General objective

The main objective of this thesis is to determine the levels of fluoride in Ethiopian Rift Valley soils.

1.4.2. Specific objectives

1. To develop a working procedure for both sample preparation and analysis of fluoride in soil sample by fluoride ion selective electrode.
2. To determine the effect of soil properties like pH, conductivity, salinity and TDS in fluoride contents of Ethiopian Rift Valley soil.
3. To correlate the fluoride concentration in soil and any nearby water sources used for irrigation.
4. To compare the levels of fluoride in the Ethiopian Rift Valley soil with the levels of fluoride in soil from the literature reports of other part of the world.
5. To comment on the effect of fluoride level in human health by consuming of agricultural products from farm lands of sample soil.
6. To determine the impact of metals on fluoride water solubility and up take by vegetables.

2. EXPERIMENTAL

2.1. Apparatuses, instruments, chemicals, reagents and standard solutions

2.1.1. Apparatuses

Stillness steel knife were used to dig the soil sample. Mortar and pestle was used to crush soil sample in to powder. 1.4 mm polyethylene sieve was used to remove large debris, stones and pebbles. Analytical balance (Larko, LA 114, 110 g/0.1 g, U.K.) with precision of ± 0.0001 g was used to weigh the soil sample. Hot plate with magnetic stirrer was used for dissolution of the soil sample and fusion cake. Plastic beakers (50 and 100 mL) and 50 mL plastic volumetric flask were used during dilution and taking prepared solution for analysis. Borosilicate volumetric flasks (50, 100, 500 and 1000 mL) were used for preparation of both fluoride and metal standard solutions, 17 M NaOH solution and 1000 mg/L NaF stuck solution. Ni crucibles (50 and 70 mL) were used for fusion of soil sample for total fluoride determination. A drying oven (Digitheat, J.P. Selecta, Spain) was used for evaporation and dryness of soil sample. Muffle furnace (Audiotronics, Wagtech International Ltd., U.K.) were used for fusion and aching soil sample. Round bottom flasks with grounded glass (100 mL) fitted with reflux condenser were employed in digesting the soil samples on Kjeldahl heating apparatus (Gallenkamp, England). Measuring cylinders (Duran, Germany), pipettes (Pyrex, USA), were used during measuring different quantities of volumes of sample solution, reagents and standard solution.

2.1.2. Instrumentation

Orion F^- ion selective electrode was used for routine determination of F^- ion in soil and water samples. A pH/ISE meter (Orion Model, EA 940 Expandable Ion Analyzer) equipped with combination fluoride-selective electrode (Orion Model 96-09) was employed. The pH was measured with pH/ion meter (WTW Inolab pH/ION Level 2, Germany) using unfilled pH glass electrode. The electrical conductivity (EC), salinity and total dissolved solid (TDS) of soil and water samples were measured using Thermo Orion EC meter (USA). Flame atomic absorption spectrophotometer (Buck Scientific

Model 210VGP AAS, East Norwalk, USA) equipped with deuterium arc back ground correctors and hollow cathode lamps with air-acetylene flame was used for the analysis of the analyte metals in soil and water samples.

2.1.3. Chemicals, reagents and standard solutions

Chemicals and reagents that were used in the analysis were all analytical grade. Sodium fluoride (99.0% NaF, BDH Chemicals Ltd, Poole, England) was used to prepare fluoride stock standard solution. Glacial acetic acid (99.5%, BDH limited, Poole, England), sodium chloride [Scharlau, European Union], sodium citrate [Research-Lab Fine Chem. Industries Mumbai 400 002, (India)] and EDTA [Reagent grade, Spain] to prepare total ionic strength adjustment buffer (TISAB) solution, sodium hydroxide [Scharlau, European Union] solution to adjust pH of TISAB solution and total fluoride determination were also used. A 0.01 M potassium chloride [A.R. Interchem (U.K.)] was used for calibration of EC meter. HNO_3 (69-72%) [Research-Lab Fine Chem Industries Mumbai 400 002 (India)] were used for acidification of water sample for metal analysis. Aqua-regia prepared from 3:1 ratio of 37% HCl [Riedel-deHaen, Germany] and (69-72%) HNO_3, and extra pure hydrogen peroxide 30% H_2O_2, [Scharlau, European Union], were used for digestion of soil sample. 37% HCl [Riedel-de-Haen, Germany] were also used for neutralization of fusion cake in total fluoride determination. Lanthanum nitrate hydrate [98%, Aldrich, USA] was used to avoid refractory interference (for releasing calcium and magnesium from their phosphates) Sock standard solution of concentration 1000 mg/L in 2% HNO_3 of the metals, Na, K, Ca, Mg, Mn, Cu, Zn, Co, Cr, Fe and Ni (Buck Scientific Puro-graphic) as nitrate salt, standard solutions were used to prepare intermediate standard solutions of metals. Deionized water (chemically pure with conductivity ≤ 1.5 µs/cm) was used for dilution of sample and intermediate standard solutions prior to analysis and rinsing glassware and sample bottles.

2.2. PROCEDURES

2.2.1. Cleaning of apparatus

Apparatus such as volumetric flasks, measuring cylinders, plastic beakers, plastic volumetric flasks, nickel crucibles, plastic containers and polyethylene bags were washed with detergents and tap water, rinsed with deionized water. The digestion flasks were soaked with 1% (w/v) potassium dichromate in 98% (v/v) H_2SO_4 and the volumetric flasks used for metal analysis were soaked in 10% (v/v) HNO_3 for 24 hours followed by rinsing with deionized water, dried in oven and kept in dust free place until analysis of metal begins. Prior to each use the apparatus were soaked and rinsed in deionized water.

2.2.2. Description of the sampling areas

Samples were collected from fluoride rich Ethiopian Rift Valley irrigation and vegetation farm lands namely Bulbulla, Adami-Tullu, Zuway, Meki, Alem-Tena, Mojo, Wonji, Debre-Zeyt, Akaki and Addis Ababa University (Arat Killo Campus) as controlling group. Except Akaki and Addis Ababa University (Arat Killo Campus) all others are located in the East Shoa zone, Oromia Region, southeast of Addis Ababa. The area is known to encompass various water bodies used for irrigation such as rivers like Bulbulla, Meki and Awash River and lakes like Zuway, Debre-Zeyt and Koka dam.

The area is under continuous cultivation throughout the year and has been supplying significant portion of a wide variety of vegetables like tomato, onion, cabbage, green pepper, potato, etc to the capital and local people consumption for a long number of years. Modern farming practices such as mechanized farming, application of agro-chemicals (fertilizers, pesticide, insecticides, fungicides, etc), and selected seeds are significant agricultural inputs for getting better yield in the area.

2.2.3. Collection and pretreatment of soil and water samples

2.2.3.1. Sample collection

Soil sampling

The soil samples were collected from the surface horizon (0-20 cm) depth of the nine sampling areas of Rift Valley vegetation farmlands and one controlling sample site. Sampling was done by taking half kilo gram of soil from five sub-sites roughly three kilo meter away from each other, homogenize and form one bulk sample finally take one kilo gram of homogenized soil put in clean polyethylene plastic bags labeled and brought to the laboratory for further pre-treatment, the same for all the ten samples.

Water sampling

For comparative analysis of fluoride and metals in soil the water samples were collected from any water source used for irrigation (River, Lake and Well) at the point where the water enters in to the farm plots. From each five sub-sites about one liter of water were collected where the soil sample were collected, mix and form one bulk sample, finally take two liter of water filled in the pre-cleaned, dried and rinsed with the sample water solution plastic bottles labeled and brought to the laboratory for further pre-treatment the same for all the nine samples.

2.2.3.2. Sample pretreatment

Soil sample pretreatment

The soil samples collected from the ten sampling area were air dried to constant weight for fifteen days, grinding using mortar and pestle and sieved through a 1.4 mm polyethylene sieve to remove large debris, stones, and pebbles. The part of the sample which passes through the sieve was returned to the original sample bag and stored ready for analysis.

Water sample pretreatment

The collected water samples were transported to the laboratory immediately as soon as possible to measure fluoride concentration and other parameters like pH, conductivity, salinity and total dissolved solid without any pre-treatment. 500 mL of water samples were filtered and preserved adding 2% (v/v) nitric acid at about 4 ^{o}C in a refrigerator for metal analysis.

2.2.4. Preparation of the samples for total fluoride content analysis

The total soil fluoride was determined using the alkaline fusion by slightly modifying the reported methods (McQuaker and Gurney [89]); 0.50 g of prepared soil samples were precisely weighed directly into the 50 mL nickel crucibles and moistened slightly with 1 mL distilled water. This was followed by the addition of 6.0 mL of a 17 M sodium hydroxide solution, placed in an oven (150 °C) for 2 h and then removed after sodium hydroxide had solidified; the crucible was placed in a muffle furnace. The temperature was then raised to 600 °C and the sample was fused at this temperature for 30 min. After cooling for 1 h, 15 mL of deionized water was added to the sample and slightly heated in hot plate for approximately 3 h to facilitate the dissolution of the fusion cake. About 7 mL of concentrated hydrochloric acid was added drop wise to decreasing the pH from 12.0-13.0 to 8.0-8.5 under the control of a pH meter. Subsequently the samples were transferred to a 50 mL plastic volumetric flask. The crucible was rinsed successively with deionized water until the final volume reached 50 mL and all the washings were mixed and filtered with Whatman filter paper (70 mm, diameter) in pre-cleaned and rinsed 50 mL plastic volumetric flask. This step eliminates most of the Al and Fe, both interfering in F^- determinations by the ion selective electrode. Before measuring the F^-, 10.0 mL total ionic strength adjusting buffer (TISAB) was added to 10.0 mL filtrate into 50 mL plastic beaker [89].

2.2.5. Soil sample preparation for water soluble fluoride analysis

2.2.5.1. Optimization of stirring time

The stirring time for the extraction of water-soluble fluoride was optimized by varying the stirring time from 5 min to 2 h on one soil sample. A stirring time of 1 h was found to be optimum for the extraction of water soluble fluoride from soil samples. The results are given in Table 1.

Table 1. Evaluation of stirring time for the extraction of water-soluble fluoride from soil sample.

Sample	Stirring time (min)	Fluoride concentration in (µg/g) Mean ± SD
Bulbulla	5	2.62 ± 0.002
	10	2.77 ± 0.020
	30	5.24 ± 0.003
	60	6.05± 0.009
	90	6.03 ± 0.015
	120	5.99 ± 0.011

It is also shown by Figure 1.

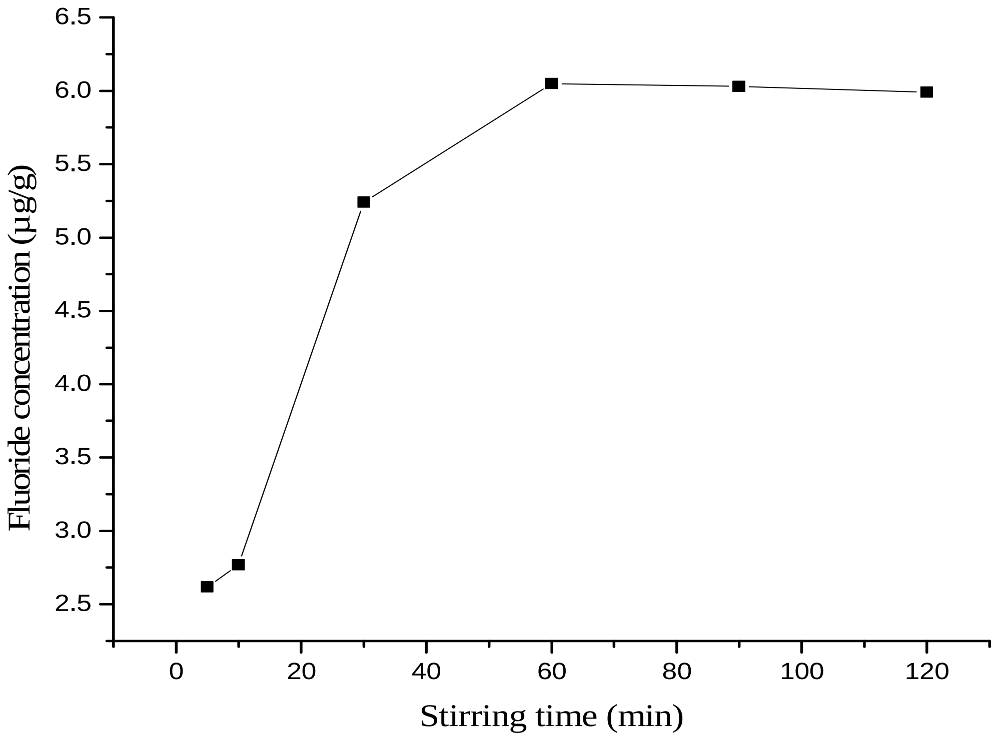


Figure 1. Evaluation of stirring time for the extraction of water-soluble fluoride from soil sample.

Using the optimized stirring time (1 h) the samples were prepared as follow; 5 g of prepared soil was weighed in 50 mL conical flask, 10 mL of deionized water was added, stirred by magnetic stirrer for one hour, filtered with Whatman No. 70 filter paper in 50 mL volumetric flask and diluted to volume. 10 mL of the clear supernatant was mixed with 10 mL TISAB in 50 mL plastic beaker and the F^- ion concentration of the solution was measured with an fluoride sensitive ISE against NaF standards.

2.2.6. Soil sample preparation for metals analysis

2.2.6.1. Digestion of soil samples

Applying the optimized condition [92], 0.5 g of dried and homogenized soil samples were transferred into a 100 mL round bottomed flask. To this 6 mL of aqua-regia (3:1

ratio of 37% HCl to (69-72%) HNO_3) and followed by 1.5 mL of 30% H_2O_2 were added and the mixture was digested on a Kjeldahl digestion apparatus fitting the flask to a reflux condenser by setting the temperature first to dial at 6 (180 ^oC) for the first 30 min and then raised to dial 8 (240 ^oC) for the next 30 min and finally raised to dial 9 (270 ^oC) for the remaining 2 h. The digest was allowed to cool to room temperature for 30 min without dismantling the condenser from the flask and for 30 min after removing the condenser. To the cooled solution 20 mL of deionized water was added to dissolve the precipitate formed on cooling and to minimized dissolution of filter paper by the digest residue while filtering with Whatman, (70 mm, diameter), filter paper into 50 mL volumetric flask. The rounded bottom flask was rinsed subsequently with 5 mL deionized water until the total volume reached around 45 mL. To this final solution, 2 mL lanthanum nitrate solution (1% w/w) was added and the solution was filled to the mark (50 mL) with deionized water. The digestion was carried out in triplicate for each bulk samples. Digestion of a reagent blank was also performed in parallel with the soil samples keeping all digestion parameters the same. The digested samples were kept in the refrigerator, until the level of all the metals in the sample solutions were determined by FAAS.

2.2.7. Analysis of soil and water samples

2.2.7.1. Fluoride determination in soil and water samples

The liquid phase F^- concentrations were measured by mixing equal volumes (10 mL) of soil, water samples or standards with TISAB in a 50 mL plastic beaker and the mixture were stirred (uniformly) thoroughly using the magnetic stirrer. The combination fluoride selective electrode was immersed in the solution and calibrates the fluoride ion selective electrode prior to each experiment over a concentration range of interest (0.1 to 10 mg/L for water soluble fluoride and 0.5 to 20 mg/L for total fluoride and water sample analysis). The method of direct potentiometry was used and the concentration of fluoride was read directly. All measurements were made in triplicates.

2.2.7.2. Determination of pH, conductivity, salinity and total dissolved solid (TDS) in soil and water samples

Soil pH, conductivity, salinity and TDS of prepared soil samples were determined by mixing 10 g of soil with 25 mL of deionized water in 50 mL preliminary flask. The mixture was stirred by magnetic stirrer for 30 minute. Then pH measured by HANNAN instruments (HI 9025 model, Singapore) microcomputer pH meter after calibrating technical pH buffer of 4.01 and 10.00 pH value, the other three parameters (conductivity, salinity and TDS) were determined by Thermo Orion conductivity meter (model 145, USA) after direct calibration by 0.01 M potassium chloride (KCl) solution. For the water samples, all the parameters are determined by measuring 30 mL water sample in 50 mL plastic beaker. In all measurements, the solutions were stirred constantly in order to homogenize the solution and triplicate.

2.2.7.3. Metal determination in soil and water samples

Flame atomic absorption spectrophotometer, FAAS, equipped with deuterium arc background corrector and standard air-acetylene flame system using external calibration curve after optimizing the parameters (burner and lamp alignment, slit width and wavelength adjustment) in to maximum signal intensity of the instrument was used for determination of metal of interest. The instrument parameters optimized according to the manufacturers are given in Table 2. All the metals were determined by absorption/concentration mode and the instrument readout was recorded for each solution manually. The three replicate of each sample, blank and working standards of each metal were determined by the same procedure.

Table 2. Instrumental operating conditions for determination of metals in soil and water samples using FAAS.

Element	Wavelength (nm)	Detection limit (mg/L)	Slit width (nm)	Lamp current (mA)	Energy (erg)
Cu	324.7	0.020	0.7	1.5	3.496
Zn	213.9	0.005	0.7	2.0	3.105
Cr	357.9	0.050	0.7	2.0	3.576
Co	240.7	0.050	0.2	4.5	2.710
K	766.5	0.010	0.7	0.2	3.410
Ca	422.7	0.010	0.7	2.0	3.604
Ni	232	0.040	0.2	7.0	2.715
Mn	279.5	0.010	0.7	3.0	3.950
Mg	285.2	0.001	0.7	1.0	3.988
Na	589	0.002	0.2	2.0	3.210
Fe	248.3	0.030	0.2	7.0	2.960

2.2.8. Instrument calibration

2.2.8.1. Calibration for fluoride analysis

The operation of ion selective electrodes is based on the fact that there is a linear relationship between the electrical potential developed between an ion-selective electrode (ISE) and a reference electrode immersed in the same solution, and the logarithm of the concentration of the ions in the solution. This relationship is described by the Nernst equation:

$$E = \text{Constant} \pm (2.303RT/zF) \times \text{Log } C \qquad (1)$$

where E = the total potential (in mV) developed between the sensing and reference electrodes, constant = constant characteristic of the particular ISE/reference pair, (it is the sum of all the liquid junction potentials in the electrochemical cell), 2.303 = the conversion factor from natural to base 10 logarithm, R = the gas constant (8.314 Joules/degree/mole), T = the absolute temperature (K), z = absolute value of the charge on the ion, F = the Faraday constant (96,500 coulombs per mole), Log C = the logarithm of the concentration of the measured ion.

The slope of electrode response is ± 2.303RT/zF (which shows plot of E (mV) against Log C is a straight line within the concentration range within linear range of the electrode response. This is an important diagnostic characteristic of an ISE. When the ion to which the electrode responds is negative charged the slope becomes negative.

Because all of the solutions are at a constant ionic strength, Equation 1 can be rewritten as follows:

$$E = \text{constant} - 0.059 \log [F^-] \qquad (2)$$

From this equation, if E is plotted against log F^-, the slope of the electrode response should be 59.2 mV per decade change in fluoride concentration. This means that for every ten fold decrease in F^-concentration, increasing by one unit in terms of -log, the potential should change 59.2 mV.

The calibration curve was obtained by plotting mV vs log mg/L F^-. In fact, each standard solution of F^- was diluted in half because 10.00 mL of TISAB was added to 10.00 mL of standard F^- solution. However, since each standard received the same treatment, the calibration curve can be used with the undiluted standard concentrations. Otherwise, simply divide by two to get the concentrations for the calibration curve and multiply by two to obtain the concentration of the measured solution.

The ion-selective electrode instrument was calibrated using five series of working standards. The working standard solutions were prepared freshly by dilution from 1000 mg/L stock fluoride solution. The concentrations of the working standards, calibration curves and values of correlation coefficient of the calibration graph for water soluble fluoride, total fluoride concentration and fluoride determination in water sample are given in (Table 3 and 4 and Figure 2 and 3).

Table 3. Calibration standard solutions and correlation coefficients of the calibration curves for total fluoride in soil, fluoride in water sample and recovery test for total fluoride in soil analysis.

No.	Items	Concentration of working standards (mg/L)	Slope in (mV/dec)	Correlation coefficient of calibration curve	Equation for calibration curve
1	Total fluoride in soil samples	0.5, 1.0, 5.0, 10, 20	- 58.9	-0.99954	Y = 116.26745 - 54.70134*X
2	Fluoride in water samples	0.5, 1.0, 5.0, 10, 20	- 57.4	-0.99841	Y = 128.11044 - 57.85622*X
3	Recovery test for total fluoride in soil	0.5, 1.0, 5.0, 10, 20	- 60.3	-0.99947	Y = 114.84724 - 54.92325*X
	Mean of the three measurements	0.5, 1.0, 5.0, 10, 20	-58.8 ± 1.45	-0.99995	Y = 119.74504 - 55.82693*X

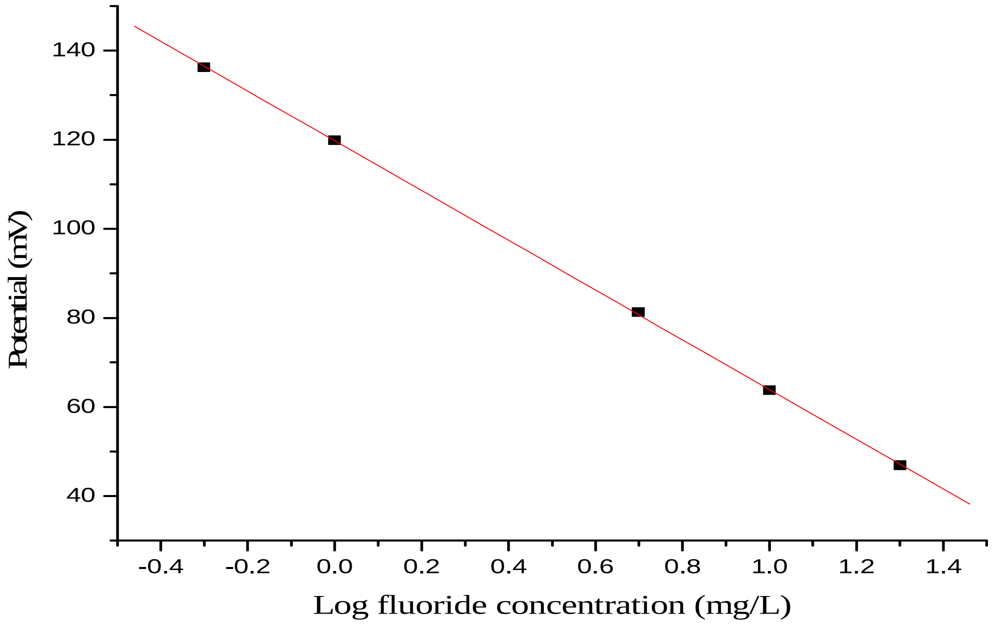


Figure 2. The calibration curves of mean of the three measurements (for the determination of total fluoride in soil samples, fluoride in water samples, and recovery test for total fluoride in soil).

Table 4. Calibration standard solutions and correlation coefficients of the calibration curves for water soluble fluoride in soil samples, optimization of stirring time for water soluble fluoride analysis and recovery test for water soluble fluoride in soil.

No.	Items	Concentration of working standards (mg/L)	Slope in (mV/dec)	Correlation coefficient of calibration curve	Equation for calibration curve
1	Water soluble fluoride in soil samples	0.1, 0.5, 1.0, 5.0, 10	- 57.6	-0.99998	Y = 103.4382 - 46.4668*X
2	Optimization of stirring time for	0.1, 0.5, 1.0, 5.0, 10	- 57.0	-0.99971	Y = 104.35154 - 48.89606*X

	water soluble fluoride determination				
3	Recovery test for water soluble fluoride in soil	0.1, 0.5, 1.0, 5.0, 10	- 57.5	-0.99972	Y = 113.61212 - 46.89302*X
	Mean of the three measurements	0.1, 0.5, 1.0, 5.0, 10	- 57.4 ± 0.322	-0.99999	Y = 107.15243 - 47.39952*X

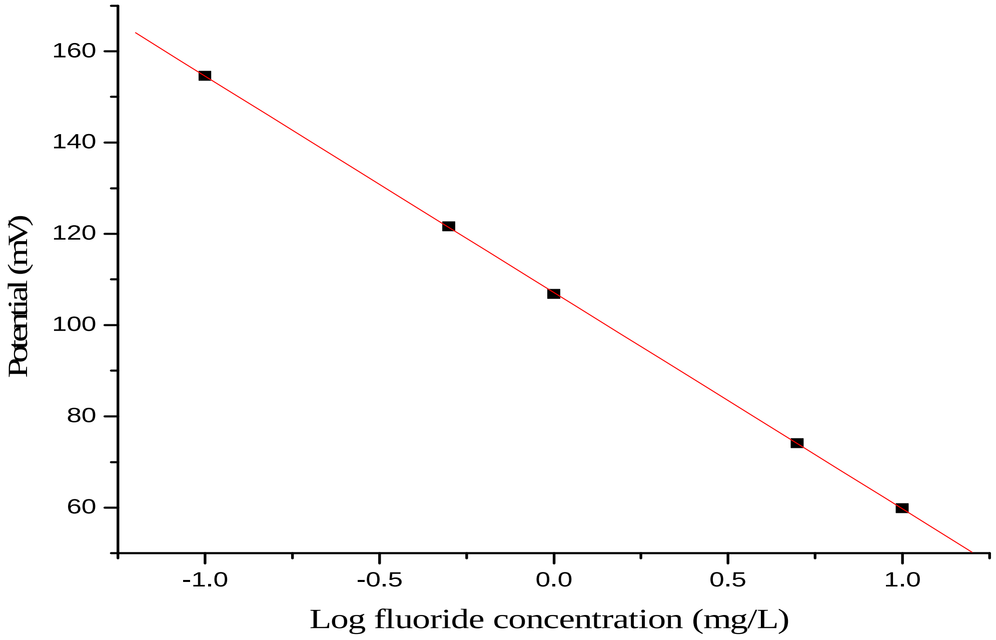


Figure 3. The calibration curves of mean of the three measurements (for the determination of water soluble fluoride in soil samples, optimization of stirring time for water soluble fluoride determination and recovery test for the water soluble fluoride in soil).

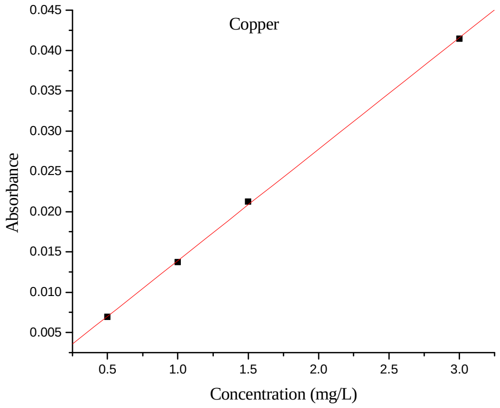
The mean and the precision of the slope in Table 3 and 4 give information about the reputability of the electrode in calibrating in different days.

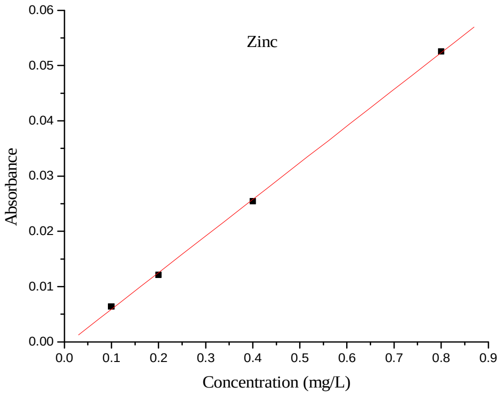
2.2.8.2. Calibration for metal analysis

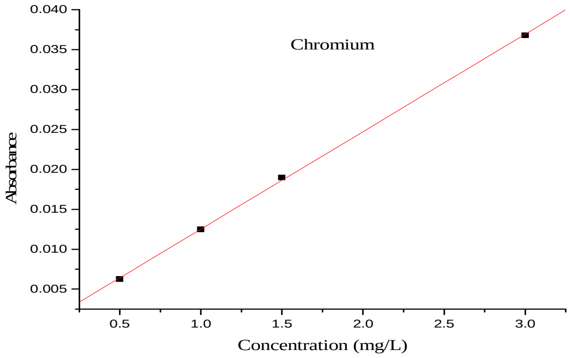
The instrument was calibrated using four series of working standards. The working standard solutions of each metal were prepared freshly by diluting the intermediated standard solutions. Concentrations of the intermediate standards, working standards, calibration curves and value of correlation coefficient of the calibration graph for each of the metals are provided (Table 5 and Figure 4).

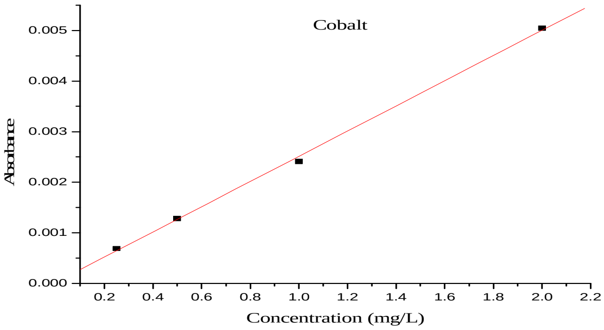
Table 5. Calibration metal standard solutions and correlation coefficients of the calibration curves.

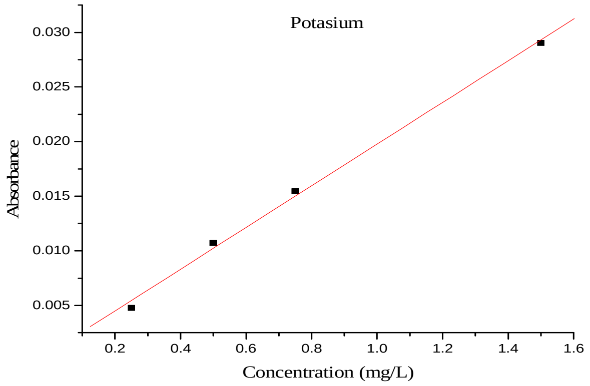
No.	Metal	Intermediate standard (mg/L)	Working standards (mg/L)	Correlation coefficient (r)	Equation for calibration curve
1	Cu	10	0.5, 1, 1.5, 3	0.99984	Y = 1.18071E-4 + 0.01382*X
2	Zn	10	0.1, 0.2, 0.4, 0.8	0.99977	Y = -7.41826E-4 + 0.06635*X
3	Cr	10	0.5, 1.0, 1.5, 3	0.99983	Y = 3.22179E-4 + 0.01221*X
4	Co	10	0.25, 0.5, 1, 2	0.99936	Y = 2.40435E-5 + 0.00249*X
5	K	10	0.25,0.5, 0.75, 1.5	0.99845	Y = 6.75107E-4 + 0.01909*X
6	Ca	10	0.5, 1, 2, 4	0.9992	Y= 1.76957E-5 + 4.85896E-4*X
7	Ni	10	0.25, 0.5, 1, 2	0.99994	Y= 2.65217E-5 + 0.005*X
8	Mn	10	0.25, 0.5, 1, 2	0.99976	Y= 4.06783E-4 + 0.01815*X
9	Mg	10	0.25, 0.5, 1, 2	0.99984	Y= -1.57304E-4 + 0.00595*X
10	Na	10	0.25, 0.5, 1, 2	1.00000	Y= -5.43478E-5 + 0.16981*X
11	Fe	10	0.5, 1, 1.5, 3	0.99977	Y= 1.62107E-4 + 0.00636*X

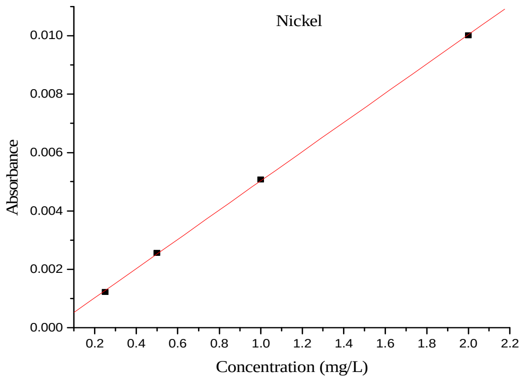

Copper
Absorbance
0.045
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.5
1.0
1.5
2.0
2.5
3.0
Concentration (mg/L)

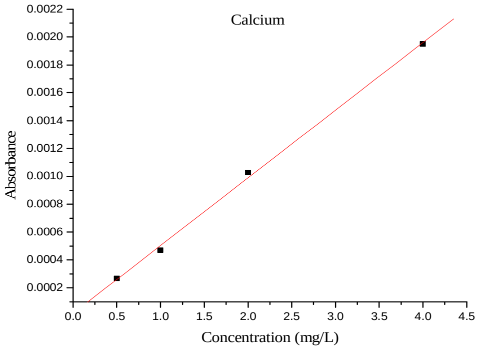

Zinc
Absorbance
0.06
0.05
0.04
0.03
0.02
0.01
0.00
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
Concentration (mg/L)

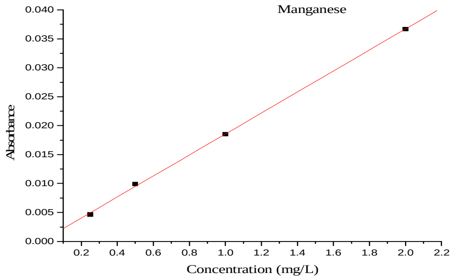

Chromium
Absorbance
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.5
1.0
1.5
2.0
2.5
3.0
Concentration (mg/L)

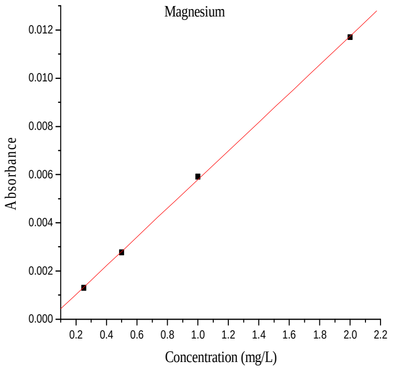

Cobalt
Absorbance
0.005
0.004
0.003
0.002
0.001
0.000
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
Concentration (mg/L)

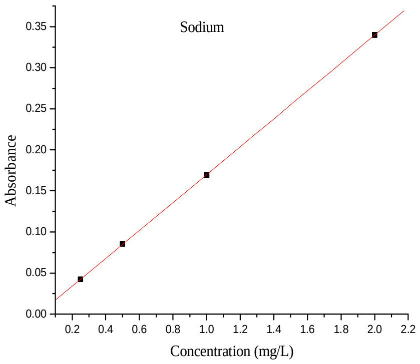

Potasium
Absorbance
0.030
0.025
0.020
0.015
0.010
0.005
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
Concentration (mg/L)


Nickel
Absorbance
0.010
0.008
0.006
0.004
0.002
0.000
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
Concentration (mg/L)


Calcium
Absorbance
0.0022
0.0020
0.0018
0.0016
0.0014
0.0012
0.0010
0.0008
0.0006
0.0004
0.0002
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
Concentration (mg/L)


Manganese
Absorbance
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
Concentration (mg/L)


Magnesium
Absorbance
0.012
0.010
0.008
0.006
0.004
0.002
0.000
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
Concentration (mg/L)


Sodium
Absorbance
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
Concentration (mg/L)

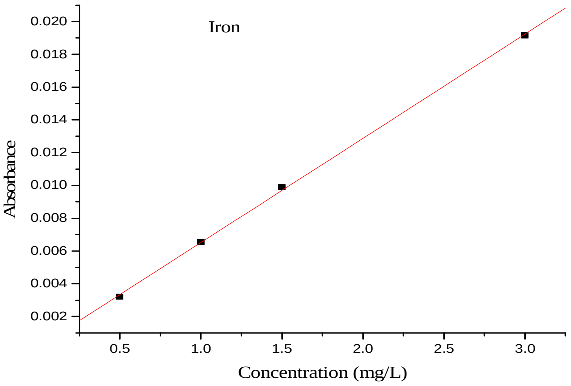


Figure 4. Calibration curves for metals determination.

2.2.9. Method validation for fluoride analysis

The efficiency of the optimized procedure is checked by various methods. These are certified standard reference material analyzing and spiking sample with known concentration of the analyte. In this work, the method validation was established by spiking experiments (recovery test). The spiked samples were prepared by adding, for Debre-Zeyt 0.3, 0.6 and 1.1 mL of 20 mg/L standard fluoride solution for water soluble fluoride and 0.3, 0.6 and 1.2 mL of 20 mg/L standard fluoride solution for total fluoride were added to 5 g and 0.5 g soil sample, respectively. For Zuway 0.2, 0.3 and 0.6 mL of 100 mg/L standard fluoride solution for water soluble fluoride and 0.9, 1.7 and 3.4 mL of 100 mg/L standard fluoride solution for total fluoride were added to 5 g and 0.5 g soil sample, respectively. For Alem-Tena 0.3, 0.5 and 0.9 mL of 100 mg/L standard fluoride solution for water soluble fluoride and 0.5, 1.0 and 1.9 mL of 100 mg/L standard fluoride solution for total fluoride were added to 5 g and 0.5 g soil sample, respectively. The spiked and non-spiked soil samples were prepared and analyzed in similar condition. Then the percentage recovery of the analyte was calculated by:

$$\%\ \text{Recovery} = \frac{C_{F^-}\text{ in the spiked sample} - C_{F^-}\text{ in non-spiked samples}}{C_{F^-}\text{ added for spiking}} \qquad (3)$$

5 g and 0.5 g for water soluble fluoride and total fluoride respectively of prepared soil samples were spiked with fluoride solution of which the fluoride content was equivalent

to 25%, 50%, or 100% of the fluoride content of the original (unspiked) soil samples. After spiking, following the procedure, determination was made in triplicates. The results of the measurements are presented in Table 6 and 7. As shown in Table 6 and 7, the percentage recoveries for the studied samples were found within acceptable range (between 90.9% and 107%).

2.2.10. Method validation for metal analysis

The method validation of metal analysis was established by spiking experiments. The spiked samples were prepared by adding a small known quantity of metal standard solutions.

For spiking soil sample, 100 µL of 100 mg/L Ca, Cr, Co, K, Ni, Mn, Mg, Na, and Fe, 100 µL of 3 mg/L Cr and 100 µL of 0.4 mg/L Zn standard solutions were added to round bottomed flask (100 mL) containing 0.5 g soil sample. The spiked and non-spiked samples were digested and analysed in similar condition. For water sample spiking, 200 µL of the same metal concentration standard solution used in soil sample spiking, were added to 100 mL of acidified and filtered water sample. Then the percentage recovery of the analyte was calculated.

3. RESULTS AND DISCUSSION

3.1. Optimization of digestion procedure of soil samples

The conventional aqua-regia digestion procedure consists of digesting soil samples are so widely used that the European Community Bureau of Reference has certified several soil and sludge samples based on it, in addition to the total elemental concentrations [90]. Wilson *et al*. reported that digesting soil samples with aqua-regia produced the most accurate, efficient and reproducible results [91]. Hur *et al.* evaluated 1:1 HNO_3:HCl, 1:3 HNO_3:HCl (aqua-regia), and 1:3:0.5 HNO_3:HCl:H_2O_2 (modified aqua-regia), and they reported that, the aqua-regia and modified aqua-regia were the most effective digestion reagents [92].

Considering the finding mentioned above, the modified aqua-regia (HNO_3 + HCl + H_2O_2) was selected as digestion reagent for soil sample digestion in this work. The optimum conditions for soil sample digestion were a reagent mixture of 6 mL aqua-regia (3:1 ratio of HCl to HNO_3) and 1.5 mL H_2O_2, digestion temperature of 270 ^{o}C and digestion time of 3 hours for 0.5 g soil samples.

3.2. Recovery results of fluoride analysis

Table 6. Recovery test results of water soluble fluoride.

Sample	Concentration in unspiked sample (µg/g)	Amount added (µg/g)	Concentration in spiked sample (µg/g)	Recovery (%)
Debre-Zeyt	4.11	1.03	5.06 ± 0.02	92.3 ± 1.4
	4.11	2.06	6.10 ± 0.05	96.7 ± 2.5
	4.11	4.11	8.38 ± 0.03	104 ± 1
Zuway	11.3	2.83	14.1 ± 0.2	97.8 ± 7.4
	11.3	5.65	16.7 ± 0.2	95.1 ± 3.7
	11.3	11.3	22.8 ± 0.1	101 ± 1
Alem Tena	16.7	4.18	20.5 ± 0.3	90.9 ± 6.3

	16.7	8.35	25.3 ± 0.4	102 ± 5
	16.7	16.7	32.9 ± 0.2	96.6 ± 0.9

Table 7. Recovery test results of total fluoride

Sample	Concentration in unspiked sample (µg/g)	Amount added (µg/g)	Concentration in spiked sample (µg/g)	Recovery (%)
Debre-Zeyt	232	58.0	285 ± 3	91.4 ± 4.9
	232	116	353 ± 4	104 ± 3
	232	232	469 ± 11	102 ± 5
Zuway	657	164	816 ± 11	97 ± 7
	657	328	980 ± 15	94.4 ± 3.2
	657	657	1363 ± 15	107 ± 2
Alem Tena	372	93	460 ± 6	94.7 ± 6.0
	372	186	560 ± 12	101 ± 6
	372	372	733 ± 8	± 2.0

3.3. Recovery results of metal analysis

As shown in Table 8 and 9, the results of percentage recoveries for the studied metal nutrients in both soil and water samples were within the acceptable range (91.3-105) in the soil and (90.6-106) in the water samples. Therefore, this verifies that the optimized digestion procedure and instrument was valid for soil sample analysis and the instrument was valid for water analysis.

Table 8. Recovery test for the optimized procedure of soil sample.

Metal	Conc. in unspiked sample (µg/g)	Amount added (µg/g)	Conc. in spiked sample (µg/g)	Amount recovered (µg/g)	Recovery (%)

Na	1942	392	2352 ± 38	410 ± 15	105 ± 4
Mg	2154	434	2562 ± 40	408 ± 28	94 ± 6
K	4389	879	5255 ± 89	866 ± 5	98.5 ± 0.5
Ca	22996	4600	27476 ± 66	4481 ± 68	97.4 ± 1.5
Cr	14.7	3.02	17.5 ± 1.1	2.74 ± 0.06	90.6 ± 1.9
Mn	476	96.2	576 ± 23	99.4 ± 16.3	103 ± 17
Co	58.3	11.3	68.7 ± 4.7	10.4 ± 1.8	92.1 ± 16.0
Cu	28.6	5.6	34.1 ± 0.5	5.4 ± 0.7	96.4 ± 12.5
Zn	56.6	11.8	67.4 ± 5.5	10.8 ± 1.3	91.3 ± 10.7
Fe	28533	5704	34107 ± 89	5574 ± 86	97.7 ± 1.5
Ni	861	172	1032 ± 3.5	172 ± 6	99.8 ± 3.4

Table 9. Recovery test for the optimized procedure of water sample.

Metal	Conc. in unspiked sample (mg/L)	Amount added (mg/L)	Conc. in spiked sample (mg/L)	Amount recovered (mg/L)	Recovery (%)
Na	54.8	11.2	65.7 ± 1.4	10.9 ± 0.3	97.6 ± 2.7
Mg	23.1	4.54	27.7 ± 1.0	4.6 ± 0.6	101 ± 12
K	16.4	3.24	19.6 ± 0.7	3.2 ± 0.1	98.8 ± 3.1
Ca	181	35.8	219 ± 2	38 ± 6	106 ± 15
Cr	0.117	0.028	0.142 ± 0.026	0.025 ± 0.002	90.6 ± 7.5
Mn	6.20	1.28	7.44 ± 0.49	1.24 ± 0.21	97.2 ± 16.1
Co	1.27	0.27	1.53 ± 0.06	0.26 ± 0.01	95.1 ± 2.2
Cu	0.146	0.031	0.175 ± 0.01	0.029 ± 0.001	94.6 ± 1.9
Zn	0.296	0.062	0.354 ± 0.015	0.058 ± 0.003	93 ± 5
Fe	23.3	4.8	28.2 ± 0.8	4.9 ± 0.7	103 ± 15
Ni	10.6	2.34	12.9 ± 1.2	2.3 ± 0.1	98.3 ± 4.3

3.4. Determination of analyte in soil and water samples

3.4.1. Determination of fluoride, conductivity, salinity and TDS in soil and water samples

Table 10 shows the results of water fluoride, pH, conductivity, salinity and total dissolved solid (TDS) determination experiments.

Table 10. Mean concentration (mean ± SD) of fluoride, pH, conductivity, salinity and total dissolved solid (TDS) of water sample.

Sample Site	Fluoride concentration (mg/L) mean ± SD	pH mean ± SD	Conductivity (µs) mean ± SD	Salinity (%o) mean ± SD	Total dissolved solid (TDS) (mg/L) mean ± SD
AAAK	0.143 ± 0.002	7.73 ± 0.04	103 ± 1	0.0 ± 0.0	48.8 ± 0.6
AK	1.09 ± 0.05	7.79 ± 0.03	489 ± 4	0.2 ± 0.0	234 ± 2
DZ	1.31 ± 0.06	7.62 ± 0.03	228 ± 1	0.1 ± 0.0	109 ± 1
MO	1.48 ± 0.09	7.94 ± 0.03	540 ± 1	0.3 ± 0.0	259 ± 1
WO	1.33 ± 0.05	8.08 ± 0.02	213 ± 2	0.1 ± 0.0	102 ± 1
AL	8.03 ± 0.29	7.91 ± 0.02	832 ± 6	0.4 ± 0.0	401 ± 3
ME	1.40 ± 0.05	7.91 ± 0.02	445 ± 3	0.2 ± 0.0	213 ± 2
ZU	1.79 ± 0.03	7.85 ± 0.02	355 ± 3	0.2 ± 0.0	170 ± 2
AD	1.85 ± 0.02	7.78 ± 0.02	352 ± 2	0.2 ± 0.0	168 ± 1
BU	2.04 ± 0.06	8.04 ± 0.12	357 ± 3	0.2 ± 0.0	171 ± 2

Table 11 shows the results of soil fluoride both (water soluble and total), pH, conductivity, salinity and total dissolved solid (TDS) determination experiments.

Table 11. Mean concentration (mean ± SD) of fluoride, pH, conductivity, salinity and total dissolved solid (TDS) of soil samples.

Sample Site	Water soluble fluoride (µg/g) mean ± SD	Total fluoride (µg/g) mean ± SD	pH mean ± SD	Conductivity (µs) Mean ± SD	Salinity (%o) Mean ± SD	Total dissolved solid (TDS) (mg/L)
AAAK	2.32 ± 0.19	209 ± 25	7.40 ± 0.07	163 ± 2	0.1 ± 0.0	77.4 ± 0.6
AK	4.73 ± 0.10	224 ± 7	7.69 ± 0.06	155 ± 3	0.1 ± 0.0	73.4 ± 0.6
DZ	4.05 ± 0.44	229 ± 10	6.53 ± 0.02	205 ± 3	0.1 ± 0.0	97.7 ± 1.2
MO	3.47± 0.67	363 ± 3	7.36 ± 0.07	43.3 ± 2	0.0 ± 0.0	20.4 ± 0.6
WO	10.6 ± 0.2	345 ± 9	8.02 ± 0.02	121 ± 1	0.1 ± 0.0	57.0 ± 0.0
AL	16.2 ± 2.7	380 ± 12	7.90 ± 0.02	262 ± 3	0.1 ± 0.0	125 ± 2
ME	5.54 ± 0.31	333 ± 23	7.59 ± 0.04	115 ± 2	0.1 ± 0.0	54.7 ± 0.6
ZU	11.5 ± 0.46	662 ± 11	8.43 ± 0.02	487 ± 6	0.2 ± 0.0	233 ± 2
AD	5.07 ± 0.33	669 ± 17	7.91 ± 0.02	134 ± 8	0.1 ± 0.0	63.7 ± 4.3
BU	6.30 ± 0.34	1210 ± 86	8.23 ± 0.03	91.1 ± 7	0.0 ± 0.0	43.4 ± 3

3.4.2. Determination of metals in soil and water samples

The concentration of eleven metals (Na, K, Ca, Mg, Fe, Zn, Cu, Co, Cr, Mn and Ni) in water and digested soil samples were analysed by flame AAS. Among the analysed metals chromium in Addis Ababa tap water was below the method detection limit (0.050 mg/L) and the concentration values of the rest metals are shown in Table 12 and 13.

Table 12. Average concentration (mean ± SD) of metals in soil samples.

Sample sites	Metal concentration in µg/g (mean ± SD)										
	Na	Mg	K	Ca	Cr	Mn	Co	Ni	Cu	Fe	Zn
AAAK	6703 ± 358	2031 ± 10	3354 ± 198	16970 ± 1382	79.3 ± 6.5	315 ± 27	74.5 ± 12	446 ± 47	40 ± 2	19665± 555	30.5 ± 2.9
AK	1455 ± 127	2190 ± 109	2432 ± 187	19730 ± 2546	53.4 ± 2.6	648 ± 55	55.8 ± 11	822 ± 94	38.8 ± 5.7	29726± 808	87.5 ± 2.2
DZ	2374 ± 22	2854 ± 44	1776 ± 277	13417 ± 1008	44.4 ± 1.9	329 ± 40	88.5 ± 16	850 ± 57	45.4 ± 1.9	24099± 209	61.9 ± 3.3
MO	869 ± 27	1681 ± 41	3324 ± 129	21283 ± 2100	27.6 ± 8.7	426 ± 47	62.8 ± 12	1288 ± 77	29.1 ± 3.2	28546± 236	71.2 ± 1.4
WO	998 ± 20	2161 ± 52	3274 ± 92	12581 ± 959	24.3 ± 2.6	143 ± 27	112 ± 6	627 ± 84	20.7 ± 1.5	32681± 205	78 ± 3
AL	1958 ± 342	2171 ± 31	4394 ± 137	22998 ± 2689	15.1 ± 3.0	481 ± 26	56.6 ± 17	860 ± 66	28 ± 3	28522± 250	59 ± 2
ME	1017 ± 16	1608 ± 72	2296 ± 80	19974 ± 2488	11.9 ± 2.3	700 ± 34	57.5 ± 18	810 ± 145	28.3 ± 1.6	31775± 131	89.2 ± 11
ZU	2555 ± 70	11229 ± 129	4267 ± 100	7547 ± 804	9.79 ± 2.72	229 ± 38	50.3 ± 14	587 ± 35	22.3 ± 0.6	13519± 152	80.3 ± 10.7
AD	684 ± 15	2234 ± 51	3265 ± 84	16968 ± 692	10.5 ± 1.4	371 ± 14	52.1 ± 13	750 ± 71	17.5 ± 2.0	18608± 618	65.9 ± 4.0
BU	845 ± 20	2163 ± 102	1887 ± 117	22535 ± 2415	10.9 ± 1.4	414 ± 17	51.3 ± 10	727 ± 77	8.85 ± 2.99	12180± 133	48.5 ± 1.8

Table 13. Average concentration (mean ± SD) of metals in water samples.

Sample Sites	Metal concentration in mg/L (mean ± SD)										
	Na	Mg	K	Ca	Fe	Cr	Mn	Co	Ni	Cu	Zn
AAAK	8.64 ± 0.23	43.4 ± 0.6	1.11 ± 0.02	16.7 ± 0.2	11.4 ± 0.3	ND	0.048 ± 0.002	1.16 ± 0.07	0.274 ± 0.008	0.157 ± 0.026	0.529 ± 0.052
AK	41.9 ± 0.1	44.4 ± 0.2	20.3 ± 1.2	184 ± 12	7.87 ± 2.28	0.149 ± 0.006	6.54 ± 0.252	1.47 ± 0.06	29.1 ± 0.8	0.088 ± 0.007	0.22 ± 0.02
DZ	9.37 ± 0.06	31.1 ± 0.5	11.3 ± 1.2	188 ± 5	37 ± 3	0.072 ± 0.004	1.94 ± 0.75	1.48 ± 0.05	16.1 ± 1.2	0.1 ± 0.0	0.154 ± 0.005
MO	57.9 ± 0.6	66.2 ± 0.3	18.6 ± 0.8	267 ± 22	47.7 ± 2.8	0.169 ± 0.059	37.2 ± 0.1	1.18 ± 0.04	16.7 ± 0.3	0.149 ± 0.006	0.383 ± 0.008
WO	17.2 ± 0.7	32.7 ± 1.3	2.54 ± 0.12	146 ± 29	18.4 ± 1.2	0.126 ± 0.006	6.6 ± 0.1	1.22 ± 0.12	15.5 ± 0.8	0.251 ± 0.007	0.562 ± 0.016
AL	55.6 ± 0.2	22.7 ± 1.4	16.2 ± 1.7	179 ± 15	24 ± 2	0.137 ± 0.049	6.37 ± 0.31	1.34 ± 0.09	11.7 ± 0.2	0.154 ± 0.007	0.308 ± 0.007

ME	44.6 ± 0.2	61.6 ± 0.9	8.04 ± 0.51	142 ± 17	28.3 ± 0.9	0.120 ± 0.005	4.47 ± 0.12	1.33 ± 0.04	22 ± 2	0.152 ± 0.046	0.311 ± 0.012
ZU	47.7 ± 0.1	25.7 ± 0.2	4.04 ± 1.23	167 ± 2	6.04 ± 2.02	0.083 ± 0.005	4.57 ± 0.12	1.21 ± 0.13	40.9 ± 0.1	0.108 ± 0.001	0.219 ± 0.009
AD	46.4 ± 0.3	36.9 ± 0.5	3.47 ± 0.55	134 ± 18	17.8 ± 1.3	0.071 ± 0.006	7.8 ± 0.6	0.354 ± 0.097	36.1 ± 2.5	0.155 ± 0.015	0.156 ± 0.011
BU	67.3 ± 0.7	28.6 ± 0.7	15.8 ± 3.6	144 ± 1	6.64 ± 1.73	0.075 ± 0.008	8.77 ± 0.35	0.979 ± 0.127	18.2 ± 2.0	0.130 ± 0.008	0.144 ± 0.006

3.5. Distribution patterns of analyte in the samples

3.5.1. Distribution patterns of fluoride in the samples

The levels of fluoride slightly differ among different soil and water samples. The distribution patterns of the fluoride in soil and water samples are discussed in the following subtopics.

3.5.1.1. Distribution patterns of fluoride in soil samples

The results of water soluble fluoride content in soil samples collected from the ten sample site are presented in Table 11. The water soluble fluoride levels varied within the range of 2.32 to 16.2 µg/g. The highest water soluble fluoride was obtained in the soil of Alem Tena and the lowest concentration was found in the soil of Addis Ababa Arat Killo campus used as controlling group. The results obtained agree with some of results reported in the literature (Table 21). Water soluble fluoride is a type of fluoride available for plant uptake and then increase total fluoride intake of human beings. Therefore, it is important to determine the amounts of fluoride in soil available for plant. The loading of fluoride on the soil arising from the use of the water for irrigation and fluoride from other sources has no negative effect on the human, because the water soluble fluoride is in the range of 2.57-16.44 µg/g soil water soluble fluoride recommendation of FAO, EPA, and WHO [113].

The results of total fluoride content of soil sample are presented in Table 11. The total fluoride levels are within a range of 209 to 1210 µg/g. The highest total fluoride was obtained in the soil of Bulbulla and the lowest concentration was found in the soil of Addis Ababa Arat Killo campus used as controlling group. The some of the results obtained are agreed with some of results reported in the literature (Table 21). Except three sample sites (Zuway, Adami Tulu and Bulbulla), others sites were found to have normal fluoride content of soils (150-400 µg/ g) [136]. The exceed values in the above three sample sites may be due to heavy clay type of soil or the acid igneous rocks contain fluoride in the range (850-1000 µg/g) are sources of surface soil or fluoride present in soils in the form of the following minerals: fluorite - CaF_2; fluoroapatite - $Ca_{10}(PO_4)_6F_2$; These minerals are sparingly soluble in water, so that only small amounts of F are taken up by plants.

3.5.1.2. Distribution patterns of fluoride in water samples

As reported in Table 10, highest fluoride concentration was found in Alem Tena irrigation dam water that is 8.03 mg/L and the lowest was Addis Ababa Arat Killo campus tap water that is 0.143 mg/L. World Health Organization (WHO) [93] have reported that fluoride becomes toxic to animals and human beings when present at more than 1 mg/L in drinking water, and toxic to some crops and animals when present at more than 10 mg/L in irrigation waters. Except Alem Tena water other water samples are at relatively lower concentration (< 2 mg/L), this is safe for irrigation, even Alem Tena water is safe for irrigation since it is below the upper limit of WHO limits of fluoride concentration for irrigation.

3.5.2. Distribution patterns of pH, conductivity, Salinity and TDS

3.5.2.1. In soil samples

As reported in Table 11, the pH range lied between 6.53–8.43. The highest pH was found in Zuway soil and the lowest pH was found in Dedre-Zeyt soil. Therefore, the pH of all soil samples are near to neutral. Therefore, no pH effect on fluoride solubility and on the availability for plant uptake. The values of other three parameters are also given in Table 11. The three parameters have positive correlation to each other. The highest value was found in Zuway that is 487 µs conductivity, 0.2 %o of salinity and 233 mg/L of total dissolved solid (TDS) and the lowest was found in Mojo that is 43.3 µs of conductivity, 0.0 %o of salinity and 20.4 mg/L of TDS.

3.5.2.2. In water samples

As reported in Table 10, the pH range lied between 7.62–8.04. The highest pH was found in Bulbulla water and the lowest pH was found in Dedre-Zeyt water. Therefore, the pH of all water samples are near to neutral and in the range of the normal pH range for irrigation water 6.5-8.4 [94]. The values of other three parameters are also reported in Table 10. The three parameters have positive correlation to each other. The highest value was found in Alem Tena water that is 832 µs conductivity, 0.4 %o of salinity and 401 mg/L of total dissolved solid (TDS) and the lowest was found in Addis Ababa Arat Killo Campus tap water that is 103 µs of conductivity, 0.0 %o of salinity and 48.8 mg/L of TDS.

The physical and chemical water quality properties are critical to the successful production of plants in any farm lands. While considered a critical parameter, water issues are frequently overlooked by most growers. Parameters deemed suitable for drinking water purposes are not necessarily acceptable for growing plants. Appropriate tests should be conducted prior to selecting appropriate irrigation water for plant growing. General guidelines for irrigation water used in plant production reported the optimum range conductivity and TDS are 0-300 µS and 0-192 mg/L, respectively [106]. Except Wonji, Debre-Zeyt and Addis Ababa Arat Killo Campus tap water other contain conductivity above the optimum range of reported guidelines of irrigation water. But, TDS of most waters are in range except Akaki, Mojo, Alem-Tena and Meki water.

3.5.3. Distribution patterns of metals in different samples

The levels of metals differ in some extent among each other and there is also slight difference between the same metals from different sampling area. The distribution pattern of the metals in both soil and water samples are discussed in the following subtopics.

3.5.3.1. Distribution patterns of metals in soil samples

The soil samples collected from ten sampling sites were found to contain detectable major (Ca, Mg, Na, and K) and trace (Cu, Co, Cr, Mn, Fe, Zn and Ni) metals. There is significant difference in concentration of different metals within soil samples and appreciable difference in the same metals of different samples. The determined concentration ranges of metals from ten soil sampling area are given in Table 14.

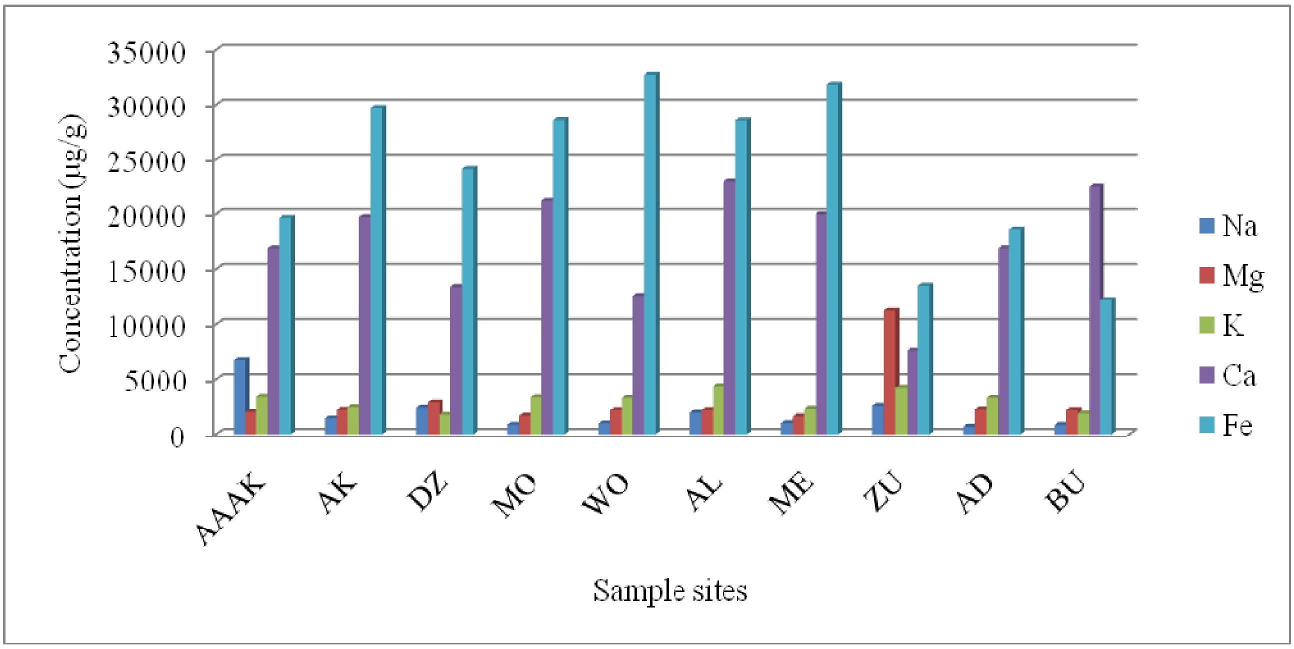
As shown in Table 14 and Figure 5, the concentration of Fe (12180-32681 µg/g) in soil exceeds much the concentration of macro-elements, Ca (7547-22998 µg/g), Mg (1608-11229 µg/g), Na (684-6703 µg/g) and K (1776-4394 µgg), this is may be due to the presence of excess amount of hematite (Fe_2O_3) in the soil.

The micro-nutrient heavy metal Ni (446-1288 µg/g) in this soil is higher compared to others Mn (143-700 µg/g), Co (50.3-112 µg/g), Zn (30.5-89.2 µg/g), Cr (9.79-79.3 µg/g) and Cu (8.85-45.4 µg/g). In general, the concentration pattern of metals in soil was decreased as Fe > Ca > Mg > Na > K > Ni > Mn > Co > Zn > Cr > Cu.

Table 14. Range of metal concentration in soil samples.

Metal	Concentration range (µg/g)	Metal	Concentration range (µg/g)
Na	684-6703	Co	50.3-112
Mg	1608-11229	Ni	446-1288
K	1776-4394	Cu	8.85-45.4
Ca	7547-22998	Fe	12180-32681
Cr	9.79-79.3	Zn	30.5-89.2
Mn	143-700		

Macro elements and Fe



Trace metals

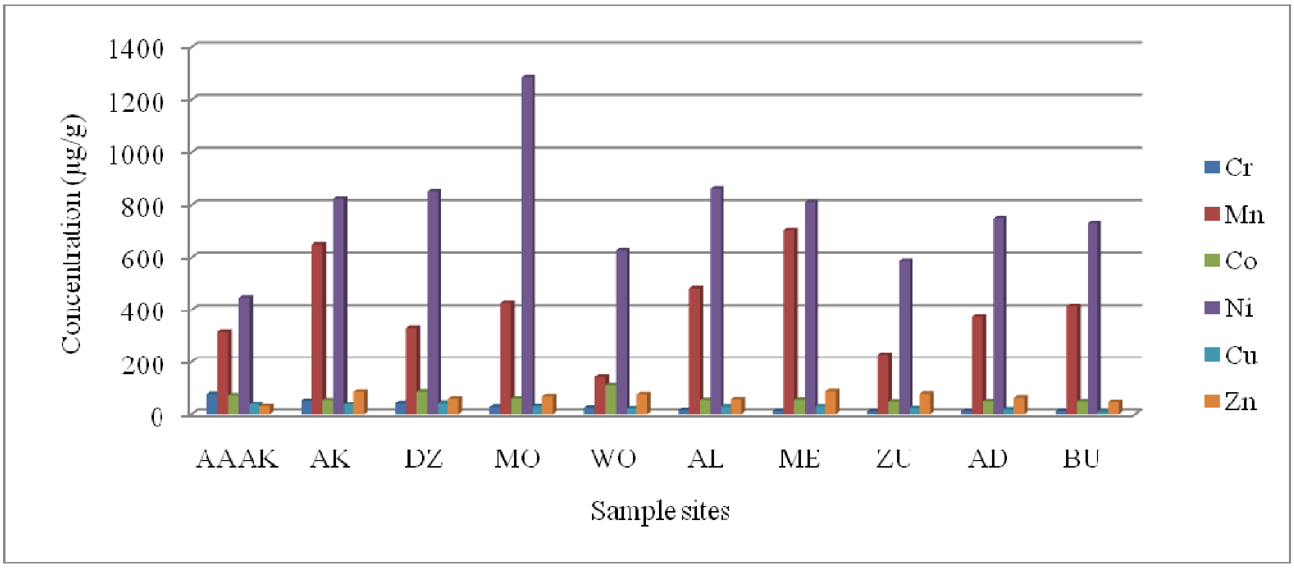


Figure 5. Distribution pattern of metals in soil sample

3.5.3.2. Distribution patterns of metals in water samples

The irrigation water sampled from lakes, rivers and wells at the point of diversion from pipes was also found to contain detectable metals Na, Ca, Mg, K, Mn, Cr, Co, Cu, Fe, Zn and Ni. The determined concentration ranges of metals from ten water sampling area are given in Table 15.

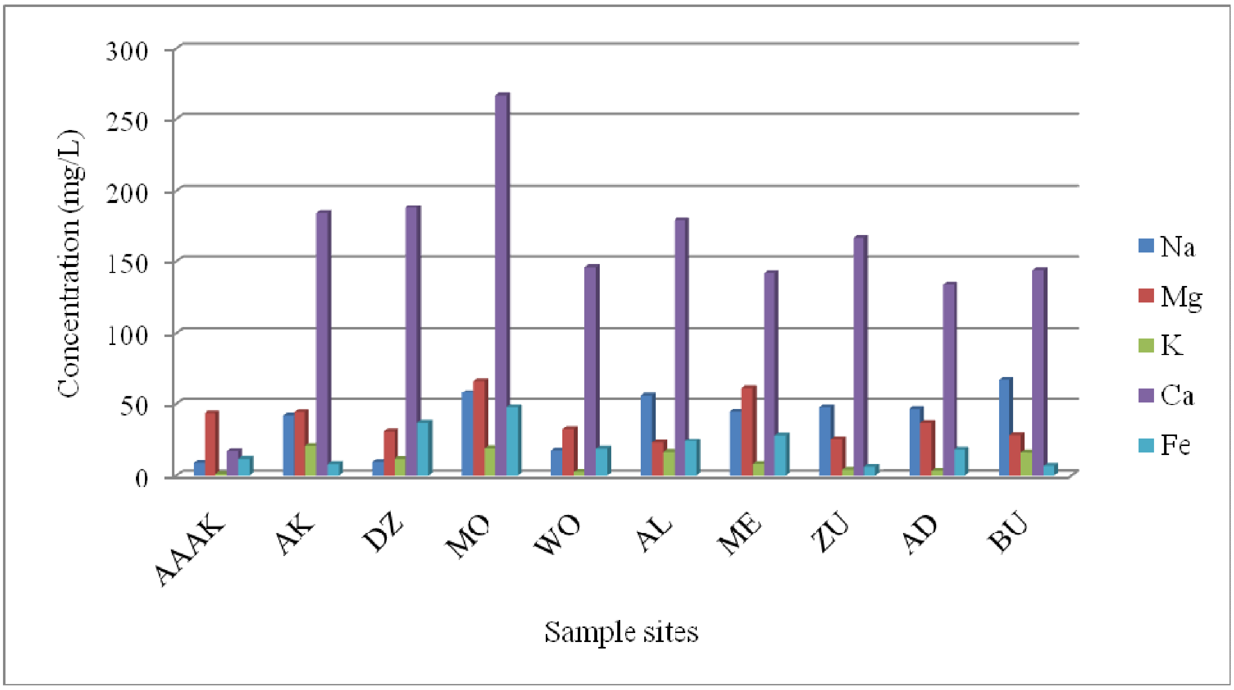
Concentration of macro-element Ca (16.7-267 mg/L) in this water samples are higher compared to other macro and micro-elements and the smallest is Cr (0.071-0.169 mg/L). In general, the concentration pattern of metals in water was in decreasing order as Ca > Mg > Na > Fe > Ni > Mn > K > Co > Zn > Cu > Cr.

General guidelines for irrigation water used in plant production were also reported the optimum range of some metals; Na (0-30 mg/L), Ca (40-100 mg/L), Mg (5-25 mg/L), K (1-10 mg/L), Fe (1-3 mg/L), Mn (0.2-1 mg/L), Zn (0-0.2) and Cu (0.05-0.15 mg/L) [106]. As shown in Table 15 most of the metals in most of sample sites are above the optimum range.

Table 15. Range of metal concentration in water samples.

Metal	Concentration range (mg/L)	Metal	Concentration range (mg/L)
Na	8.64-67.3	Co	0.354-1.48
Mg	22.7-66.2	Ni	0.274-40.9
K	1.11-20.3	Cu	0.088-0.251
Ca	16.7-267	Fe	6.04-47.7
Cr	0.071-0.169	Zn	0.144-0.562
Mn	0.048-37.2		

Macro elements and Fe



Trace metals

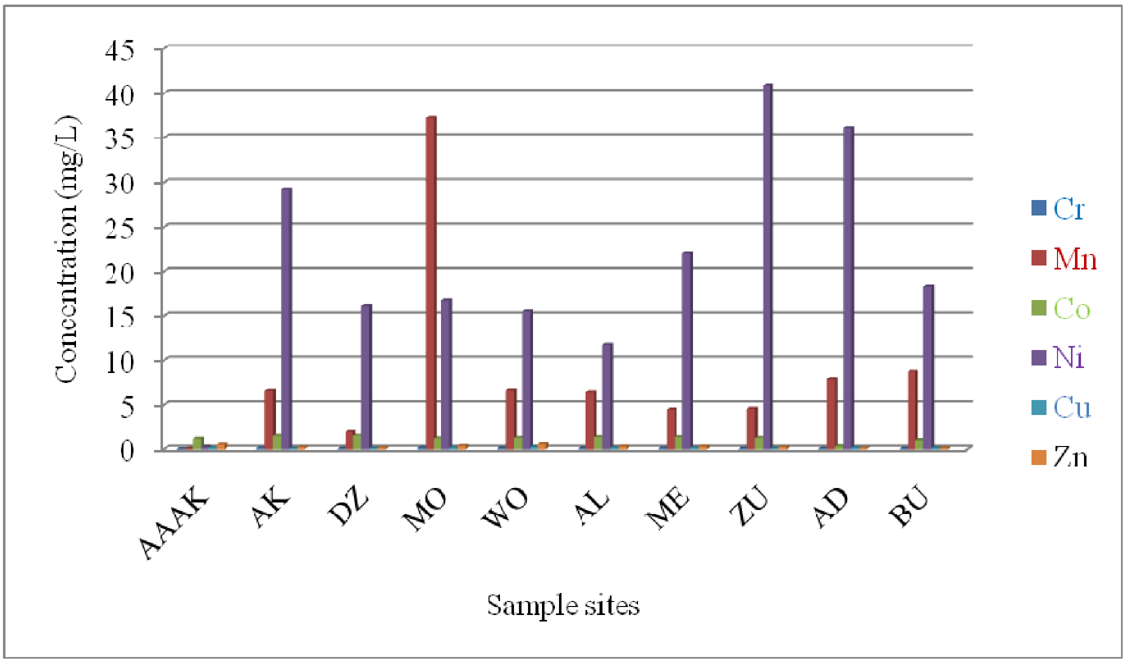


Figure 6. Distribution pattern of metals in soil sample

3.6. Comparison between results

3.6.1. Comparison of fluoride between water and soil samples

All the soil samples were collected from the irrigation farm lands of Ethiopian Rift Valley and the corresponding water sample were collected from any water source used for irrigation. The water soluble fluoride concentrations in soil samples have two major sources; one is from rapidly soluble fluoride complex like cryolite (Na_3AlF_6) found in water and soil and the second is from phosphate fertilizers. Therefore, the fluoride concentration in water directly affects fluoride concentration in soil samples. The comparison of fluoride in water and water soluble fluoride in soil samples are verified in Figure 7.

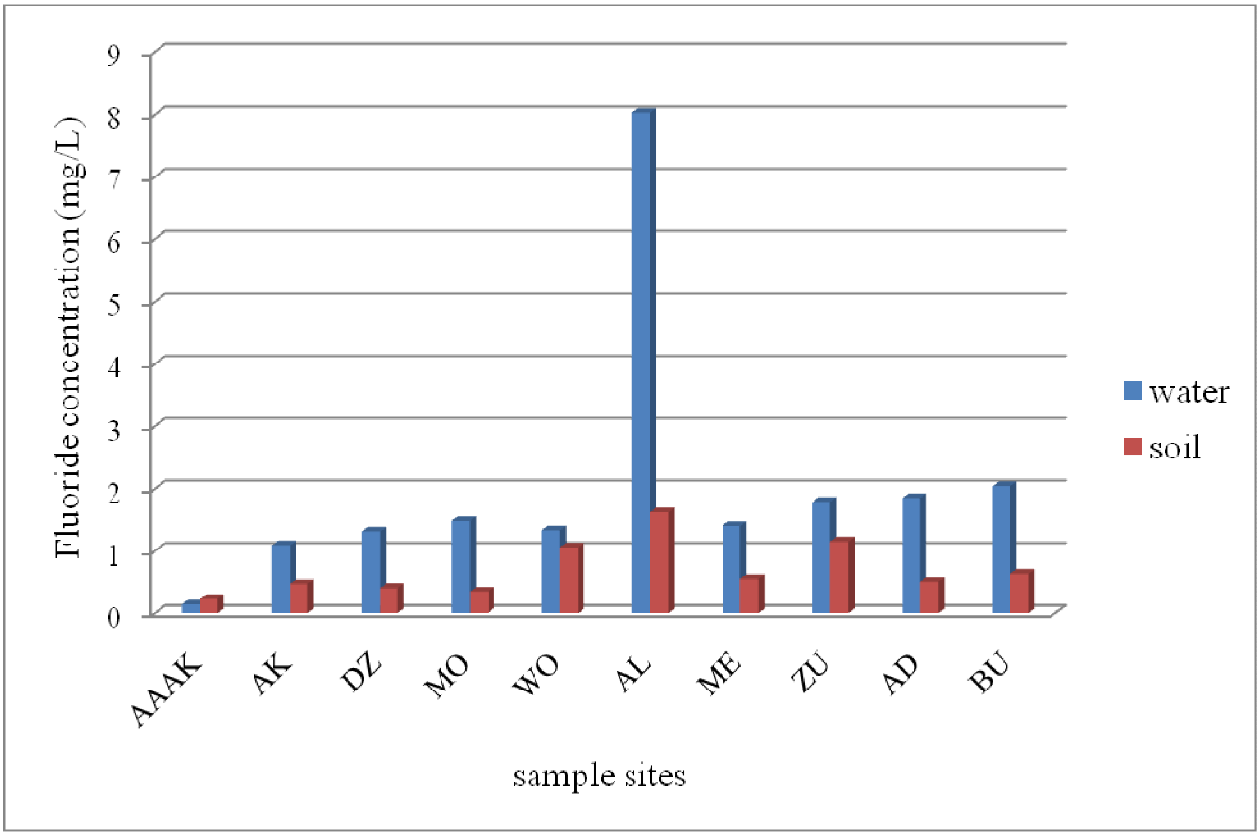


Figure 7. Comparison of fluoride in water and water soluble fluoride in soil samples

Except Arat Killo Campus soil used as controlling group and the tap water, in all other samples the fluoride concentration in water samples are greater than in soil sample; this may be due to soluble fluoride is washed by soil erosion in to any water sources like river, lake and well. Fluoride concentrations in water have positive correlation with both total and water soluble fluoride in soil; but the degree of correlation between fluoride in water and water soluble fluoride in soil is strong (correlation coefficient(r) = 0.796) and the degree of correlation between fluoride in water and total fluoride in soil is very weak (r = 0.086). Therefore, the levels of fluoride in water is more depend on the contents of water soluble fluoride in soil than total fluoride found in soil.

3.6.2. Comparison of water soluble and total fluoride in soil samples

Significant differences between the investigated soils have been obtained for water soluble fluoride content, which amounts from 2.32 to maximum 16.2 mg/kg. As shown in Table 16, water soluble fluoride is expressed in percentage from the total fluoride content, obtained values are very lower and are in the range from 0.52 to 4.27%. Therefore, relative to total, low water soluble fluoride content in the investigated soil samples were obtained, this may be different soils can bound soluble fluoride, Precipitation of F with Ca in solution and/or the complexing of Ca–F in the soil have been suggested as reasons for decreased fluoride solubility. Also, fluoride availability is much more dependent on soil's capacity for its bounding than on total fluoride content. For that reason, statistically small correlation coefficient between the total and water soluble fluoride content has been obtained (r = 0.144).

Table 16. Percentage of total fluoride that is extracted with water from the soil samples.

Sample site	AAAK	AK	DZ	MO	WO	AL	ME	ZU	AD	BU
% Fluoride extracted	1.11	2.12	1.77	0.956	3.08	4.27	1.67	1.74	0.758	0.521

The comparison of water soluble and total fluoride is verified in Figure 8.

.

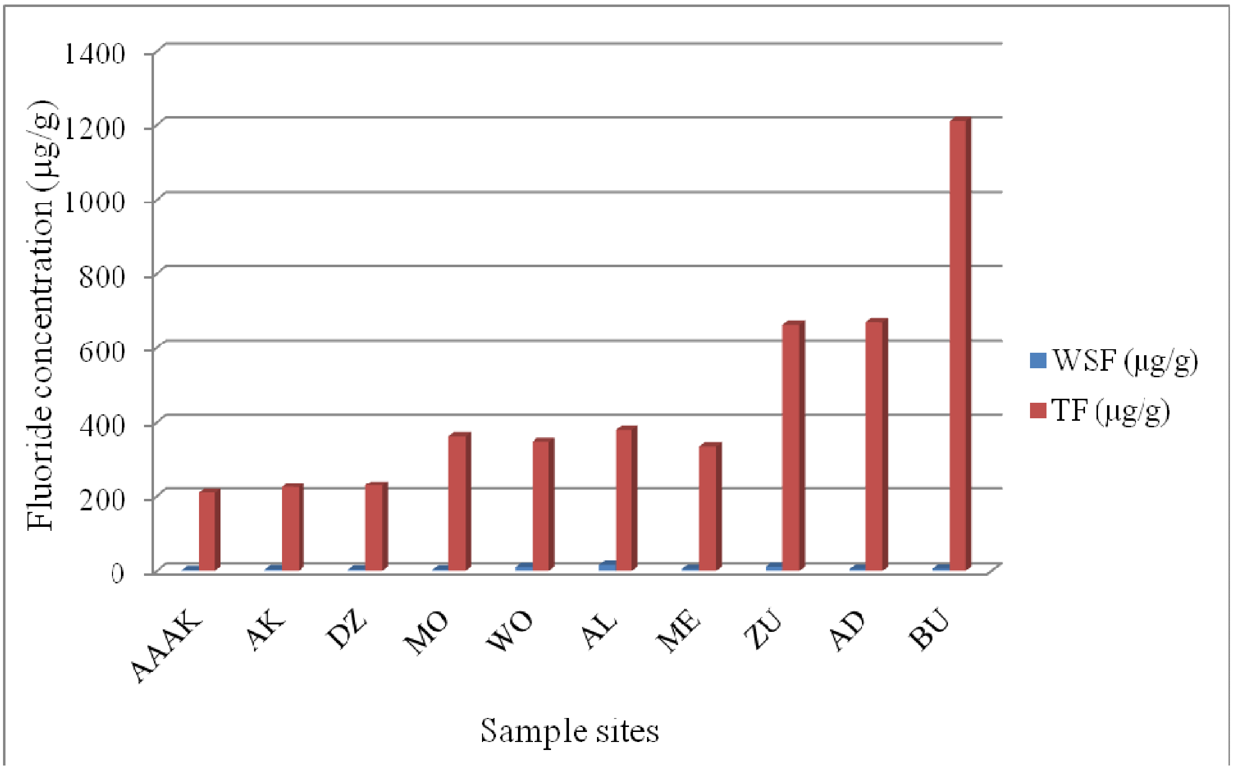


Figure 8. Comparisons of water soluble and total fluoride

3.6.3. Comparison of fluoride with pH, conductivity, salinity and TDS

The solubility of fluoride in soil increases with decreasing pH, this is due to the formation of soluble fluoride complexes of Al in acidic soil (pH < 5.5) and although the percentage of HF increased, HF uptake rate by plant was orders of magnitude higher than F^- at similar ion activities because HF readily diffused across the cell membrane [137].

The aqueous concentrations of fluoride are proportional to HCO_3^- concentration and pH values. Consequently, high fluoride water is usually HCO_3^- dominated which favors the dissolution of fluoride from soils and rocks. Therefore, water with high fluoride concentration can form in the areas where alkaline, i.e. carbonate-containing, waters are in contact with fluoride bearing rocks. Fluoride concentrations are relatively independent of the other water soluble components but noteworthy correlation exists between fluoride and pH values. The fluoride solubility in soil is lowest in the pH range of 5.0-6.5. At higher pH values, ionic exchange occurs between F^- and OH^- ions (illite, chlorite, micas and amphiboles) resulting in increase of F^- concentration in groundwater. At $pH < 6$, both F^- and Al^{3+} combine into water and formation of $[AlF]^{2+}$ and $[AlF_2]^+$ complexes mainly takes place in solution. Observed that the formation of $[MgF]^+$ complexes on the account of F^- ions intensifies while the saltiness of groundwater, Ca^{2+} and temperature increases [138]. But in this study, the pH of all soil samples is more than 6.53 and not extends from neutral. Therefore, no significant effect of pH on fluoride solubility in top soils of collected soil samples.

Electrical conductivity (EC), salinity, or total dissolved solids (TDS). These terms are all comparable and all quantify the amount of dissolved "salts" (or ions, charged particles) in a given sample. However, TDS is a direct measurement of dissolved ions and EC is an indirect measurement of ions by an electrode. EC measures salinity from all the ions dissolved in a sample. This includes negatively charged ions (e.g., Cl^-, NO_3^-) and positively charged ions (e.g., Ca^{++}, Na^+) [94]. As a result, it have very strong positive correlation coefficient (r) among them in both soil and water sample analysis.

3.6.3.1. In water sample

Total soluble salts are easily measured by monitoring the electrical conductivity (EC) of the solution. Note that soluble salts may disassociate in water to form charged ions. Therefore, high conductivity in sample indicates high concentration of fluoride. But electrical conductivity meter simply measures the total relative amount of either the dissolved anions and the dissolved cations. Pure water, with few or no dissolved salts, would be a poor conductor of electrons so the electrical conductivity value would be very low or approaching zero. Electrical conductivity measurements do not indicate the relative amounts of any specific salt or ion. Additional specific tests typically run by outside laboratories must determine concentrations of specific ions. The relative concentration of fluoride and the other three parameters are shown in Figure 9.

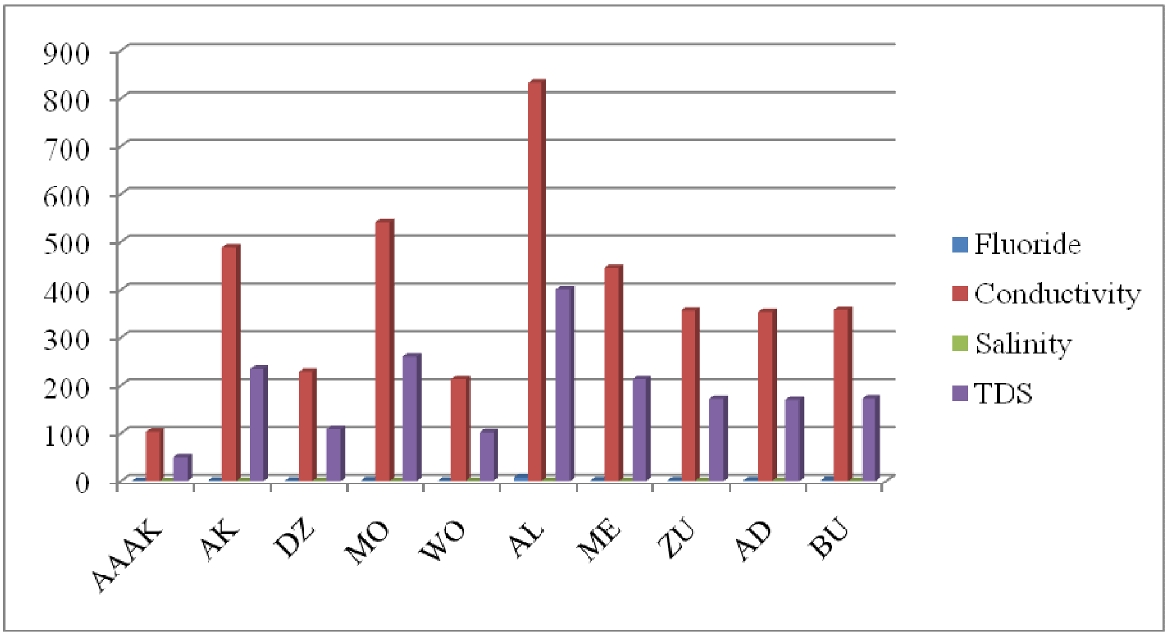


Figure 9. The relative concentration of fluoride and the other three parameters (Conductivity, Salinity and TDS) in water sample.

The maximum values of conductivity, salinity and TDS were found in Alem Tena water, it also contianed the highest concentration of fluoride and the lowest concentration were obtianed in the soil of Addis Ababa Arat Killo campus. The corelation coffecent between fluoride and the three parametrs are (r = 0.815, 0.777, 0.817), fluoride with conductiviy, salinity and TDS respectivily in water sample. Therefore, all the three parametrs are strong positive correlation with fluoride in water sample.

3.6.3.2. In soil sample

The relative concentration of total fluoride and the other three parameters in soil sample are shown in Figure 10.

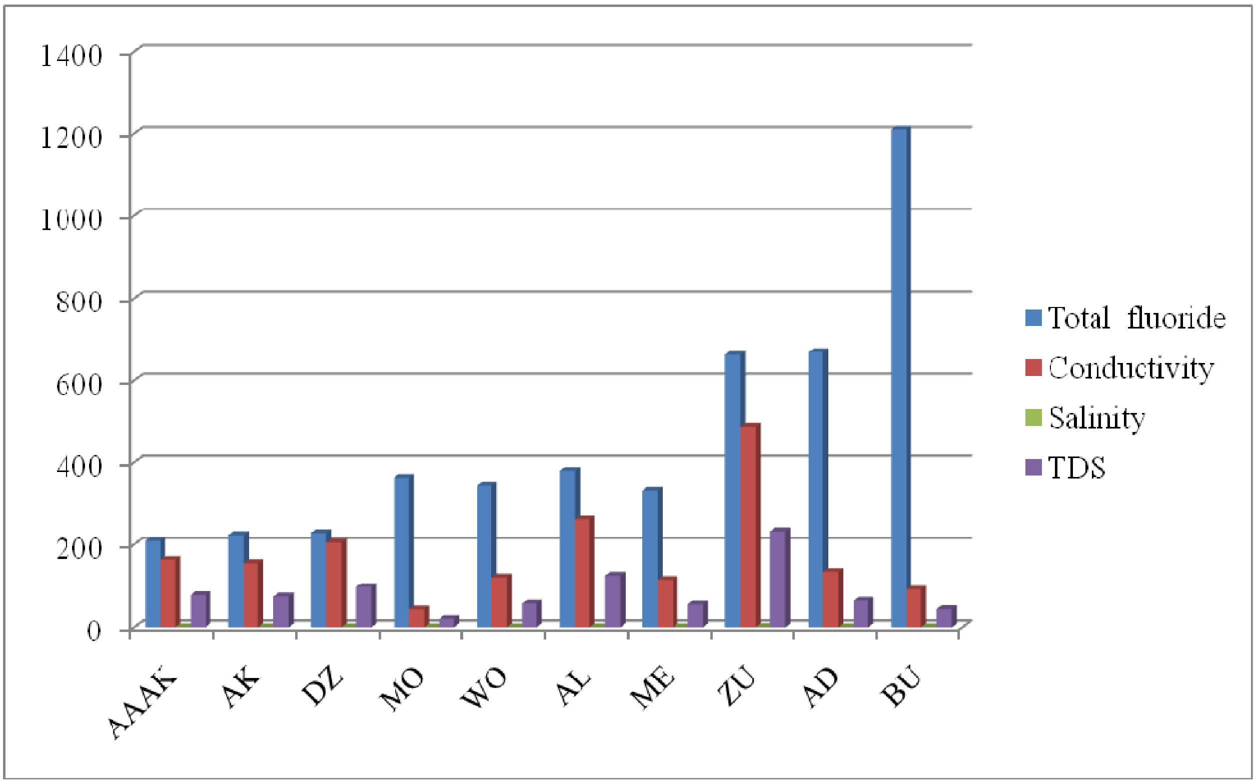


Figure 10. The relative concentration of total fluoride and the other three parameters in soil sample.

As shown in Figure 10, relations between total fluorides concentrations with the three parameters are not significant. The correlation coefficients are (r = 0.035, -0.284, 0.037) between total fluoride in soil with conductivity, salinity and TDS respectively. Therefore, no correlation between total fluoride and the three parameters were obtained.

The relative concentration of water soluble fluoride and the other three parameters in soil sample are shown in the Figure 11.

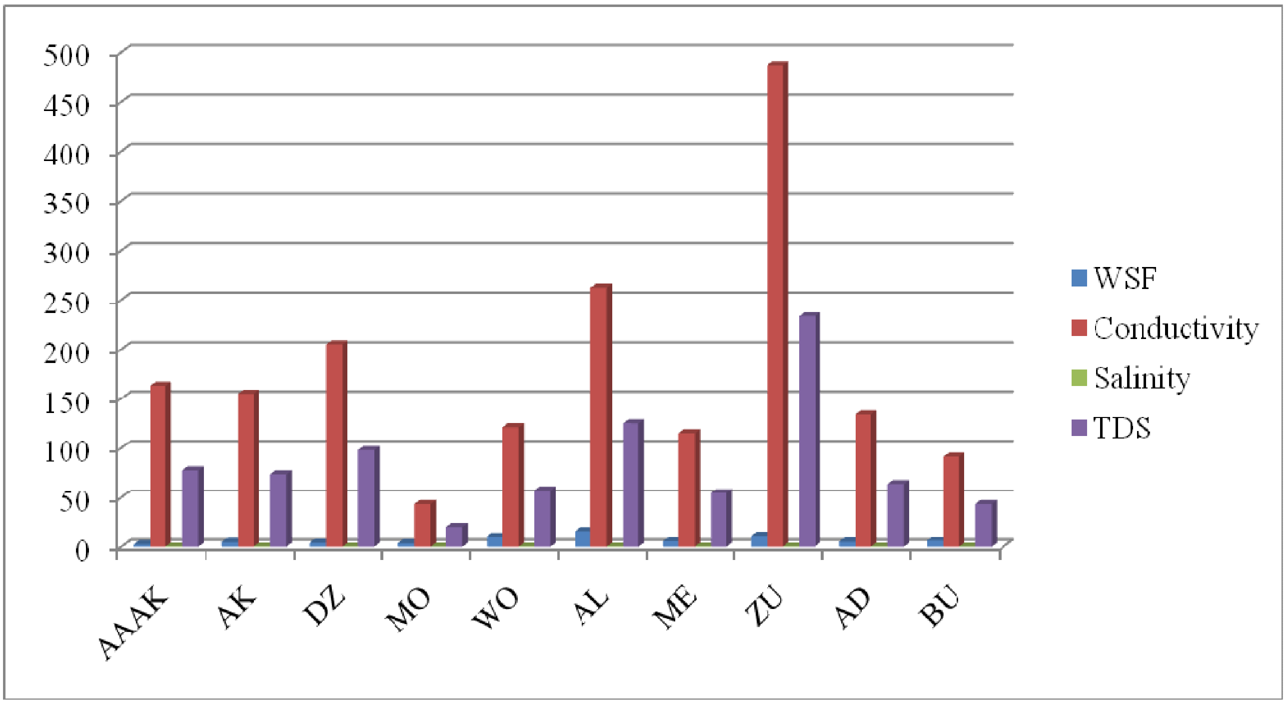


Figure 11. The relative concentration of water soluble fluoride and the other three parameters in soil sample.

The maximum water soluble fluoride was obtained in Alem Tena and the minimum was in Addis Ababa University Arat Killo Campus, but the maximum conductivity, salinity and TDS was found in Zuway and the minimum was obtained in Mojo. The correlation coefficients of water soluble fluoride in soil with conductivity, salinity and TDS are (r = 0.555, 0.0555, 0.555), respectively. Relative to total fluoride water soluble fluoride have moderate positive correlation with the three parameters. It may because of the soluble fluoride is increase total ions in soil than the complex form of fluoride.

3.6.4. Comparisons of metals with fluoride, pH, conductivity, salinity and TDS

3.6.4.1. In soil sample

The relationship between fluoride and other metal elements in soil samples was investigated. As shown in Table 18, positive correlation between total fluoride and Mg, Ca and Cu was determined in soils. Coefficients of correlation were 0.224, 0.120 and

0.830, respectively, and negative correlation between total fluoride and Na, K, Cr, Mn, Co, Ni, Fe and Zn. Coefficients of correlation were -0.362, -0.111, -0.604, -0.143, -0.450, -0.111, -0.726 and -0.192, respectively. The degree of correlation total fluoride with metals are; highly positive correlation with Cu ($r > 0.7$) and highly negative correlation with Fe ($r < -0.7$). The degree of correlation between total fluorides with Na, Cr and Co is moderate negative correlation ($r = -0.3$ to -0.7). Total fluoride also weak negative and posetive correlation with Mg, Ca, K, Mn, Ni and Zn ($r = -0.3$ to 0.3).

The correlation between water soluble fluoride and metals are shown in Table 17. Positive correlation between water soluble fluoride and Na, Mg, K and Fe was obtained in soils. Coefficients of correlation were 0.206, 0.368, 0.639 and 0.081, respectively, and negative correlation between water soluble fluoride and Ca, Cr, Mn, Co, Ni, Cu and Zn. Coefficients of correlation, -0.113, -0.532, -0.205, -0.018, -0.133, -0.351, and -0.121, respectively. The degree of correlation between water soluble fluorides with metals are; water soluble fluoride has moderate positive correlation ($r = 0.3$ to 0.7) with Mg and K, and moderate negative correlation ($r = -0.3$ to $–0.7$) with Cr and Cu. Water soluble fluoride also weak positive and negative correlation with Na, Ca, Mn, Co, Ni and Zn ($r = -0.3$ to 0.3).

The solubility of fluoride increases as Na concentration increases and Ca and Mg concentration decreases [138]. As a result, the highest water soluble fluoride was obtained in Alem-Tena sample. The highest concentration of Ca was also obtained in Alem-Tena and Mg and Na concentration in this site was comparable with other site. The highest concentration of water soluble fluoride in the site may be due to highest concentration of K and also form fluoride rich irrigation water. The levels of total fluoride in lower altitude of the site (Zuway, Adami-Tullu and Bulbulla) soil were excess the normal fluoride concentration of the soil reported in [136]. This may be because of the highest levels of Mg in Zuway, the lower concentration of Na in Adami-Tullu and Bulbulla and high concentration of Ca in Bulbulla.

The correlations of metals with other parameters (pH, Conductivity, Salinity and TDS) in soil are almost have similar trained except Cr and Co has positive correlation salinity and negative correlation with other three parameters; Cu has negative correlation with pH and positive correlation with other parameters. Metals have negative correlation with Ca, Mn, Ni and Fe and positive correlation with Na, Mg, K and Zn. There degrees of correlation are; Mg has highly positive correlation with all the four parameters and Ca has highly negative correlation with salinity. K with all four parameters and Na with salinity have moderate positive correlation and Ca and Fe with pH, conductivity and TDS and Ni with conductivity, salinity and TDS have moderate negative correlation. Na with pH, Conductivity and TDS, Cr, Mn, Co, Cu and Zn with all four parameters, Ni with pH and Fe with salinity have weak positive and negative correlation.

Table 17. Correlation coefficients between metals with fluoride (both water soluble and total) and other parameters (pH, conductivity, salinity and TDS) in soil samples.

	Na	Mg	K	Ca	Cr	Mn	Co	Ni	Cu	Fe	Zn
Total fluoride	-0.362	0.224	-0.111	0.120	-0.604	-0.143	-0.450	-0.111	0.830	-0.726	-0.192
Water soluble fluoride	0.206	0.368	0.639	-0.113	-0.532	-0.205	-0.017	-0.133	-0.351	0.081	-0.121
pH	0.119	0.993	0.479	-0.698	-0.286	-0.361	-0.278	-0.299	-0.177	-0.488	0.253
Conductivity	0.274	0.902	0.544	-0.644	-0.157	-0.312	-0.209	-0.412	0.053	-0.388	0.120
Salinity	0.303	0.704	0.448	-0.745	0.0	-0.234	0.023	-0.572	0.214	-0.086	0.298
TDS	0.273	0.902	0.543	-0.643	-0.159	-0.311	-0.212	-0.411	0.051	-0.390	0.119

3.6.4.2. In water samples

The relationship between fluoride and other metals in water samples was investigated. As shown in Table 18, positive correlation between fluoride and Na, K, Ca, Cr, Co, Fe and Cu was determined in the water samples. Coefficients of correlation were 0.429, 0.339, 0.253, 0.175, 0.084, 0.050 and 0.087, respectively, and negative correlation between fluoride and Mg, Mn, Ni and Zn. Coefficients of correlation were -0.442, -0.006, -0.097 and -0.134, respectively. The degree of correlation of fluoride with metals are; fluorides has moderate positive correlation with Na and K and moderate negative correlation with Mg. Fluoride in water also has no correlation with Ca, Cr, Mn, Co, Ni, Cu, Fe and Zn.

The correlations of metals with other parameters (pH, conductivity, salinity and TDS) in waters are; Na, Mg, K, Ca, Mn and Cr with all the four parameters, Co, Fe and Ni with three the parameters (conductivity, salinity and TDS) and Cu and Zn with pH have positive correlation. Cu and Zn with the three parameters (conductivity, salinity and TDS) and Co, Ni and Fe with pH have negative correlation. There degrees of correlations are; Na has strong positive correlation with salinity. Cr and Mn with all the four parameters, K and Ca with three parameters (conductivity, salinity and TDS), Na with pH, conductivity and TDS, Cu and Zn with pH have moderate positive correlation. Zn with salinity has moderate negative correlation. Mg, Co, Ni and Fe with all the four parameters, K and Ca with pH and Cu and Zn with the three parameters (conductivity, salinity and TDS) have no correlation. The significant positive correlation between conductivity and TDS with Na, K, Ca and Cr is due to the fact that conductivity depends on the constituents of TDS in water are Na^+, K^+ and Ca^{2+}.

Table 18. Correlation coefficients between metals with fluoride and other parameters (pH, conductivity, salinity and TDS) in water samples.

	Na	Mg	K	Ca	Cr	Mn	Co	Ni	Cu	Fe	Zn
Fluoride	0.429	-0.442	0.339	0.253	0.175	-0.006	0.084	-0.097	0.050	0.087	-0.134
pH	0.498	0.025	0.110	0.191	0.321	0.343	-0.087	-0.037	0.603	-0.099	0.315
Conductivity	0.699	0.025	0.668	0.578	0.570	0.362	0.160	0.121	-0.171	0.243	-0.238
Salinity	0.803	0.003	0.630	0.670	0.486	0.481	0.004	0.242	-0.142	0.276	-0.317
TDS	0.697	0.022	0.667	0.577	0.569	0.360	0.161	0.118	-0.168	0.243	-0.236

3.6.5. Comparisons of metals between water and soil samples

The relationship between metals in water and soil samples are shown in Table 19, some metals (Ca, Cr, Mn, Co, Ni and Fe) have positive correlation; but other metals (Mg, K, Cu and Zn) have negative correlation in water and soil samples. The degrees of correlation of Cr and Fe in soil with that in water samples are moderate positive and Na, Mg, Cu and Zn are negative moderate correlation. Some metals (K, Ca, Mn, Co and Ni) in soil have no correlation with that in water samples. The concentration of each individual metal in soil is higher relative to corresponding metals in the water.

Table 19. Correlation coefficients of metals between water and soil samples.

Metal	Na	Mg	K	Ca	Cr	Mn	Co	Ni	Cu	Fe	Zn
Correlation coefficient (r)	-0.591	-0.404	-0.263	0.147	0.337	0.077	0.285	0.030	-0.357	0.512	-0.327

3.6.6. Comparison of fluoride levels in this study with literature values

3.6.6.1. In soil samples

The comparative study of the fluoride concentration of soil sample determined in this study and reported literature values are presented in Table 20. The fluoride concentration in this study has wide variation between sample sites relative to the reported values in the literature; it may because of the variation of soil type, climate, altitude and so on. Except the value reported by US NAS, Washington DC, America [107], Smith *et al.*, America [108] is lower than this study, others Toma *et al.*, Moldova [117], Shomar *et al.*, Israel [111], Zhang *et al.*, China [115] and others have comparable value of total fluoride with this study. The water soluble content of soil in this study was a bit higher than that of reported in literature, but comparable values also reported in America [107] and New Zealand [109].

Table 20. Summary of fluoride concentrations of soil reported in literature

No.	Country	Total fluoride concentration (µg/g)	Water soluble fluoride concentration (µg/g)	Reference
1	Ethiopia	209-1210	2.32-16.2	This study
2	America For soil developed from non-fluoride containing minerals	0.2-0.3		107
	for soil developed from fluoride containing minerals	7-38		108
	sample collected from highly contaminated sites	286 - 590	7 -36	114
3	New Zealand	106-454	0.318-9.08	109

4	India		0.15-1.89	110
5	India	18–39		112
6	Israel	100-475		111
7	Nigeria		0.075 - 0.200	113
8	Turk		1.24-1.52	116
9	China Fluoride concentrations in Pb-Zn mining agricultural soils	409-1553		115
10	China Topsoil in the paddy fields and in the aerated field	378-508		120
11	Moldova	64 – 1120	0.2 – 14	117
12	Pomoravlje Serbia	285-391	0.1-0.9	118
13	Podgorica	217-696	0.06-2.67	119

3.6.6.2. In water samples

The comparative study of the fluoride concentration of water sample determined in this study and reported literature values are presented in Table 21. The fluoride concentration in water sample is highly dependent on the water source. The river water of this study has slightly higher concentration of fluoride than the other study of Ethiopia reported in literature [131]. Except Israel [123] and Ethiopia [131], slightly higher concentration, the fluoride concentration of ground water in this study is lied the range of reported values in the literature. The fluoride concentration in lake of this study varied widely between sample sites, it may depend on different altitudes of Ethiopian Rift Valley. But the fluoride concentration lied in the range of values reported in Kenya [132], slightly higher than that reported in India [132] and some sites are comparable with that reported in Ethiopia [131].

Table 21. Summary of fluoride concentrations of water reported in literature

No.	Country	Type of water	Fluoride (mg/L)	Reference
1	Ethiopia	River	1.09-2.04	This study
		Lake	1.31-8.05	
		Well	1.48	
1	India	Ground water	1.50-11.82	127
2	Iran	Well	0.70-2.13	128
3	South Africa	Ground water	0.64-2.87	130
4	Ethiopia		0.4–36	131
		Lake	>5	
		River	<1.5	
		Ground water	4.5	
5	Israel	Ground water	2.6-4.4	123
6	Kenya	Lake	0.1-39.4	132
7	India	Lake	0.02-1.62	132

3.6.7. Comparison of metal levels in this study with literature values

3.6.7.1. In soil samples

The natural content of metals in the soil is directly related to the mineralogic and granulometric composition and the origin of the matrix soil. The metal concentration in soil is very wide range. The comparative study of the metal concentration of soil sample determined in this study and reported literature values are presented in Table 22. From the major metals, the content of Na was comparable to that reported in USA [122] and lower than that reported in Pakistan [134]. K was lower than that reported in USA [122] and Pakistan [134]. Ca was lower than that reported in USA and higher than that reported in Pakistan. The values of Mg in the literature lie in the range of this study.

The trace metal Mn in Turkey [124], Fe in USA [122], Zn in Ireland [121] and Turkey [124], Cu in USA, Turkey and Ireland and Cr in USA and Turkey are comparable to the values of fluoride in soil obtained in this study. But Mn and Zn in USA were higher and Fe in Turkey, Ni and Co in USA and Turkey were lower than the values compared to the result obtained in this study.

Table 22. Summary of metal concentrations of soil reported in literature

Metal	Concentration (μg/g)	Country	Reference
Na	4500	USA	122
	10026	Pakistan	134
	684-6703	Ethiopia	This study
K	10520	USA	122
	9242	Pakistan	134
	1776-4394	Ethiopia	This study
Ca	45180	USA	122
	6726	Pakistan	134
	7547-22998	Ethiopia	This study
Mg	2670	Ireland	121
	9857	Pakistan	134
	4000	USA	122
	1608-11229	Ethiopia	This study
Mn	749	USA	122
	139-320	Turkey	124
	143-700	Ethiopia	This study
Fe	26220	USA	122
	7368-10344	Turkey	124
	12180-32681	Ethiopia	This study
Zn	42.33	Ireland	121
	38-74	Turkey	124
	128	USA	122
	30.5-89.2	Ethiopia	This study
Ni	16	USA	122
	32-54	Turkey	124
	446-1288	Ethiopia	This study
Co	10	USA	122
	4.20-12.4	Turkey	124
	50.3-112	Ethiopia	This study
Cu	8.27	Ireland	121
	7.50-38.3	Turkey	124
	30	USA	122
	8.85-45.4	Ethiopia	This study
Cr	42	USA	122

	10.9-31.7	Turkey	124
	9.79-79.3	Ethiopia	This study

3.6.7.2. In water samples

The comparative study of the metal concentration of water sample determined in this study and reported literature values are presented in Table 23. The concentration of Na in this study is lower than those reported in literature. K was bit higher in this study of the well water than Israel [123] and comparable in the lower end of the range reported in Kenya [132] and India [129, 132]. The concentration of Ca in the lake of this study lie in the range of reported in Kenya [132], but bit higher in the well of this study relative to the reported value of Israel [123] and India [129]. Mg in the lake of this report is lie in the range of reported literature value of Kenya and India [132] and also comparable in the well of this study with literature values.

Mn and Fe content in this study are comparable with that reported in literature of Nigeria [125]. Zn in the river of this study is comparable with the literature values reported in Nigeria [125], but bit lower than that reported in the surface water of the same place in Nigeria [126]. Ni concentration in this study is higher than the result reported in Nigeria [126]. Co in the lake water is bit higher than the reported value in Ethiopia [133]. Cu in lake water of this study is also higher than reported in Ethiopia [133], but comparable to the result reported in Nigeria [125, 126]. Cr concentration is bit higher in this study than the literature value reported in Nigeria [125], Ethiopia [133] and India [129].

Table 23. Summary of metal concentrations of water reported in literature

Metal	Water type	Concentration (mg/L)	Country	Reference
Na	Ground water	406-1058	Israel	123
	Lake	115-33562	Kenya	132
	Ground water	170-550	India	129
	Lake	186-1835	India	132
	River	17.2-67.3	Ethiopia	This study
	Lake	9.37-55.6		
	Well	57.9		

K	Ground water	4.7-9.7	Israel	123
	Lake	15-4681	Kenya	132
	Ground water	20-135	India	129
	Lake	19-246	India	132
	River	2.54-20.3	Ethiopia	This study
	Lake	4.04-16.2		
	Well	18.6		
Ca	Ground water	67-182	Israel	123
	Lake	2.8-1293	Kenya	132
	Ground water	71-223	India	129
	Lake	11-70	India	132
	River	134-184	Ethiopia	This study
	Lake	167-188		
	Well	267		
Mg	Ground water	42-56	Israel	123
	Lake	2.0-216	Kenya	132
	Ground water	52-147	India	129
	Lake	17-146	India	132
	River	28.6-61.6	Ethiopia	This study
	Lake	22.7-31.1		
	Well	66.2		
Mn	River	3.13-6.80	Nigeria	125
	River	4.47-8.77	Ethiopia	This study
	Lake	1.94-6.37		
	Well	37.2		
Fe	Ground water	44-113	Israel	123
	Ground water	0.1-0.4	India	129
	River	5.64-13.14	Nigeria	125
	River	6.64-28.3	Ethiopia	This study
	Lake	6.04-37.0		
	Well	47.7		
Zn	River	0.36-1.04	Nigeria	125
	Surface water	0.647-1.382	Nigeria	126
	River	0.144-0.562	Ethiopia	This study
	Lake	0.154-0.308		
	Well	0.383		
Ni	Surface water	0.096-1.561	Nigeria	126
	River	15.5-36.1	Ethiopia	This study
	Lake	11.7-40.9		
	Well	16.7		
Co	Lake	0.05-0.064	Ethiopia	133
	River	0.354-1.47	Ethiopia	This study
	Lake	1.21-1.48		
	Well	1.18		
Cu	River	0.05-0.10	Nigeria	125

	Lake	0.03-0.04	Ethiopia	133
	Surface water	0.153-0.438	Nigeria	126
	River	0.088-0.251	Ethiopia	This study
	Lake	0.1-0.154		
	Well	0.149		
Cr	River	0.02-0.06	Nigeria	125
	Lake	0.06	Ethiopia	133
	Ground water	0.09-1.0	India	129
	River	0.071-0.149	Ethiopia	This study
	Lake	0.072-0.137		
	Well	0.169		

3.6.8. Statistical analysis

3.6.8.1. Pearson correlation of metals

The correlation between two variables reflects the degree to which the variables are related. The most common measure of correlation is the Pearson Product Moment Correlation (called Pearson's correlation in short). When measured in a population the Pearson Product Moment correlation is designated by the Greek letter rho (ρ). When computed in a sample, it is designated by the letter "r" and is sometimes called "Pearson's r." Pearson's correlation reflects the degree of linear relationship between two variables. It ranges from +1 to -1. A correlation of +1 means that there is a perfect positive linear relationship between variables and a correlation of -1 means perfect negative linear relationship between variables [135]. The scatter plot shown in Table 24 and 25 indicates such relationship.

3.6.8.1.1. Pearson correlation of metals with in soil sample

Table 24. Correlation matrices for metals in soil sample

	Na	Mg	K	Ca	Cr	Mn	Co	Ni	Cu	Fe	Zn
Na	1										
Mg	0.131	1									
K	0.215	0.447	1								
Ca	-0.224	-0.736	-0.221	1							
Cr	0.759	-0.260	-0.173	-0.026	1						
Mn	-0.252	-0.403	-0.344	0.681	-0.023	1					
Co	0.146	-0.238	-0.131	-0.38	0.336	-0.553	1				
Ni	-0.562	-0.325	-0.114	0.487	-0.237	0.391	-0.177	1			
Cu	0.528	-0.142	-0.103	-0.094	0.771	0.198	0.277	0.079	1		
Fe	-0.249	-0.513	-0.029	0.242	0.127	0.358	0.440	0.404	0.395	1	
Zn	-0.649	0.224	-0.025	-0.205	-0.428	0.330	-0.054	0.318	-0.046	0.497	1

From the results depicted in Table 25, high positive correlation is obtained for Cr with Na and Cu. High negative correlation between Ca and Mg. Na with Cu, Mg with K, Ca with Mn and Ni, Cr with Co, Mn with Ni, Fe and Zn, Co with Fe, Ni with Fe and Zn and Fe with Zn have moderate positive correlation. Na with Ni and Zn, Mg with Mn and Ni and Fe, K With Mn, Ca with Co, Cr with Zn and Mn with Co have moderate negative correlation. The positive correlation may come from common anthropogenic or natural sources of soil as well as similarity in chemical properties. The other metals have weak positive or negative correlation indicates that the presence or absence of one metal affect in very less extent on the other metal.

3.6.8.1.2. Pearson correlation of metals with in water sample

Table 25. Correlation matrices for metals in water sample

	Na	Mg	K	Ca	Cr	Mn	Co	Ni	Cu	Fe	Zn
Na	1										
Mg	0.072	1									
K	0.550	0.182	1								
Ca	0.478	0.206	0.683	1							
Cr	0.171	0.566	0.533	0.623	1						
Mn	0.482	0.572	0.489	0.698	0.588	1					
Co	-0.270	0.072	0.380	0.234	0.440	-0.098	1				
Ni	0.402	-0.116	-0.035	0.332	-0.378	0.004	-0.333	1			
Cu	-0.226	0.031	-0.474	-0.223	0.204	0.072	-0.227	-0.3511	1		
Fe	-0.049	0.529	0.279	0.579	0.375	0.608	0.190	0.27697	0.099	1	
Zn	-0.458	0.272	-0.379	-0.329	0.630	0.097	0.203	-0.6057	0.743	0.109	1

In water samples, there is high positive correlation between Cu and Zn. Moderate positives correlation Na with K, Ca, Mn and Ni, Mg with Cr, Mn and Fe, K with Ca, Cr, Mn and Co.Ca with Cr and Mn, Cr with Mn and Co and Mn with Fe. Moderate negative correlation Na with Zn, K with Cu and Zn, Ca with Zn, Cr with Ni, Co with Ni and Ni with Cu and Zn. Other metals have very weak positive and negative correlation.

4. CONCLUSION AND RECOMMENDATIONS

The levels of fluoride, macro and trace metals and same physical parameters like pH, conductivity, salinity and TDS in soils of vegetation farmlands and surrounding water used for irrigation were assessed in this study. The efficiency of sample preparation and instrument were tested by assessing standard deviation, conducting recovery experiment.

The concentration of total fluoride in soil was found in the range of 209-1210 µg/g, the values in some sites are exceeded from the reported normal total fluoride content of soils (150-400 µg/g); this may be due to fluoride rich acid igneous rocks as source of surface soil. The water soluble fluoride in soil was found in the range 2.32-16.2 µg/g, the value within normal fluoride levels of soil (2.57-16.44 µg/g). So, danger from fluoride accumulation in vegetations does not exist, while the food produced in the investigated area is in regard of fluoride content, is unpolluted.

The levels of fluoride in irrigation water samples were in the range of 0.143-8.03 mg/L. The result is below WHO limit of fluoride in irrigation water (10 mg/L). Therefore, the irrigation water is not toxic to some crops and animals.

The concentration of metals in soil samples in this study is in the following order Fe (12180-32681 µg/g) > Ca (7547-22998 µg/g) > Mg (1608-11229 µg/g) > Na (684-6703 µg/g) > K (1776-4394 µg/g) > Ni (446-1288 µg/g) > Mn (143-700 µg/g) > Co (50.3-112 µg/g) > Zn (30.5-89.2 µg/g) > Cr (9.79-79.3 µg/g) and Cu (8.85-45.4 µg/g). The order fit with the relative abundance of metals in earths crest.

The concentration pattern of metals in water is in the following decreasing order as Ca (16.7-267 mg/L) > Mg (22.7-66.2 mg/L) > Na (8.64-67.3 mg/L) > Fe (47.7-6.04 mg/L) > Ni (0.274-40.9 mg/L) > Mn (0.048-37.2 mg/L)> K (1.11-20.2 mg/L) > Co (0.354-1.48 mg/L) > Zn (0.144-0.562 mg/L) > Cu (0.088-0.251mg/L) and Cr (0.071-0.169 mg/L). Relative to General Guidelines for Irrigation Water Used in Plant Production, this result exceeds the reported optimum range of some metals.

The fluoride and metal results in this study are comparable with the data reported in the literature for some countries.

The pH range in soil sample was 6.53-8.43, indicates no pH effect on fluoride solubility and its availability for vegetation uptake.

The three parameters (conductivity, salinity and TDS) have strong positive correlation with fluoride in water sample and moderate positive correlation with water soluble fluoride in soil sample, but no significant correlation with total fluoride in soil.

Fluoride concentrations in water have strong positive correlation with water soluble fluoride in soil, but weak positive correlation with total fluoride in soil. Therefore, the levels of fluoride in water are more dependent on the contents of water soluble fluoride in soil than total fluoride found in soil.

The percentage of total fluoride that extracted with water from the soil is very small (in the range of 0.52-4.27%) and the correlation between them is not significant. So, fluoride availability is much more dependent on soil's capacity for its bounding than on total fluoride content.

Total fluoride have positive correlation with Ca, Mg and Cu and negative correlation with Na, K, Cr, Mn, Co, Ni, Fe and Zn, but the degree of correlation is strong positive with Cu and strong negative correlation with Fe. It has also moderate negative correlation with Na, Cr, and Co. Water soluble fluoride have positive correlation with Na, K, Mg and Fe and negative correlation with Ca, Cr, Mn, Co, Ni, Cu, and Zn, but the degree of correlation is moderate positive with Mg and K and moderate negative correlation with Cr and Cu. Therefore, the less solubility of fluoride in soil sample may be because of high concentration of Ca, Cu and Mg and low concentration of Na, K, and Fe. Except, Na and K which have moderate positive correlation with fluoride, other metals have no significant correlation with fluoride in water sample.

Generally, the concentrations of major metals in soil have vital input for determination of fluoride solubility than trace metals.

The present study gives brief information about fluoride concentration in soil and irrigation water and its correlation with same selected metals. It might be useful in pointing directions for studies that will be conducted. Aluminum is the way of fluoride transportation for plant uptake from soil, therefore, it is recommended to assess Al analysis in soil. Other than soil, air is also a source of fluoride, therefore, recommended to conduct vegetation analysis of fluoride.

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