SINET: Ethiop. J. Sci., 37(1):43–52, 2014
 ISSN: 0379–2897

LEVELS OF FLUORIDE IN STAPLE CEREALS AND LEGUMES PRODUCED IN SELECTED AREAS OF ETHIOPIA

Seid Mustofa [1], Bhagwan Singh Chandravanshi [2,*], Feleke Zewge [2]

[1] Department of Chemistry, Faculty of Natural and Computational Sciences, Wolayta Sodo University, PO Box 138, Sodo, Ethiopia. E-mail: seydchem@gmail.com
[2] Department of Chemistry, College of Natural Sciences, Addis Ababa University, PO Box 1176, Addis Ababa, Ethiopia. E-mail: bscv2006@yahoo.com

ABSTRACT: The main objective of this study was to determine the levels of fluoride in cereals (tef, wheat, corn and barley) and legumes (pea, lentil and chickpea) produced in selected areas of Ethiopia. The samples were collected from the rift valley and outside rift valley areas of Ethiopia: Arsi Negele, Adola, Wonji, Ada, Gonder, Bure (Gojam) and Dessie towns. The samples were collected from local markets in the areas where they are cultivated in large amount. Levels of total fluoride in cereal and legume grain samples were determined by fluoride ion selective electrode. Fluoride levels in cereals were found between 0.98 mg/kg in corn from Adola and 10.98 mg/kg in tef from Wonji. Fluoride levels in legumes ranged from 1.52–11.07 mg/kg both in the pea with the lowest and highest levels from Bure and Ada, respectively. Fluoride levels in cereals from rift valley areas were higher than those from outside the rift valley areas. Generally, cereal samples from Arsi Negele and Wonji were found to contain higher levels of fluoride, ranging from 3.70 mg/kg in corn from Wonji to 10.98 mg/kg in tef from Wonji. The highest level of fluoride was found in pea (11.07 mg/kg) from Ada, and the lowest level in chickpea (1.52 mg/kg) from Dessie and in pea (1.52 mg/kg) from Bure. Fluoride contents of legume samples from Ada were found to be higher than those from Gonder, Bure and Dessie. In general, the levels of fluoride in Ethiopian cereals and legumes from non-rift valley areas are comparable to those from other countries.

Keywords/phrases: Cereals, Ethiopia, fluoride, legumes, staple food

INTRODUCTION

A staple food is generally defined as food that is eaten regularly and supplies a major proportion of energy and nutrient needs. Staple foods vary by location but typically include grains, tubers, legumes or seeds (World Bank, 2012). Grains such as tef, corn, wheat, barley and sorghum are the basis of Ethiopian indigenous diet. Most of Ethiopian main meals consist of breads made of cereal grains (tef, wheat, corn, barley and sorghum) (Abbebe Kifleyesus, 2011). Grain legumes are edible seeds of annual legumes and produced throughout the world (Janzen *et al.*, 2006). They are the next important food crop after cereals. Legumes include plants such as field peas, lentils, dry edible beans, chickpeas, soybeans, fenugreek, faba beans and other minor plants. Food legumes play an important and diverse role in the diets of poor people around the world (Janzen *et al.*, 2006; Akibode and Maredia, 2011). Legumes are multipurpose crops and are consumed either directly as food or in various processed forms (Akibode and Maredia, 2011).

Tef (*Eragrostis tef*) is one of the major staple food crops of Ethiopia (MoARD, 2009; Melese Temesgen, 2013). It is primarily grown to prepare Ethiopian bread, porridge and some native alcoholic drinks (Hailu Tefera and Seyfu Ketema, 2001; MoRAD, 2009; Melese Temesgen, 2013). There are three types of tef varieties in Ethiopia: white, brown and mixed. White tef is the most preferred and expensive one. Brown tef is becoming more popular related to its increased iron content (Piccinin, 2007). Considering the country as a whole, tef is produced in seven regions to varying degrees. Amhara (East and West Gojam, North and South Gonder, North Shewa and South Wello) and Oromiya (North

---

* Author to whom all correspondence should be addressed.

Shewa, East and West Shewa, East and West Welega and Jimma) regions are the largest producer of tef, followed by Southern Nations Nationalities and Peoples Region (SNNPR) and Tigray. The crop contains iron and has high amount of calcium, potassium and other essential minerals found in an equal amount than in other cereal grains (Melese Temesgen, 2013).

Wheat (*Triticum aestivum*) is one of the various cereal crops largely grown on the highlands of Ethiopia. It is produced largely in the southeast, central and northwest parts of the country. Small amount is produced in the rest of the north and south regions (MoARD, 2009).

Corn (*Zea mays* L.) is widely produced in the country. In Ethiopia, corn is also used as staple food. Corn is largely produced in Western, Central, Southern and Eastern regions of Ethiopia. It is consumed as bread, porridge and roasted grain (popcorn). In addition to the above, it is also used to prepare *tella* and *arekie* (MoARD, 2009).

Barley (*Hordeum vulgare* L.) is one of the most important staple food crops on the highlands of Ethiopia. In Ethiopia barley is the fifth most important cereal crop next to corn, tef, sorghum and wheat (Melese Temesgen, 2013). Barley is the most preferred grain, after tef, for making the traditional bread (*injera*), which can be used either solely or in combination with tef flour or other cereal flours. It is used to prepare various types of foods (*kollo*, *besso, kitta*), local drinks (*tella*, *araki*, *borde* and *buqri*) and industrial beverages (MoARD, 2009; Melese Temesgen, 2013). *Genfo* (thick porridge), *kollo* (roasted grain), *kinche* (thick cooked) are most popular when made from barley grain, but can be prepared from other cereals also. Other recipes, such as *dabbo* (bread), *kitta* (thin, unleavened, dry bread) and *atmit* (gruel) can be prepared with barley or blended with other cereal flours. Local beverages t*ella* and *borde* can be made from barley grain. Barley is also traditionally used in the preparation of gruel utilized as weaning food (Melese Temesgen, 2013).

In Ethiopia, pea (*Pisum sativum*) is a highly consumed pulse in the daily diet of the society in urban and rural areas (Ethiopian Export Promotion, 2004). Pea is eaten as whole, split or milled usually fresh, fried, boiled or mixed with other cereals to make various types of stews and soups (Ethiopian Export Promotion, 2004). Pea is widely used for food because of its highest protein contents in the form of *shiro*, *kik wot*, *nifro* and soup (Ethiopian Export Promotion, 2004).

Lentil (*Lens culinarus*) is one of the important legume crops heavily consumed in Ethiopia (Ethiopian Export Promotion, 2004). It is a popular ingredient of every day diet in the majority of households. Lentil is widely used as whole, split in stews, soups and various forms of sandwiches (Ethiopian Export Promotion, 2004). It is usually consumed as fried, roasted and boiled whole or split in the form of wot (stews), vegetable soups mixed with other beans. It is also ground to powder to prepare *shiro wot* (stew).

Chickpea belongs to *Leguminoseae* family (Steenbergen *et al*., 2011). Chickpea is an important crop in Ethiopia. It is the fourth most produced and cultivated pulse after faba, field and haricot beans (EATA and MOA, 2012). There are two main varieties of chickpea in Ethiopia: Kabuli or White Gram and Desi or Brown Gram. Although Ethiopia primarily consumes most of its chickpea production domestically, it is also the 7th largest global exporter, contributing 3.7% of global exports in 2010 (Ethiopian Export Promotion, 2004; EATA and MOA, 2012). Chickpea is grown across the highlands and semi-arid regions, mostly in the Oromiya and Amhara regions, which account for 90% of chickpea production nation-wide (Steenbergen *et al*., 2011). The major growing areas in the country include Eastern Showa, Western Showa, Gondar, Gojam, and Wello.

Fluoride is not considered to be essential for human growth and development but it is considered to be beneficial in the prevention of dental caries and skeletal fluorosis (SCHER, 2010). Fluoride is strongly retained by soil, forming complexes with soil components (CDC, 2001). The amount of fluoride taken up by plants depends on the type of plant, the nature of the soil, and the amount and form of fluoride in the soil (WHO, 2002). Plants accumulate fluoride in different extents, depending on the type of the plant and of the soil where they grow (WHO, 2002). Among beverages tea has exceptionally high fluoride content (Mahapatra, 2007). Tea plants are well known to accumulate high fluoride. Seafoods are also known to accumulate high levels of fluoride (WHO, 2002; USDHS, 2003). Some foodstuffs such as vegetables and fruits normally contain fluoride though at low concentration (0.1 mg/kg–0.4 mg/kg) and thus contribute to fluoride intake by humans (Yadav *et al*., 2012). Fluoride exposure is not limited to its presence in fluoridated drinking water (Ahokas *et al*., 1999). Food generally contains low levels of fluoride (USDHS, 2003); however, food grown in areas where soils have high amounts of fluorides or where phosphate fertilizers are used may have higher levels of fluoride (CDC, 2001; USDHS, 2003). Besides water, food items especially agricultural crops are heavily contaminated with fluoride bearing rocks (Sunitha and Reddy, 2008). Fluoride level in the food depends on mainly: fluoride level in the soil, fluoride level in the atmosphere, use of fertilizers and pesticides and other sources of contamination (Sunitha and Reddy, 2008). Total exposure to fluoride depends on contributions from several sources such as drinking water, water-based beverages, food, food supplements, use of toothpaste and to a lesser extent from several environmental sources (SCHER, 2010). The major factor that determines the extent of adverse effect depends on the fluoride content of natural drinking-water, the total amount ingested daily, the duration of ingestion and the efficiencies of intestinal absorption and renal excretion (WHO, 1996; Tamiru Alemayehu, 2006). The total intake of adults is usually within the range 0.2–2.0 mg of fluoride/day but higher intakes are common where the fluoride content of drinking water is high (WHO, 1996).

Fluorosis is endemic in at least 25 countries around the world with India, China and East African countries being the countries with the highest prevalence rates (Mahapatra, 2007). Dental fluorosis is widespread in eastern part of Africa (Malde *et al*., 1997). In certain parts of Ethiopia, especially rift valley areas, fluorosis has been observed to be a public health problem (Dagnew Tadesse *et al*., 2010). Fluorosis is assessed as a risk for a population of close to 8.5 million in Ethiopia. The population at risk lives mainly in the Rift Valley — spread over different regional states: Afar, Amhara, Oromyia and Southern Nations, Nationalities and Peoples (SNNPR) (Steenbergen *et al*., 2011).

The moderately high fluoride concentrations (1.5–5.0 mg/L) are found on the highlands of Ethiopia, indicating that fluorosis is not confined to the Rift Valley (Tamiru Alemayehu, 2006). In the Rift Valley region of Ethiopia, the problem of high fluoride concentrations in natural waters, especially groundwater, is severe and widespread (Dagnew Tadesse *et al*., 2010). There is wide difference in fluoride among different water bodies. Fluoride concentration varies from 1.9 to 250 mg/L in lakes, 2 to 150 mg/L in hot springs, from non-detectable to 6.4 mg/L in boreholes and 2 to 68 mg/L in geothermal wells (Tamiru Alemayehu, 2006). The Wonji area and its surroundings contain high fluoride in the groundwater attributed to the high thermal activity (Tamiru Alemayehu, 2006).

The fluoride level in dry legume and cereal grains has been reported in different parts of the world. Study by Sunitha and Reddy (2008) reported that cereal and legume crops grown in fluoride endemic areas of India had the following fluoride levels in their grains: wheat (4.6 mg/kg), corn (5.9 mg/kg), soybean (4.0 mg/kg). In India, Yadav *et al.* (2012) found fluoride levels in wheat crops- 3.24–14.30 mg/kg, which were cultivated in Dausa District (Rajasthan, India) where fluorinated water (5.6–14.7 mg/L) was used for irrigating those crops.

Recently, Meseret Dessalegne (2011) and Tesfaw Ashagrie (2011) determined fluoride levels in cereals and legume-based foods consumed in the Rift Valley area (Bidara Fuka and Dibibisa Kebeles, located in rural part Rift Valley), and Dura Woreda (East Shewa Zone of Oromiya) of Ethiopia; the levels of fluoride reported in bread prepared from cereal mixture (wheat and corn) and (corn and sorghum) is 3.54±0.004 mg/kg and 5.33±0.76 mg/kg, respectively while in bread prepared from corn only is 3.91±0.015 mg/kg and bread prepared from wheat only is 2.47±0.01 mg/kg (Tesfaw Ashagrie, 2011). Meseret Dessalegne (2011) determined the levels of fluoride in corn flour (12.2 mg/kg) and tef flour (15.1 mg/kg), which are food ingredients used for preparation of food and beverages consumed by the population living in Dugda Woreda.

The staple food ingredients can accumulate varied amounts of fluoride in their edible parts, which may thus affect human health. However, there is no systematic study conducted to determine the levels of fluoride in the staple cereals and legumes widely consumed by most people throughout the country. Therefore, this research focused to determine levels of fluoride in staple cereals (tef, wheat, corn and barley) and legumes (pea, lentil and chickpea) produced in selected areas (including the Rift Valley and non-Rift Valley regions) of Ethiopia.

MATERIALS AND METHODS

Instrumentation

Orion fluoride ion selective electrode was used for the determination of fluoride ion in cereals and legume 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.

Chemicals and reagents

All reagents used in this work were of analytical grade. Distilled-deionized water was used for the preparation of reagents and standard solutions. Sodium fluoride (99.0% NaF, BDH Chemicals Ltd., Poole, England) was used to prepare fluoride stock standard solution. Glacial acetic acid (99.5%, BDH Chemicals Ltd., Poole, England), sodium chloride (Scharlau, European Union), sodium citrate (Research-Lab Fine Chem Industries Mumbai, 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 hydrochloric acid (Scharlau, European Union) to adjust pH of the sample solution.

Sample collection

For this study, four types of cereals (tef, wheat, corn and barley) and three types of legume (pea, lentil and chickpea) from selected areas of Ethiopia were collected. The samples were collected in localities within the Ethiopian Rift Valley (Arsi Negele, Wonji, Ada) and from areas located outside the Rift Valley (Adola, Gondar, Bure, Desse). All samples were collected from local accessible markets in the area where they are cultivated in large amounts. Cereals were collected from Arsi Negele, Adola, Wonji and Gonder, and legumes from Gonder, Bure, Desse and Ada. Wonji, Arsi Negele and Ada are located in theRrift Valley areas. A total of 28 samples, *i.e.* 4 types of cereals from four sample areas and 3 types of legumes from four sample areas, were collected.

Sample preparation for fluoride analysis

The determination of fluoride in cereal and legume using fluoride ion selective electrode was done by slightly modifying the method of Malde *et al.* (1997. The cereals and legume grains were separately washed with tap water and then with distilled water. After washing, they were sun dried. Then, they were ground using a blender device in the laboratory and sieved with about 0.457 mm sieve. A 0.5 g powdered sample from each sample was accurately weighed and placed into 50 mL nickel crucibles. 5 mL of 8 M NaOH was added. Then, the samples and sodium hydroxide solutions were carefully mixed. The crucibles were placed on a hot plate for evaporation until the mixed NaOH and sample was solidified. The crucible was then placed in a muffle furnace and set at 200°C for 2 h, after which the temperature was increased to 525°C and kept there for 3 h in muffle furnace in order to fuse the sample in the crucible. The crucible was then placed in a hood and allowed to cool. 10 mL distilled water was added and placed on hot plate to facilitate the dissolution of the fusion cake. After 2 h, the sample solution was transferred to plastic volumetric flask, made up to volume with distilled water and filtered through a Whatman No. 40 filter paper. The pH of the filtrate was adjusted to pH 7.2–7.5 using concentrated HCl or 5 M NaOH. The sample solution was transferred into 50 mL volumetric flask and made up to the mark. Then, these digested samples were kept in the refrigerator until the analysis. All the analysis was made in triplicate. The fluoride content of cereals and legumes was then determined based on the calibration curve plotted using standard solutions.

Calibration of the fluoride electrode

Standard solution was prepared by dissolving 2.21 g of NaF in 1000 mL deionized water. Five standard solutions (0.5, 1.0, 5.0, 10.0 and 20.0 mg/L) were prepared by serial dilution from 1000 mg/L standard solution. The concentration of the samples was determined by constructing a calibration curve from these standards. At room temperature, the ISE was placed in a beaker containing 5 mL of standard solution, along with 5 mL of TISAB. Adding TISAB to standards and to samples breaks fluoride complexes of Fe and Al, providing a constant ionic strength (Buck and Cosofret, 1993). Instrument detection limit was 0.02 mg/L.

Validation of the procedure

In this study, the procedure was validated by analyzing fluoride concentration of sample prepared by alkali fusion and spiked with known amounts of fluoride. Validation of the method used was checked by performing recovery tests. The spiked samples were prepared by adding a known quantity of fluoride standard solution to cereal and legume sample by applying similar procedure to prepare the sample and analyzed for the levels of fluoride to calculate the recovery percent. Each cereal and legume sample was spiked with fluoride solution of which the fluoride content was equivalent to 25%, 50%, or 100% of the fluoride content of the original (unspiked) samples. Thus, percent recovery was obtained by comparing the results between the fluoride found and the fluoride added.

RESULTS AND DISCUSSION

Recovery results of fluoride determination

The percentage recovery of method was evaluated by calculating percentage recovery (% R). Recoveries for cereals and legumes were found in the range 93–102% and 93–102% (Tables 1 and 2). These recoveries were within the acceptable range (100±10%).

Table 1. Recovery test for cereal samples.

Type of grain	Percentage of F in unspiked sample (%)	Amount added mg/kg of F in unspiked sample	Concentration in unspiked 0.5 g sample (mg/kg)	Concentration in spiked 0.5 g sample (mg/kg)	Recovery (%)
Tef (Gonder)	25	1.06	3.84±0.28	4.91±0.06	101±6
	50	2.13	3.84±0.28	6.01±0.11	102±5
	100	4.23	3.84±0.28	7.96±0.3	93±7
Wheat (Wonji)	25	1.80	7.51±0.60	9.27±0.15	98±8
	50	3.60	7.51±0.60	11.01±0.19	97±6
	100	7.20	7.51±0.60	14.30±0.56	93±7
Corn (Arsi Negele)	25	1.13	4.20±0.14	5.26±0.08	93±7
	50	2.27	4.20±0.14	6.33±0.11	94±6
	100	4.53	4.20±0.14	8.39±0.08	93±2
Barley (Wonji)	25	1.03	4.23±0.34	5.25±0.07	99±5
	50	2.06	4.23±0.34	6.33±0.13	102±6
	100	4.11	4.23±0.34	8.13±0.13	96±4

Table 2. Recovery test for legume samples.

Type of grain	Percentage of F in unspiked sample (%)	Amount added mg/kg of F in unspiked sample	Concentration in unspiked 0.5 g sample (mg/kg)	Concentration in spiked 0.5 g sample (mg/kg)	Recovery (%)
Chickpea (Ada)	25	2.07	8.10±0.48	10.18±0.14	101±8
	50	4.13	8.10±0.48	12.08±0.23	96±6
	100	8.25	8.10±0.48	15.71±0.54	93±7
Pea (Gonder)	25	1.33	5.02±0.25	6.28±0.10	95±8
	50	2.67	5.02±0.25	7.55±0.07	94±3
	100	5.33	5.02±0.25	10.36±0.46	100±9
Lentil (Ada)	25	1.71	6.65±0.47	8.39±0.09	102±5
	50	3.42	6.65±0.47	9.93±0.20	96±6
	100	6.83	6.65±0.47	13.07±3	94±2

Levels of fluoride in cereal and legume grains

Fluoride levels found in the samples of this study are presented in Tables 3 and 4, with the highest in the pea from Ada and lowest in corn from Adola.

Table 3. Average levels (mean ± SD, n = 9, mg/kg dry weight) of fluoride in cereals grains (tef, wheat, corn and barley) from four sample sites.

Type of grains	Sample site	Fluoride level mean (mg/kg) ± SD
Tef	Arsi Negele*	8.00 ± 0.56
	Wonji*	10.98 ± 0.66
	Gonder	3.20 ± 0.56
	Adola	2.20 ± 0.18
Wheat	Arsi Negele*	10.30 ± 0.49
	Wonji*	7.20 ± 0.47
	Gonder	1.76 ± 0.34
	Adola	5.60 ± 0.36
Corn	Arsi Negele*	4.53 ± 0.28
	Wonji*	3.70 ± 0.22
	Gonder	2.54 ± 0.10
	Adola	0.98 ± 0.06
Barley	Arsi Negele*	6.07 ± 0.25
	Wonji*	4.11 ± 0.20
	Gonder	3.83 ± 0.23
	Adola	3.68 ± 0.09

* Areas located in the Rift Valley.

Table 4. Average levels (mean ± SD, n = 9, mg/kg dry weight) of fluoride in legume grains (pea, lentil and chickpea) from four sample sites.

Type of grains	Sample site	Fluoride level mean (mg/kg) ± SD
Chickpea	Ada*	8.25 ± 1.22
	Gonder	4.99 ± 0.43
	Bure	2.31 ± 0.16
	Dessie	1.52 ± 0.09
Pea	Ada*	11.07 ± 0.66
	Gonder	5.33 ± 0.31
	Bure	1.52 ± 0.06
	Dessie	2.65 ± 0.19
Lentil	Ada*	6.83 ± 0.31
	Gonder	6.32 ± 0.92
	Bure	2.63 ± 0.13
	Dessie	2.89 ± 0.06

* Areas located in the Rift Valley.

Distribution pattern of fluoride in cereal samples

Table 3 shows the levels of fluoride in cereal grains from Arsi Negele, Wonji, Gonder and Adola. Fluoride levels in cereals were found to range between (0.98 mg/kg) in corn from Adola and (10.98 mg/kg) in tef from Wonji. Fluoride levels in cereals from rift valley areas were higher than those from outside rift valley areas. Generally, cereal samples from Arsi Negele and Wonji were found to contain higher levels of fluoride, ranging from (3.70 mg/kg) in corn from Wonji to (10.98 mg/kg) in tef from Wonji. Fluoride levels in tef and wheat from Arsi Negele and Wonji were found to be higher, while similar cereals from other areas were found to be lower (Table 3). It was found that fluoride levels in cereals from Arsi Negele were found in the order of: wheat (10.30 mg/kg) > tef (8.00 mg/kg) > barley (6.07 mg/kg) > corn (4.53 mg/kg).

The fluoride levels of cereals from outside rift valley areas were between (0.98 mg/kg) in corn from Adola to (5.60 mg/kg) in wheat from Adola. In cereals from rift valley areas, fluoride levels ranged between (3.70 mg/kg) in corn from Wonji and (10.98 mg/kg) in tef from Wonji. The comparison of fluoride levels in the four types of cereals is shown in Figure 1.

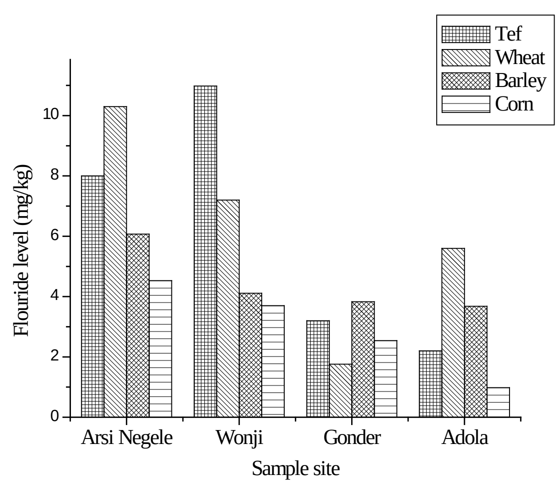

Figure 1. Comparison of levels of fluoride in cereal samples.

Distribution pattern of fluoride in legume samples

Table 4 shows the fluoride levels of legume grain samples from Ada, Bure, Gonder and Dessie. The comparison of fluoride levels among three legume samples is shown in Figure 2. The highest level of fluoride was found in the pea (11.07 mg/kg) from Ada, and the lowest level in chickpea (1.52 mg/kg) from Dessie and in pea (1.52 mg/kg) from Bure (Table 4). Fluoride content of legume samples from Ada were found to have higher than those from outside rift valley sample sites. When chickpea from four sample sites are compared, the highest value 8.25 mg/kg was found from Ada followed by 4.99 mg/kg from Gonder and 2.31 mg/kg from Bure.

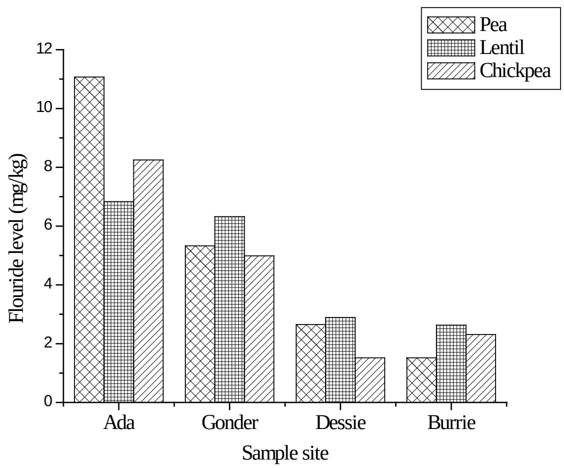

Figure 2. Comparison of levels of fluoride in legume samples.

Generally, there is significant difference ($p < 0.05$) in the fluoride levels between legumes from Ada and Bure or Dessie. Although lentil (6.32 mg/kg) from Gonder was from outside rift valley area, it was found to contain almost similar fluoride level as lentil (6.83 mg/kg) from Ada. Lentil (2.63 mg/kg) from Bure and lentil (2.89 mg/kg) from Dessie were almost similar in their values. Fluoride level in chickpea (5.33 mg/kg) was about two times that of the pea (2.65 mg/kg) from Dessie. Fluoride level in legumes from Ada ranged from 6.83 to 11.07 mg/kg, both the highest in pea and the lowest in lentil (Table 4).

Cereal and legume-based diets make large contribution to the diets of majority of the people in Ethiopia. A study conducted by Meseret Dessalegne (2011) showed that cereal food ingredients such as corn and tef had higher levels of fluoride. Generally in this study, legumes were found to contain lower levels of fluoride when compared to cereals: corn (0.98–4.53 mg/kg), barley (3.68–6.07 mg/kg), wheat (1.76–10.30 mg/kg), tef (2.20–10.98 mg/kg), lentil (2.63–6.83 mg/kg), chickpea (1.52–8.25 mg/kg) and pea (1.52–11.07 mg/kg) (Tables 3 and 4).

The fluoride levels in most of the cereals and legumes in this study (Table 3 and 4) were found to be above the ranges reported in other studies (Table 5). Fluoride levels in cereals might be increased from irrigation of crops with fluoridated water (Sunitha and Reddy, 2008; Gautam *et al.*, 2010). Both cereal and legume samples from rift valley areas were found to be higher in fluoride levels than those from outside rift valley areas. This is consistent with the work of Gautam *et al*. (2010), who determined the levels of fluoride in grains cultivated in fluoride endemic area of India, and they found that barley grains cultivated in those areas had fluoride levels of 3.84 mg/kg and 5.66 mg/kg, which were irrigated by water having 10.32 mg/L and 14.62 mg/L, respectively (Gautam *et al.*, 2010).

Fluoride may be added to soils from agricultural inputs such as fertilizers and pesticides. Crops subjected to fertilizers and pesticides that contain fluoride might have higher levels in their edible parts. Generally, cereal samples from outside rift valley area were lower in their fluoride values. However, cereal samples from outside rift valley sites (Adola and Gonder) were found to contain higher fluoride than that of rift valley sites (Arsi Negele and Wonji). This suggests that higher level fluoride in the cereals from Adola and Gonder might be due to fertilizers applied to the soil where crops were grown (Ahokas *et al.*, 1999; CDC, 2001; WHO, 2002; USDHS, 2003; Gautam *et a*l., 2010). Similarly, the fluoride level of legumes from Ada (fluoride endemic areas) was higher than other sites, which suggests that fluoride in the soil and water is likely to be available to the plant (WHO, 2002; Sunitha and Reddy, 2008; Australian Government, 2007).

Phosphetic fertilizers especially the superphosphates are the most important sources of fluoride in agricultural lands (Gautam *et al.*, 2010). Some cereals from outside rift valley areas were found to contain higher level of fluoride: wheat (5.60 mg/kg) from Adola, barley (3.83 mg/kg) from Gonder, barley (3.68) from Adola. This might be due to the higher agricultural fertilizer and pesticides in the soil where crops are cultivated (CDC, 2001; USDHS, 2003).

In this study, variations in the levels of fluoride in the same types of cereals but from different sample sites might be due to physical and chemical characteristics of the soil (WHO, 2002; Australian Government, 2007). The fluoride level in wheat (10.30 mg/kg) from Arsi Negele was about five times higher than in wheat (1.76 mg/kg) from Gonder. However, wheat from Adola was found to contain higher levels of fluoride, this may be due to content of fluoride in the soil where crops were grown or due to fertilizer application on the farmland (CDC, 2001; WHO, 2002; Gautam *et al.*, 2010; Tamiru Alemayehu, 2006; Australian Government, 2007).

Several factors can influence the availability of fluoride in soil, such as pH, content of clay, organic matter, Al and Fe oxides/hydroxides (USDHS, 2003; WHO, 2002). Fluoride from insoluble or sparingly soluble substances is less efficiently absorbed. Some cereals such as corn (4.53 mg/kg) from Arsi Negele and barley (4.11 mg/kg) and corn (3.70 mg/kg) from Wonji were found to contain lower levels of fluoride than other cereals of the same site.

In the soil containing higher levels of metals such as Ca, Mg and Al, fluoride ion can form a complex with those metals, thus reducing fluoride uptake by plant. Some cereals and legumes from rift valley areas were found to contain lower levels of fluoride. This might be due to the soil containing higher levels of metals such as Ca, Mg and Al form complex, thus reducing up-take of fluoride by crops from the soil (WHO, 2002; Australian Government, 2007).

High fluoride concentration is often found in food items rich in minerals and trace elements. Tef, for example, is a positive food item because of its high content of Fe, Zn, and Ca (Malde *et al.*, 1997). From all samples, tef from the Wonji was found to contain the highest level of fluoride (10.98 mg/kg). The higher fluoride levels in tef might be due to higher level metals such Fe, Zn and Ca in tef, but requires further research.

Comparison of fluoride levels of this study with literature values

The comparative studies of fluoride levels in the samples of this study and those reported in literature are presented in Table 5. Levels of fluoride in wheat (0.51–14.30 mg/kg) from India and corn (5.1 mg/kg) from Burundi (Gautam *et al.*, 2010; Sunitha and Reddy, 2008; Bhargava and Bhardwaj, 2009; Yadav *et al.*, 2012) have comparable values with results from this study. The fluoride level in corn (0.3 mg/kg) reported by Gautam *et al.* (2010) in Tanzania is lower than the level found in this study. The fluoride level in barley (3.84 mg/kg) reported by Gautam *et al.* (2010) is comparable to the level found in this study, except for barley (6.07 mg/kg) from Arsi Negele.

Processes such as milling of cereals to flour result in lowering of residue levels (WHO, 1997). Traditionally, cereal grains can be milled into flour ingredients, with or without washing. Fluoride levels in corn powder (12.2 mg/kg) and tef powder (15.1 mg/kg) reported by Meseret Dessalegne (2011) was higher than in this study (Table 5). The possible reasons of higher levels of

Table 5. Comparison of fluoride levels in cereals and legumes with previously reported values.

Grain type		Concentration in mg/kg dry wt	Origin	Reference
Cereals	Tef	2.20–10.98	Ethiopia	Present study
	Red tef (powder)	15.1	Ethiopia	(Meseret Dessalegne, 2011)
	Tef (red) flour	6.9	Ethiopia	(Malde *et al.*, 1997)
	Wheat	3.24–14.3	India	(Yadav *et al.*, 2012)
		4.6	India	(Sunitha and Reddy, 2008)
		0.51–5.98	India	(Bhargava and Bhardwaj, 2009)
		1.76–10.30	Ethiopia	Present study
		6.96	India	(Gautam *et al.*, 2010)
	Corn	5.1	Burundi	(Gautam *et al.*, 2010)
		5.9	India	(Sunitha and Reddy, 2008)
		0.3	Tanzania	(Gautam *et al.*, 2010)
	Corn (powder)	12.2	Ethiopia	(Meseret Dessalegne, 2011)
	Corn	0.98–4.53	Ethiopia	Present study
	Barley	3.84	India	(Gautam *et al.*, 2010)
		0.45–3.65	India	(Bhargava and Bhardwaj, 2009)
		3.68–6.07	Ethiopia	Present study
Legumes	Chickpea	1.52–8.25	Ethiopia	Present study
	Pea	8.34	India	(Gautam *et al.*, 2010)
		0.042–0.086	Brazil	(Gautam *et al.*, 2010)
	Pea (yellow)	1.6	Tanzania	(Malde *et al.*, 1997)
	Pea	1.52–11.07	Ethiopia	Present study
	Lentil	2.63–6.83	Ethiopia	Present study
	Beans (yellow)	1.1	Tanzania	(Malde *et al.*, 1997)
	Beans (red)	4.4		
	Beans	1.0	Burundi	
		0.015	India	(Sunitha and Reddy, 2008)
	Gram	2.5	India	(Sunitha and Reddy, 2008)

fluoride in tef and corn might be milling of unwashed cereal grains into flour. This might contribute additional fluoride levels in the cereals. In this study, samples were washed by distilled water and dried, before they were changed into powder samples.

Generally, most of fluoride levels of legumes in this study were found to contain higher values than those reported elsewhere except pea (1.52 mg/kg) from Bure. With the exception of pea (11.07 mg/kg) from Ada, fluoride levels in pea from this study were found to have lower values than pea (8.34 mg/kg) reported by Gautam *et al*. (2010) in India. Fluoride level in pea (1.52 mg/kg) from Gonder was found to contain the lowest value when compared to all legumes in this study. The content of fluoride in pea (0.042–0.086 mg/kg) reported by Casarin *et al*. (2007) in Brazil is much lower than values reported in this study (Table 5). Tables 4 and 5 show that the fluoride level in pea (11.07 mg/kg) from Ada was higher than that of pea (8.34 mg/kg) reported by Gautam *et al*. (2010) in India. The fluoride level of legumes in this study was found to be higher than values in yellow beans (1.1 mg/kg) and red beans (4.4 mg/kg) in Tanzania, reported by Malde *et al*. (1997).

In this study, the fluoride level in pea (1.52 mg/kg) from Bure was almost similar to the values reported in yellow pea (1.6 mg/kg) (Malde *et al*., 1997) from Tanzania. The fluoride level in pea from Ada was found to be 11.07 mg/kg, which is above the value (8.34 mg/kg) reported by Gautam *et al*. (2010) in India.

Analysis of variance

Variation in the mean levels of fluoride between the samples were tested whether it was from a random error or treatment (difference in fluoride contents of soil, water, atmosphere; variation in application of agrochemicals like fertilizers, pesticides, herbicides, or other variations in cultivation procedures). Analyses of variance (ANOVA) are widely used statistical methods to compare groups, whether the source for variation was from sampling or heterogeneity among the samples. One way ANOVA was used to compare whether there was difference in the mean levels of fluoride among samples. The statistical analysis in this study was made using SPSS 15.0 Window Evaluation Version program.

There was a significant difference ($p<0.05$) in the mean levels of fluoride among cereals and among legumes collected from four sites. This implies that variations in fluoride levels among sample sites is not due to random errors introduced during the sampling to analysis, but rather it is real. The factors that contribute to such variations are likely to be differences in the physical and chemical characteristics of fluoride content of the soil and variety of crops. Similarly, statistical analysis revealed that there were significant differences ($p<0.05$) observed among legume grain seeds in their fluoride levels.

CONCLUSION

This study showed that fluoride levels in cereals from Adola and Gonder (both are out of rift valley) were found to contain lower levels of fluoride than samples from Arsi Negele and Wonji (both from rift valley region). In general, the levels of fluoride in the cereals and legumes from the places away from the rift valley region of Ethiopia are comparable to the similar grains from other countries. The levels of fluoride in the cereals and legumes from the rift valley region of Ethiopia were found to be higher than similar grains from other countries. Analysis of variance showed that there was a significant difference at 95% confidence level in the mean fluoride levels in the samples.

ACKNOWLEDGMENTS

The authors express their gratitude to the Department of Chemistry, Addis Ababa University, Ethiopia, for providing the laboratory facilities. Seid Mustofa is thankful to Wolayta Sodo University, Ethiopia, for sponsoring his study.

REFERENCES

1. Abbebe Kifleyesus (2011). The construction of Ethiopian national cuisine. Available at http://www.ethnorema.it/pdf/numero2/Abbebe Kifleyesus - The Construction of Eth... Accessed in April, 2013.
2. Ahokas, J.T., Demos, L., Donohue, D.C., Killalea, S., McNeil, J. and Rix, C.J. (1999). Review of water fluoridation and fluoride intake from discretionary fluoride supplements Review for NHMRC, Centre for Applied and Nutritional Toxicology and Department of Applied Chemistry, RMIT-University, Melbourne, Australia.
3. Akibode, S. and Maredia, M. (2011). Global and regional trends in production, trade and consumption of food legume crops. Department of Agricultural, Food and Resource Economics Michigan State Univer-

sity. Report Submitted to SPIA March 27, 2011, pp. 1–50.

4. Australian Government (2007). A Systematic Review of the Efficacy and Safety of Fluoridation. Part A: Review of methodology and results, pp. 17–22.
5. Bhargava, D. and Bhardwaj, N. (2009). Study of fluoride contribution through water and food to human population in fluorosis endemic villages of North-Eastern Rajasthan. *Afr. J. Basic Appl. Sci.* **1**:55–58.
6. Buck, R.P. and Cosofret, V.V. (1993). Recommended procedures for calibration of ion-selective electrodes. *Pure Appl. Chem.* **65**:1849–1858.
7. Casarin, R.C.V., Fernandes, D.R.M., Lima-Arsati, Y.B.O. and Cury, J.A. (2007). Fluoride concentrations in typical Brazilian foods and in infant foods. *Rev. Saúde Públ.* **41**:1–7.
8. CDC (2001). Recommendations for using fluoride to prevent and control dental caries in the United States. The Morbidity and Mortality Weekly Report (MMWR) **50**:14, August 17, 2001, pp. 8–10.
9. Dagnew Tadesse, Assefa Desta, Aberra Geyid, Woldemariam Girma, Solomon Fisseha and Schmolla, O. (2010). Rapid assessment of drinking-water quality in the Federal Democratic Republic of Ethiopia: Country Report of the Pilot Project Implementation in 2004–2005, pp. 5–24.
10. EATA and MOA (2012). The Business Case for Investing in a Chickpea Flour Processing Plant in Ethiopia.
11. Ethiopian Export Promotion (2004). Ethiopia: Land of Crops Diversity. Ethiopian Pulses Profile, pp. 1–12.
12. Gautam, R., Bhardwaj, N. and Saini, Y. (2010). Fluoride accumulation by vegetables and crops grown in Nawa Tehsil of Nagaur District (Rajasthan, India). *J. Phytol.* **2**:80–85.
13. Hailu Tefera and Seyfu Ketema (2001). Production and importance of tef in Ethiopian agriculture. **In**: *Narrowing the Rift: Tef Research and Development. Proceedings of the International Workshop on Tef Genetics and Improvement,* Debre Zeit, Ethiopia. 16–19 October 2000, pp. 3–5, (Hailu Tefera, Getachew Belay and Mark Sorrells, eds). Ethiopian Agricultural Organization.
14. Janzen, E., Flaskerud, G. and Bartsch, E. (2006). Pulse Crop Market Guide. North Dakota State University (NDSU).
15. Mahapatra, K.M. (2007). Fluoride Menace in Orissa (India). RCDC Centre for Water for Life, Perfect Print and Graphics Pvt. Ltd., pp. 2–10.
16. Malde, M.K., Maage, A., Macha, E., Julshamn, K. and Bjorvatn, K. (1997). Fluoride content in selected food items from five areas in East Africa. *J. Food Comp. Anal.* **10**:233–245.
17. Melese Temesgen (2013). Nutritional status of Ethiopian weaning and complementary foods: A review. *Open Access Sci. Rep.* **2**:2–9.
18. Meseret Dessalegne (2011). Assessment of daily fluoride intake of adult Person living in selected households of Dugda Woreda, Ethiopia. MSc Thesis, Environmental Science Programme, Addis Ababa University, Ethiopia.
19. MoARD (2009). Animal and Plant Health Regulatory Directorate, Crop Variety Registration Issue No. 13, Addis Ababa, Ethiopia, June 2009, pp. 10–20.
20. Piccinin, D. (2007). More about Ethiopian Food: Tef. Ethnomed, University of Washington.
21. Sunitha, V. and Reddy, M.R. (2008). Fluoride in ground water and fluorosis. *e-J. Earth Sci. India* Popular Issue, October, 2008. Available at: www.earthscienceindia.info.
22. SCHER (2010). Critical review of any new evidence on the hazard profile, health effects, and human exposure to fluoride and the fluoridating agents of drinking water, the 7th plenary, May 2010, pp. 2–4.
23. Steenbergen, F.V., Tekle Haimanot Redda, and Sidelil Aschalew (2011). High fluoride, modest fluorosis: investigation in drinking water supply in Halaba (SNNPR, Ethiopia). *J. Water Res. Prot.* **3**:120–126.
24. Tamiru Alemayehu (2006). Groundwater Occurrence in Ethiopia, A report. Addis Ababa University, Ethiopia, 106 pp.
25. Tesfaw Ashagrie (2011). Total dietary fluoride intake and its observed health effect in young children: Case of Bidara Fuka and Dibibisa Kebeles in SNNPR and Oromiya Regions; Ethiopian Rift Valley. MSc Thesis, Environmental Science Programme, Addis Ababa University.
26. World Bank (2012). Africa Can Help Feed Africa: Removing Barriers to Regional Trade in Food Staples.
27. WHO (1996). Trace Elements in Human Nutrition and Health. World Health Organization (WHO), Geneva.
28. WHO (1997). Guidelines for predicting dietary intake of pesticide residues. World Health Organization (WHO), Geneva.
29. WHO (2002). Environmental Health Criteria 22 (EHC 227): Fluorides. World Health Organization (WHO), Geneva.
30. USDHS (2003). Public Health Service Agency for Toxic Substances and Disease Registry (2003). Toxicological Profile for Fluorides, Hydrogen Fluoride, and Fluorine, Agency for Toxic Substances and Disease Registry (ATSDR), Atlanta.
31. Yadav, R.K., Sharma, S., Bansal, M., Singh, A., Panday, V. and Maheshwari, R. (2012). Effects of fluoride accumulation on growth of vegetables and crops in Dausa District, Rajasthan, India. *Adv. Biores.* **3**:14–16.