

Levels of Selected Essential and Non-Essential Metals in Rice and the Underlying Soil in Major Rice-Growing Areas of Ethiopia

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Abstract

The concentrations of essential metals (Ca, Mg, Cr, Cu, Fe, Mn, Ni, and Zn) and non-essential metals (Cd and Pb) were determined in Ethiopian white rice cultivated in Fogera, Metema, and Pawe areas with their corresponding growing soils. The amounts of metals in rice and soil were determined by flame atomic absorption spectrometry, after digesting the powdered rice and soil samples with a mixture of HNO₃, HClO₄, and H₂O₂. The accuracy of the digestion procedure was assessed using the spiking method, where an acceptable percentage metal recovery was obtained in the range of 86.6%-106.7% and 87.15%-112.8% for rice and soil, respectively. The concentrations (mg/kg) of metals found in rice and soil, respectively, were in the ranges of Mg 414.28-560.89, 618.70-709.43; Fe 49.36-167.95, 11673.60-12916.67; Ca 45.21-57.71, 281.60-655.20; Mn 27.40-57.71, 168.60-416.60; Cu 12.01-61.19, 59.98-139.66; Zn 24.19-28.07, 26.59-55.85; Cr 17.65-27.45, 12.75-12.76; Ni 3.16-8.61, 2.07-11.87; Cd 1.08-1.55, 1.08-3.43 and Pb 1.08-1.55, 4.17-9.38. The pH of the studied soil farms was in the range of 5.30-5.95. Among the analyzed metals Cr showed the maximum transfer factor from soil to rice grain. Pearson correlation indicated a strong correlation for some elements between or within rice and soil samples. One way analysis of variance results indicated that for all metals in rice, the difference between means in the three sampling sites was insignificant ($p > 0.05$), while the significant difference among soil samples was observed only for Mg, Zn, Mn, and Cd. Except for Cr, Cd, and Pb in rice and Cu and Cd in metema soil, the determined concentrations of metals were below the world health organization allowed limit.

Keywords: White rice • Essential metal • Non-essential metal • Rice farming • Concentration

Introduction

Over half of the population of the world uses rice as a principal food crop [1]. It is the third most prevalent cereal crop next to maize and wheat in the world with an annual global production of approximately 600 million tons [2,3]. It is among the most important foods in the world supplying as much as half of the daily calories of the world population. In Asia alone; more than 2 billion people obtain 60-70 percent calories from rice and its products with a daily consumption per person of between 200 and 400 g. It is an important source of energy, vitamins, mineral elements, and rare amino acids for humans [4]. Rice is grouped under the family "Gramineae" and the genus "Oryza". There are about 25 species of rice in the genus "Oryza". The dominant rice species is *Oryza sativa*, which is believed to have originated somewhere in South East Asia. *Oryza sativa* has nearly completely displaced the local species *Oryza glaberrima*, which was once the dominant staple crop in Western Africa.

New types known as NERICA (new rice for Africa) were developed through crosses between African rice (*Oryza glaberrima*) and Asian rice (*Oryza sativa*) [5].

Rice is also Africa's fastest growing food source, and it plays a significant role in food security and self-sufficiency in an increasing number of low income food deficit nations. As a result, increasing rice output can help with hunger relief, poverty reduction, national food security, and economic growth [6]. Rice farming is a relatively new occurrence in Ethiopia, having been preceded by its use as a food crop. According to some reports, rice production in Ethiopia began in the early 1970's in the Fogera and Gambella plains. The largest rice-producing regions in Ethiopia are now Fogera, Gambella, Metema, and Pawe. The potential rain-fed rice-producing area in Ethiopia is estimated to be over thirty million hectares, based on GIS techniques and rice agro ecological requirements [7].

Both the acreage and productivity of Ethiopian rice cultivation have increased since 2006. Rice has become a crucial commodity for

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internal use as well as an export market for economic growth in various places of Ethiopia. It has tremendous potential as a country's emergency and food security crop. Additionally, the crop is valued for its diversity of applications, for example in the manufacture of local food and drinks, such as local bread (enjera), bread, couscous, tella, porridge, and katikalla, either alone or coupled with other crops like as teff, millet, wheat, barley, and maize. Even though rice is not a traditional staple food in Ethiopia, the knowledge of its mineral nutrition is of particular interest. Certain elements are vital for plant growth and animal and human health but if present in excessive concentrations they become toxic. Other elements are non-essential and toxic to human health even at a trace level. The elements necessary for living organisms can be classified either based on their importance or the amount needed by the body. Based on their importance, they can be essential (like K, Mg, Ca, Mn, Fe, Co, Cu, and Zn) and very important for growth and health, or they may be non-essential (like Cd and Pb). Nutritionally (based on the amount needed), minerals are grouped into Bulk (macro-minerals) and trace (micro-minerals). Essential trace elements include elements like Mn, Cr, Fe, Co, Cu, Zn, Se, Mo, F, and I, whereas essential macro elements include Ca, Mg, and K [8].

In addition to the amount of minerals in food, speciation is important when assessing the potential threat to human health [9]. So, analysis of mineral profile in rice grain with the underlying soil is therefore important on an essential, nutritional and toxicological level [10]. In addition to plant materials, the analysis of soil is an important investigative tool for identifying nutrient deficiency or excess. The identification of macro and micro constituents, as well as contaminants and the establishment of hazard levels are only possible if the soil composition is known [11]. It is composed of mineral constituents, organic matter (humus), living organisms, air, and water, and it regulates the natural cycles of these components [12].

Further, air, food, soil, and water pollution are widely expected and described in manufacturing and closely populated areas. In Ethiopia, there is not sufficient industry to cause substantial pollution. The major source of contamination comes from agricultural activities. Hence, an increasingly important aspect of food quality should be to control the levels of trace metals in food. Few papers have been reported on the mineral profile of Ethiopian rice. However, correlations of elemental concentrations of rice with its supporting soil are scarce in the literature. As this issue has not been much studied in Ethiopia the main objective of this study was to determine the amounts of essential (Ca, Mg, Cr, Cu, Fe, Mn, Ni, and Zn) and nonessential metals (Cd and Pb) in white rice and the corresponding growing soil from some major cultivation areas of Ethiopia by using flame atomic absorption spectrometry and to evaluate the Transfer Factor (TF) of metals from soil to rice grain.

Materials and Methods

Description of sampling sites

Fogera (situated at 11°46 to 11°59 latitude North and 37° 33 to 37°52 longitude east, altitude ranges from 1774 to 2410 m) located in South Gondar zone of Amhara region, Metema (latitude and longitude of 12°58'N 36°12'E with an altitude of 685 m) located in

West Gondar Zone of Amhara region and pawe (latitude: 11° 19' 60.00" N longitude: 36° 19' 60.00" E) located in Metekel zone of Benshangul Gumz regional state as shown in Figure 1.

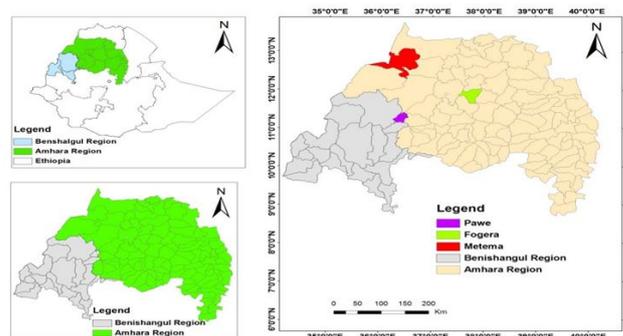


Figure 1. Map of the study sites.

Instruments

Flame atomic absorption spectrometer (Buck scientific model 210 VGP, East Norwalk, USA) and hollow cathode lamps with air acetylene flamer were used for the determination of the analyte metals in rice and soil samples. Hot plate (SH₃, STERILINE LTD, UK) to digest the dried and powdered rice and soil samples, pH meter, electric precision balance (Citizone, CTG 1200-1200, India) was used for weighing samples, blender (IKA-WERKE, Germany) was used for grinding and homogenizing rice samples and mortar and pestle was used for grinding dried soil samples. Conical flasks (100 mL) for digesting the sample on hot plate heating apparatus, fume cupboard (envair ltd, England) used as safety hood to suck the fume released during digestion, filtration funnels with Whatman filter paper (No.42) for filtration of sample solution after digestion and volumetric flasks (50 and 100 mL) were used during dilution and preservation of samples and preparation of metals standard solutions. Measuring cylinders, micropipettes (10-50 μ L, 100-1000 μ L) were used during measuring different quantities of volumes of sample solution, acid reagents and metal standard solutions. Sieve (0.5 and 2 mm, ASTM E 11, UK) to remove large debris, stones, and pebbles.

Reagents and chemicals

Reagents that were used in the analysis were all analytical grade. (69%-72%) HNO₃ (Blulux laboratories, Haryana, India), HClO₄ (70%) (Blulux fine chem, India) and H₂O₂ (30%) (Okhla industrial area, Newdelhi, India) were used for digestion of rice and soil samples. Lanthanum chloride hydrate (Blulux laboratories, Haryana, India) was used to minimize the precipitation of Ca and Mg ions in the form of phosphates and sulfates. Stock standard solutions (1000 mg/L) of the metals Ca, Mg, Fe, Zn, Cr, Cu (Blulux laboratories, Haryana, India), Ni, Mn, Cd and Pb (Loba Chemie, Mumbai, India) were used for preparation of calibration standards and in the spiking experiments.

Sample collection

Rice samples were gathered from Pawe, Metema, and Fogera from the farmers. Sampling sites were selected according to the areas in which rice is highly cultivated. About 4.5 kg of white rice samples were brought from farmers from each site separately. From a specific main site, three sub-sites were taken. About 1.5 kg of the sample from three farmers per each subsite (a total of nine

white rice samples from nine farmers in each site, 500 g from each farmer). Soil samples were gathered from the surface horizon (10-20 cm) depth of the sampling area of the rice. Soil sampling was done similar to sampling done on the rice. Then the collected sub-samples were packaged separately into clean polyethylene plastic bags, labeled, and brought to the university of Gondar chemistry department laboratory room for analysis.

Sample pretreatment

To avoid any dust particles on the grain, all raw rice samples were rinsed with distilled water before being dried to a constant weight. The dry rice sample was then pulverized in the lab with a blender and sieved to eliminate big particles using a 0.5 mm sieve. The soil samples obtained from the sampling locations were air dried for ten days to achieve a consistent weight, sieved using a 2 mm sieve to remove big debris and stones, and then mashed using a mortar and pestle to pass through a 0.5 mm sieve, homogenized, and ready for digestion.

Optimization of digestion procedure

Different rice and soil digestion conditions were optimized by using HNO₃, HClO₄, and H₂O₂ mixtures by changing parameters such as digestion time, digestion temperature, and acid mixture volume by hot plate to get a clear colorless sample solution suitable for FAAS analysis. These optimum conditions were selected based on the clarity of the digests, the amount of reagent used, the amount of time it took to digest the sample completely, and the minimum temperature used.

Digestion of rice samples

By using the optimized condition, 1 g of homogenized and dried rice powder samples were transferred into 100 ml digestion flasks. Then 7 ml of (4:2:1) ratio of HNO₃ (69%-72%), HClO₄ (70%), and H₂O₂ (30%) respectively were added. After that, the assortment was digested on a hotplate digestion apparatus by setting the temperature at 160°C for 1 hour until a clear solution was obtained. The digested solutions were permitted to cool for 30 minutes as it is closed by the watch glass and for 10 minutes after removing the watch glass. 2-5 ml of distilled water was added to the cooled solution, and gently swirled to reduce dissolution of the filter paper by digest residue. The cooled digested samples were filtered into a 50 mL standard volumetric flask with a whatman filter paper (42 mm) to remove any suspended or turbid matter. Subsequent rinsing of the digestion flask with 5 mL distilled water was followed until the volume reached the mark. 1% matrix modifier lanthanum chloride hydrate was added to each sample so lanthanum may bind the phosphate and released Ca and Mg in case large phosphate exists in the sample. Each sub-site sample was digested and determined separately and their mean value was taken. A reagent blank was also digested in parallel with the sample keeping all digestion parameters the same. The digested samples were kept in the refrigerator, and then the total amounts of metals in the sample solutions were analyzed by flame atomic absorption spectrometry.

Digestion of soil samples

Applying the optimized condition 1 g of dried, grounded, and homogenized soil samples were transferred to 100 ml digestion flasks. To this 9 ml of (4:3:2 ratio) HNO₃ (69%-72%), HClO₄ (70%), and H₂O₂ (30%) respectively were added and the mixture was digested by hot plate digestion apparatus with flasks covered by watch glass at 240°C for 2 h and 30 min until it forms clear and colorless solution. The rest of the steps were similar for both rice and soil sample digestion procedure.

Analysis of rice and soil samples for metal levels

For the analysis of the samples, calibration of the instrument with the known concentration of standards was done for each metal of interest. Immediately after calibration using the standard solutions, the sample solutions were aspirated into the AAS instrument and direct readings of the metal absorbance were recorded. The same analytical procedure was employed for the determination of elements in digested blank solutions.

Sample preparation for pH determination

A 5 g air-dried soil sample was weighed and transferred into a 100 ml beaker. 15 ml distilled water was added and the suspension was stirred vigorously for 20 min. The suspension was allowed to stand for about 30 min for the suspended clay to settle out the suspension. The pH meter was calibrated with pH buffer 4, 8, and 11. The electrode of the pH meter and thermometer were inserted into the partly settled suspension. The pH value and temperature were then read and recorded immediately [13].

Method performance and validation

Precision

Precision was expressed as the Relative Standard Deviation (RSD) of the three replicate results and the spiked samples were then subjected to the same digestion procedure as the actual sample. RSD of the samples were obtained as $\%RSD = (\text{standard deviation} / \text{mean value}) \times 100$. The precision determined at each concentration level should not exceed 15% of the RSD [14].

Instrumental Detection Limit (IDL)

It is the lowest signal that an instrument can reliably detect over background noise. IDL for each metal was determined from the examination of three replicates of calibration blank. $IDL = 3 \times S_{bl}$, where S_{bl} is the standard deviation of the calibration blank [15].

Limit of Detection (LOD)

It is the minimum concentration of analyte which can be detected but not certainly quantified with an acceptable uncertainty. LOD was calculated for each metal from the analysis of three replicates of method blanks which were digested in the same digestion procedure as the actual samples. $LOD = 3 \times s_{bl}$, where s_{bl} is the standard deviation of the method blank.

Limit of Quantification (LOQ)

The lowest concentration of an analyte in a sample can be quantitatively determined with acceptable uncertainty. LOQ

was obtained from triplicate analysis of three method blanks which were digested in the same digestion procedure as the actual samples. $LOQ=10 \times Sbl$, where Sbl is the standard deviation of the method blank.

Recovery

An identified amount of analyte was added to the natural test sample, and the amount of analyte recovered was calculated. It was

discovered by replication analysis of samples containing known levels of the analyte and digested in the same way as the genuine sample. $\% \text{ Recovery} = \frac{\text{Conc. in spiked sample} - \text{Conc. in un spiked sample}}{\text{actual spike conc.}} \times 100$. The acceptable ranges of percentage recovery are within 80%-120% for metal analysis [16]. The recovery data for rice and soil were given in Tables 1 and 2 below.

Element	Conc. in sample (mg/L)	Amount added (mg/L)	Amount recorded in spiked (mg/L)	% R for rice samples
Mg	5.81	3	8.755 ± 0.11	98.1 ± 3.7
Ca	0.925	1	1.84 ± 0.07	91.67 ± 7.2
Cr	0.353	1	1.235 ± 0.00	88.24 ± 0.0
Mn	0.37	0.35	0.72 ± 0.03	100.25 ± 7.9
Fe	0.54	1	0.72 ± 0.03	100.25 ± 7.9
Ni	0.02	0.065	0.085 ± 0.00	97.2 ± 0.0
Cu	0.113	0.1	0.210 ± 0.01	97.6 ± 13
Zn	0.524	0.45	0.932 ± 0.04	90.5 ± 9.3
Cd	0.017	0.3	0.304 ± 0.01	95.6 ± 2.7
Pb	0.188	0.34	0.483 ± 0.03	91.58 ± 8.27

Table 1. Recovery results (Mean ± SD, n=3) for rice samples.

Element	Conc. in sample (mg/L)	Amount added (mg/L)	Amount recorded in spiked (mg/L)	% R for soil samples
Mg	6.994	6	13.6 ± 0.10	109.55 ± 0.90
Ca	10.113	5	14.76 ± 0.40	92.2 ± 8.03
Cr	0.25	0.34	0.627 ± 0.03	110.98 ± 10.00
Mn	6.88	3	9.624 ± 0.06	91.44 ± 1.80
Fe	12.23	7.5	19.22 ± 0.82	93.24 ± 10.90
Ni	0.085	0.15	0.216 ± 0.00	87.15 ± 0.00
Cu	0.66	0.65	1.284 ± 0.02	95.32 ± 3.46
Zn	0.869	2	2.67 ± 0.01	89.8 ± 0.40
Cd	0.059	0.025	0.0874 ± 0.00	112.8 ± 0.00
Pb	0.188	0.36	0.517 ± 0.03	91.58 ± 8.27

Table 2. Recovery results (Mean ± SD, n=3) for soil samples.

Analysis of Variance (ANOVA)

One-way ANOVA was used to compare the means between all the three rice and soil samples and the calculations were made. The ANOVA results indicated that at a 95% confidence level for all metals in rice, the difference between means in three sampling sites was insignificant ($p > 0.05$). There exist statistically significant differences at a 95% confidence level in the mean concentration of Mg, Zn, Mn, and Cd between the three soil samples ($p < 0.05$). The source for this significant variation between sample means may be the difference in mineral levels of soil, pH of the soil, agrochemicals applied on agricultural land.

Results and Discussion

Optimum conditions for sample digestion

From the optimization procedures, the acid mixture of 4 mL of HNO_3 (69-70%), 2 mL of HClO_4 (70%), and 1 mL of H_2O_2 (30%) digestion time of 1 hour and digestion temperature of 160 °C was found the optimal condition for 1 g rice sample and the acid mixture of 4 mL of HNO_3 (69%-70%), 3 mL of HClO_4 (70%), and 2 mL of H_2O_2 (30%) digestion time of 2:30 hours and digestion temperature of 240°C was found the optimal condition for 1 g soil sample.

Analytical characteristics of the method

Accuracy and precision: The mean percentage recovery of metals in the spiked rice and soil samples was found to be in the range of 86.6%-106.7% and 87.15%-112.8% respectively, which is under the range of acceptable limit. This confirms that the method was accurate. The lower recovery for some elements may be attributed to the matrix analyte interaction which might be high and that is why their recovery values decreased. The %

RSD values obtained for rice and soil samples ranged from 0%-13.33% and 0%-11.7% respectively, which was under the required control limits of $\leq 15\%$. These results indicated that the proposed method was precise. The correlation coefficients of all the calibration curves were ≥ 0.998 and these correlation coefficients showed that there is a very good correlation (relationship) between concentration and absorbance (Table 3).

Detection limits

Element	IDL	MDL		LOQ	
		Rice	Soil	Rice	Soil
Ca	0.11	0.22	0.37	0.72	1.25
Mg	0.01	0.266	0.017	0.888	0.056
Cr	0.06	0.25	0.1	0.85	0.34
Mn	0.04	0.08	0.08	0.28	0.28
Fe	0.58	0.67	0.58	2.22	1.92
Ni	0.034	0.06	0.03	0.19	0.11
Cu	0.025	0.04	0.06	0.13	0.21
Zn	0.014	0.05	0.02	0.17	0.08
Cd	0.012	0.02	0.02	0.08	0.08
Pd	0.03	0.09	0.11	0.3	0.36

Table 3. IDL, LOQ and MDL (mg/L, n=3).

Concentration of metals in rice samples

All the metals mentioned above were found in all rice samples and their values are given in Table 4 below.

$$\text{Concentration (mg/kg)} = (\text{Concentration (mg/l)} \times V) / M.$$

Where,

V=Final volume (50 ml) of the solution, and

M=Initial weight (1 g) of the sample measured.

Rice samples				
Elements	Fogera	Metema	Pawe	WHO/FAO safe limit (2001)
Ca	45.21 ± 1.09	57.71 ± 1.73	48.33 ± 1.06	1000
Mg	560.89 ± 23.18	414.28 ± 25.60	546.22 ± 11.57	-
Cr	22.55 ± 1.49	17.65 ± 0.44	27.45 ± 1.90	2.3
Mn	40.19 ± 5.99	27.43 ± 5.28	29.82 ± 4.67	500
Fe	167.95 ± 60.07	71.79 ± 27.54	49.36 ± 24.20	425.5
Ni	8.61 ± 0.22	3.16 ± 0.89	3.16 ± 0.91	67
Cu	33.78 ± 6.82	41.67 ± 3.71	12.01 ± 1.95	73.3
Zn	28.07 ± 3.21	24.19 ± 4.70	24.37 ± 3.06	99.4
Cd	1.32 ± 0.81	1.08 ± 0.41	1.55 ± 0.71	0.2
Pd	1.32 ± 0.81	1.08 ± 0.41	1.55 ± 0.71	0.3

Table 4. Mean concentration (Mean ± SD, n=3, mg/kg) in rice samples.

As shown in Table 4, from the whole rice analyzed for metal level determination Mg was highest in concentration followed by Fe and Ca respectively, while Pb and Cd were lowest in the samples. This is because metals such as Mg, Fe, and Ca are mobile into plant tissue.

The maximum availability of Mg compared with other metals indicated that it is the major component of plant nutrients [17]. It is relatively more abundant in the parts of plants concerned with vital processes, such as seeds and leaves than in storage parts such as stems and roots.

Ca and Mg are highly translocated from old plant tissue to new plant tissue. The other possible cause for the higher amount of Mg is if the soil which has been used for cultivating the rice, is highly fertilized with manure and organic residues, it will have high in available Ca and Mg.

The accessibility of Fe to plants increases with the organic matter contents of the soil. Soils with low pH contain a high amount of available Fe to plants and the ions are readily transferred from the soil and accumulate in plants. The high concentration of Ca in rice samples may be due to a broad range of Ca-bearing minerals in soil and water which are usually abundant and can easily be absorbed by the rice plant. For normal fat and sugar metabolism, Cr (III) is a crucial ingredient. It is useful for managing diabetes and it is a cofactor with insulin. While Cr (VI) has long been understood to be poisonous and carcinogenic, Cr (III) and related derivatives are not considered to pose a health risk. The levels of Cr in rice samples were discovered to be 22.55, 17.65, and 27.45 mg/kg in sample sites of Fogera, Metema, and Pawe, respectively. Therefore, the study showed that these values were higher than the maximum permissible limit of 2.3 mg/kg, FAO/WHO, 2001. These may be due to the high transfer factor of Cr from soil to rice grain. So, the levels of Cr obtained in the present study can lead to a potential health hazard to consumers.

Nickel (Ni), plays some roles in body functions including enzyme functions. It may be advantageous to stimulate various systems in very little concentration, but its toxicity is more apparent at higher levels. Cd is a highly poisonous non-vital heavy metal and it does not have a function in the biological process of living things. Thus, even in low concentrations, Cd possibly will be harmful to living things. Cd poisoning in man could lead to anemia, renal injury, bone disorder, and cancer of the lungs. The amounts of Cd in rice samples were found to be 1.32, 1.08, and 1.55 mg/kg in sample sites of Fogera, Metema, and Pawe, respectively. The maximum FAO/WHO safe limit for Cd concentration in cereal samples is 0.2 mg/kg. The results obtained in this study in all three rice samples were above the recommended limit. So, the levels of Cd obtained in the present study indicated a potential health hazard to consumers. Pb poisonous is known to cause renal, musculoskeletal, immunological, ocular, neurological, reproductive, and developmental effects [18]. The concentrations of Pb in the studied samples were similar to Cd in all sample sites. The maximum FAO/WHO safe limit for Pb concentration

in cereal samples is 0.3 mg/kg. The results found in this study in all three rice samples were above the recommended limit. This may be due to the high transfer factor and availability of Pb for rice plant uptake. So, the concentrations of Pb found in this study indicated a toxic to consumers.

These variations in the amount of the above metals in rice grains by sample site may be resulted due to the availability of the minerals in the soluble and usable forms, the natural occurrence of these minerals in the areas, and the degree of contamination of the soil by these metals, the use of fertilizers of different chemical compositions like NPK fertilizer, pH of the agricultural soil, treatment of soil acidity, water used for irrigation and also the storage conditions of the products.

Distribution patterns of metals in the rice samples

Plants absorb whatever is in the soil medium, and as a result, metals are absorbed and bio-accumulated in the roots, stems, fruits, grains, and leaves of the plant, which can then be passed down the food chain to humans. Mineral uptake in plants is a function of mineral concentrations in soil, cation exchange capacity, soil pH, the ionic strength of the soil solution, the presence of competing ligands, the simultaneous presence of competing metals, organic matter content, types and varieties of plants and age of the plant. There was large a difference in the concentration of different metals within the rice sample and a slight variation in metals of the same type along with the geographical location. In general, the concentration pattern of metals in rice was decreased as.

Fogera: Mg>Fe>Ca>Mn>Cu>Zn>Cr>Ni>Cd=Pb

Metema: Mg>Fe>Ca>Cu>Mn>Zn>Cr>Ni>Cd=Pb

Pawe: Mg>Fe>Ca>Mn>Cr>Zn>Cu>Ni>Cd=Pb

Comparison with literature values

As the comparison in the Table 5 showed most of the values reported in the literature are lower than the present study. The variation of rice species, environmental condition, pH, and amount of minerals in the agricultural soil are the possible reasons for the difference.

Metals	Concentration	Origin
Ca	13.5 ± 8.6	Iran
	42.7 ± 12.8	Brazil
	50.42 ± 1.29	Ethiopia
Mg	182.675 ± 12.3	Turkey
	99.5 ± 0.7	Ethiopia
	507.13 ± 23.99	Ethiopia
Cr	3.8-13.8	India
	0.63 ± 0.075	Turkey
	22.55 ± 1.28	Ethiopia

Mn	5.884 ± 0.378	Turkey
	5.03-11.11	Pakistan
	32.48 ± 13.65	Ethiopia
Fe	19.6-38.8	India
	2.5 ± 1.7	Brazil
	96.37 ± 37.27	Ethiopia
Ni	9.8-14.6	India
	0.379 ± 0.03	Turkey
	3.24-13.28	Pakistan
	4.98 ± 0.67	Ethiopia
Cu	1.16-1.46	Pakistan
	45-63	India
	29-15 ± 4.16	Ethiopia
Zn	0.05-14.87	Nigeria
	11.56 ± 2.61	China
	14.1-35.1	Korea
	25.54 ± 3.66	Ethiopia
Cd	0.003-0.141	Korea
	0.045 ± 0.04	Iran
	0.01 ± 0.01	China
	1.32 ± 0.64	Ethiopia
Pd	0.04-0.197	Korea
	0.002 ± 0.003	China
	0.060 ± 0.034	China
	1.32 ± 0.64	Ethiopia

Table 5. Comparison of levels of metals in this study with values reported in the literature (mg/kg).

Concentration of metals in soil

The result revealed that all the analyzed metals accumulated in the soil at different concentrations as shown in Table 6. Therefore, the presence of these analyzed metals in the rice samples might be due to the high content of metals present in the soil. The differences

in the levels of metals in soil arise mainly due to the extent of pollution of the geosphere, modern large scale agricultural activities (use of agrochemicals), use of sewage sludge, and frequent use of heavy metal contaminated water in the agricultural fields gradually enriched the soil with heavy metals [19].

Soil Samples (mg/ kg)				
Elements	Fogera	Metema	Pawe	The maximum safe limit in soil (mg/kg)
Ca	439.79 ± 27.90	655.21 ± 30.45	281.67 ± 22.84	
Mg	709.43 ± 14.90	707.98 ± 24.20	618.70 ± 22.74	
Cr	12.75 ± 1.49	12.75 ± 8.49	12.76 ± 8.49	100
Mn	294.58 ± 8.72	416.59 ± 21.22	168.58 ± 15.36	2,000
Fe	12618.06 ± 98	12916.67 ± 94	11673.61 ± 51	50,000

Ni	9.69 ± 0.90	11.87 ± 0.99	2.07 ± 0.80	50
Cu	85.52 ± 3.01	139.66 ± 5.52	59.98 ± 3.45	100
Zn	55.85 ± 1.50	52.33 ± 1.55	26.59 ± 1.72	300
Cd	2.26 ± 0.12	3.43 ± 0.11	1.08 ± 0.08	3
Pb	9.38 ± 0.00	4.17 ± 0.51	6.77 ± 0.54	100

Table 6. Concentrations of metals (Mean ± SD, n=3, mg/kg) in soil samples.

As shown above, in Table 6, the highest amount of Fe among the metals analyzed from all the sample sites might be due to its abundance because iron is the fourth most plentiful element in the earth's crust and makes up about 5 percent by weight of the earth's crust and must be present in all soils. Iron is absorbed by the plant as Fe²⁺ and it can be transported to root surfaces as iron chelates. The most abundant element next to iron was Mg. The third abundant element next to Mg in the studied soil samples was Ca. The highest amount of Ca content in the soils may be due to the presence of a high amount of CaCO₃ value. It is available naturally in the soil in addition it is applied to agricultural soil to neutralize soil acidity. The pH of the studied soil farms was in the range of 5.30-5.95, which was acidic. A considerable quantity of Mn²⁺ in the water-soluble and exchangeable form can be found in soils with a pH of less than 5.5. With increasing soil pH, Mn²⁺ is converted into its higher oxides (Mn³⁺ and Mn⁴⁺) which are insoluble in water and therefore, unavailable to plants. The high Mn values in rice indicated the high availability of Mn for plant uptake in the rice farming area.

The amount of Cu in metema soil was higher than the maximum permissible limit. The high levels of Zn in these agricultural sites could probably be due to the extensive use of herbicides and fertilizers. The extensive use of pesticides and fertilizers may have contributed to increased Ni availability in the soil. The comparatively high levels of Pb might have resulted from the accumulation of lead through air pollution such as automobile exhaust fumes, from some pesticides, such as lead arsenates applied during cultivation and, leaching from road construction sites. Cd was the least abundant element in the soil samples studied. In Metema soil it was higher than the recommended maximum limit. The high level of Cd might be due to the use of cadmium containing phosphate fertilizers and contamination from cadmium containing dust.

In general, the outcomes of the heavy metals analyzed in the study areas showed that their concentration levels were below the standard guidelines for the maximum limit proposed for agricultural soil except in the case of cadmium and copper in metema soil. Even though most

of these heavy metal concentrations fell below the critical permissible concentration level, it seems that their persistence in the soils of the study site may lead to increased uptake of these heavy metals by plants.

Distribution patterns of metals in the soil samples

The variation is probably attributed to its natural mineral composition; the application of agrochemicals and the environmental condition is also the reason for the difference. The pattern of the overall concentration of metals in three soils samples was in the order:

Fogera: Fe>Mg>Ca>Mn>Cu>Zn>Cr>Ni>Pb>Cd

Metema: Fe>Mg>Ca>Mn>Cu>Zn>Cr>Ni>Pb>Cd

Pawe: Fe>Mg>Ca>Mn>Cu>Zn>Cr>Pb>Ni>Cd

The Concentrations of metals found in the soil samples of the study were comparable to the values in other literature.

The pH of soil samples

According to USDA natural resources conservation service soil pH ranges, Fogera and Metema soils were very moderately acid whereas Pawe soil was strongly acidic as shown in Table 7. The acidification of soil is caused by acidic precipitation in its true sense, that is H⁺ ions in precipitation, the deposition from the atmosphere of acidifying gases or particles such as Sulfur Dioxide (SO₂), Ammonia (NH₃), and Nitric and Hydrochloric acids (HNO₃, HCl), the application of acidifying fertilizers such as elemental Sulfur (S), Urea or Ammonium (NH₄⁺) salts, the growth of legumes and the mineralization of organic matter. Soil pH is one of the most influential parameters that control the conversion of immobile solid phase metal forms to more mobile and or bioavailable solution phase forms. The solubility of heavy metals is generally greater as pH decreases within the pH range of normal agricultural soils (approximately pH 5.0 to 7.0).

Soil sample site	pH	Acidity or alkalinity
Fogera	5.95	Moderately acid
Metema	5.9	Moderately acid
Pawe	5.3	Strongly acid

Table 7. The pH of the soil samples.

Soil-plant Transfer Factor (TF)

Metals can translocate from the soil to the edible regions of the food crop and can be determined by TF. It is the proportion of the

level of the element within the grain to the underlying soil and it became calculated for each rice sample to quantify the

effect of rice on the uptake of metals from the soils as shown in Table 8. The amounts of metals in the extracts of the soil and crops are calculated based on dry weight using the following simplified equation $T=Cr/Cs$ [20]. Cr and Cs represent metal concentrations in grain and the underlying soil respectively. If the

ratios >1 , the rice grains have accumulated elements, the ratios around 1 indicate that the rice grains are not influenced by the elements, and ratios <1 show that rice plants avoid (exclude) the elements from the uptake.

Sites			
Metal	Pawe	Fogera	Metema
Ca	0.17	0.1	0.09
Mg	0.88	0.79	0.59
Cr	2.15	1.76	1.38
Mn	0.18	0.14	0.07
Fe	0.01	0.01	0.01
Ni	1.53	0.89	0.27
Cu	0.2	0.4	0.44
Zn	0.92	0.5	0.46
Cd	1.44	0.58	0.32
Pd	0.23	0.44	1

Table 8. Soil to grain Transfer Factor (TF) of metals.

As shown above in Table 8 most of the TF results were below 1, indicating the bio-concentration factor was high in soil relative to rice grain. In other word; TF below 1 indicates high metal concentration in soil in relation to levels in rice grain and therefore low uptake of metals by rice plant. It denotes that the plant only absorbs the metal but does not accumulate it. Cr showed the maximum transfer factor value.

Correlation of metals between/within rice and soil

To check associations of the same metal in soil with rice grains as well as to check whether the ions of one kind present in the soil, either facilitate or interfere with the uptake of the other kind of ions, the pearson correlation coefficient was used. Soil pH is the dominant factor controlling rice metal uptake. This may be because the bioavailability of metals increased with decreasing soil pH. Agricultural practices that reduce soil acidification may help minimize the bioavailability of heavy metals in soil, thus resulting in reduced plant uptake and accumulation in

plants. Interactions among the coexisting elements occurring in the root surface and within the plants also affect their uptake and accumulation in plants. Metals interact with other metals in the uptake process by the plants because some metals have similar chemical properties. The concentration of metals in the soil measured by the total metal determination method cannot be used as a predictor of metal concentration in rice grain because the total metal contents of soil contain all exchangeable metals, carbonate bound metals, oxides bound metals, organic matter bound metals and residues, while metals which are bioavailable for plant uptakes are found in the exchangeable forms [21]. High correlation coefficient (near +1 or -1) means a good relationship between two variables, and its correlation around zero means no relationship between them at a significant level of 0.05%, it can be strongly correlated, if $r>0.7$ or $r < -0.7$, whereas r values between 0.5 and 0.7 (between -0.5 and -0.7) shows a moderate correlation between two deferent parameters (Table 9).

Correlation of metals within rice samples

	Ca	Mg	Cr	Mn	Fe	Ni	Cu	Zn	Cd	Pb	pH
Ca	1										
Mg	-0.9886	1									
Cr	-0.7209	0.817	1								
Mn	-0.8092	0.7115	0.1762	1							
Fe	-0.5537	0.4219	-0.178	0.9373	1						
Ni	-0.6931	0.5766	0	0.9844	0.984	1					
Cu	0.7651	-0.8533	-0.9978	-0.2408	0.1126	-0.0661	1				

Zn	-0.7221	0.6097	0.0411	0.9908	0.9759	0.9992	-0.107	1			
Cd	-0.7293	0.824	0.9999	0.1882	-0.1659	0.0123	-0.9986	0.0534	1		
Pb	0.2778	-0.4193	-0.866	0.3396	0.6462	0.5	0.8311	0.464	-0.8598	1	
pH	0.2148	-0.3594	-0.8317	0.4	0.6944	0.5552	0.7932	0.5205	-0.8248	0.9979	1

Table 9. Pearson Correlations of metals in rice.

Correlation of metals within soil samples

The negative correlation values indicate that as one variable increases in value, the second variable decreases in value. Some

elements have weak negative or positive correlations indicating that the presence or absence of one element affect to a lesser extent the other (Table 10).

	Ca	Mg	Cr	Mn	Fe	Ni	Cu	Zn	Cd	Pb
Ca	1									
Mg	0.8104	1								
Cr	0.9068	0.4879	1							
Mn	0.9952	0.8637	0.8613	1						
Fe	0.9288	0.9699	0.6859	0.9605	1					
Ni	0.9217	0.9743	0.6721	0.9551	0.9998	1				
Cu	0.9933	0.7372	0.9495	0.9773	0.8796	0.8705	1			
Zn	0.7503	0.9954	0.4015	0.8111	0.9419	0.948	0.6687	1		
Cd	0.9959	0.8602	0.8648	1	0.9585	0.953	0.9787	0.8071	1	
Pb	-0.5735	0.0151	-0.8655	-0.491	-0.229	-0.2108	-0.6645	0.1113	-0.4969	1

Table 10. Pearson correlation of metals within the soil.

Correlation of elements between rice and soil samples

The elements Ca and Cu exhibited a high positive correlation, Zn (moderate positive correlation), Fe, and Ni (weak negative correlation) between rice and soil samples as shown in Table 11. The high positive correlation indicated that the more accumulation of the elements in soil, the more the level of elements in the rice grain. Cr

does not show a correlation between samples ($r=0$). Cd exhibited a strong negative correlation (-0.999), and Mg, and Mn showed (a weak negative correlation) in rice and soil samples. These are the results to be expected, because the plants absorb the soluble metal ions and decrease their concentration in soils.

Metal	Ca	Mg	Cr	Mn	Fe	Ni	Cu	Zn	Cd	Pd
R	0.7792	-0.4065	0	-0.167	0.4532	0.3052	0.9905	0.5587	-0.9999	0.0011

Table 11. Pearson correlation coefficient for elements between rice and soil samples ($n=3$).

Conclusion

The concentrations of all analyzed elements were higher in soil compared to rice samples except Cr. Cr showed the maximum transfer factor value and the levels of some of the metals in the studied rice samples showed a positive correlation with the levels found in soil samples. The results obtained in the present study were compared with international guidelines for rice and soil. Except for Cr, Cd, and Pb in rice and Cu and Cd in metema soil, the levels of metals in the samples were below the WHO/FAO allowed limit. The pH of the studied soil farms was in the range of 5.30-5.95, which was acidic. The ANOVA results indicated that for all metals in rice, at the 95% confidence level, the difference between means in three sampling

sites was insignificant, and there exist statistically significant differences in the mean concentration of Mg, Zn, Mn, and Cd between the three soil samples.

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References

1. Belayneh, Tilahun, Zemene Atnafu, and Alle Madhusudhan. "Determinations of the level of essential and non-essential metals in rice and soil samples." *Int J Mod Chem Appl Sci* 2 (2015): 65-72.
2. Ummah, Humayatul, Dadang A Suriamihardja, Mary Selintung, and Abdul Wahid Wahab, et al. "Analysis of chemical composition of

- rice husk used as absorber plates sea water into clean water." *ARPN J Eng Appl Sci* 10 (2015): 6046-6050.
3. Emumejaye K. "Heavy and trace elements in some brands of rice consumed in delta state, Nigeria." *IOSR J Appl Phys* 6 (2014): 1-5.
 4. Tegegne, B., B. S. Chandravanshi, and F. Zewge. "Levels of selected metals in commercially available rice in Ethiopia." *Int Food Res J* 24 (2017): 711-719.
 5. Hagos, Afework, and Lemma Zemedu. "Determinants of improved rice varieties adoption in Fogera district of Ethiopia." *Sci Technol Arts J* 4 (2015): 221-228.
 6. Belayneh, Tamirat, and Jember Tekle. "Review on adoption, trend, potential, and constraints of rice production to livelihood in Ethiopia." *Int J Res Granthaalayah* 5 (2017): 644-658.
 7. Jorhem, Lars, Christina Astrand, Birgitta Sundstrom, Malcolm Baxter, Penny Stokes, John Lewis, and K. Petersson Grawe. "Elements in rice from the Swedish market: 1. Cadmium, lead, and arsenic (total and inorganic)." *Food Addit Contam Part A Chem Anal Control Expo Risk Assess* 25 (2008): 284-292.10.
 8. Gebrellbanos, Alem, Tesfahun Kebede, and Kassa Belay. "Quantitative determination of the level of selected heavy metals in the cows' milk from the dairy farm of the Haramaya University, Eastern Ethiopia." *Int J Chem Sci* 3 (2015): 240-248.
 9. Desta, Adane, and Almaz Ataklti. "Profile of essential and non-essential metals in soil and hat (*Catha Edulis* Forsk) leaves cultivated in Southern Region, Ethiopia." *Am J Phys Chem* 4 (2015): 58-64.
 10. Addis, Wodaje, and Alemayehu Abebaw. "Determination of heavy metal concentration in soils used for cultivation of *Allium sativum* L. (garlic) in East Gojjam Zone, Amhara Region, Ethiopia." *Cogent Chem* 3 (2017): 1419422.
 11. Tegegne, Wodaje Addis. "Assessment of some heavy metals concentration in selected cereals collected from local markets of Ambo City, Ethiopia." *J Cereals Oilseeds* 6 (2015): 8-13.
 12. Lokeshappa B, Kandarp Shivpuri, Vivek Tripathi, and Anil K Dikshit, et al. "Assessment of toxic metals in agricultural produce." *Food Public Health* 2 (2012): 24-29.
 13. Falahi E, R Hedaiati, and AR Ghiasvand. "Survey of iron, zinc, calcium, copper, lead, and cadmium in rice samples grown in Iran." *Food Addit Contam Part B Surveill* 3 (2010): 80-83.
 14. Aksu, Filiz, Duygu Tarhan, Sema Sandikci Altunatmaz, and Alev Meltem Ercan, et al. "Determination of some elements (Cr, Cu, Fe, Mg, Mn, Zn, Al, Cd, As, B, Ni, Pb) in rice and rice flour retailed in Turkey." *Fresenius Environ Bull* 30 (2021): 1311-1317.
 15. Tegegne, Bisratewongel, Alemayehu Belay, and Tsegaye Gashaw. "Nutritional potential and mineral profiling of selected rice variety available in Ethiopia." *Chem Int* 6 (2020): 21-29.
 16. Sharma MS Rakesh, and NS Raju. "Correlation of heavy metal contamination with soil properties of industrial areas of Mysore, Karnataka, India by cluster analysis." *Int Res J Environ Sci* 2 (2013): 22-27.
 17. Tariq, Farah, Xiukang Wang, Muhammad Hamzah Saleem, and Zafar Iqbal Khan, et al. "Risk assessment of heavy metals in basmati rice: Implications for public health." *Sustain* 13 (2021): 8513.
 18. Kong, Xiangyu, Ting Liu, Ziheng Yu, and Zhe Chen, et al. "Heavy metal bioaccumulation in rice from a high geological background area in Guizhou Province, China." *Int J Environ Res Public Health* 15 (2018): 2281.
 19. Kunhikrishnan, Anitha, Woo-Ri Go, Jin-Hee Park, and Kwon-Rae Kim, et al. "Heavy metal (loid) levels in paddy soils and brown rice in Korea." *Korean J Soil Sci Fert* 48 (2015): 515-521.
 20. Huang, Zhu, Xiao-Dong Pan, Ping-Gu Wu, and Jian-Long Han, et al. "Health risk assessment of heavy metals in rice to the population in Zhejiang, China." *PLoS one* 8 (2013):75007.
 21. Abebe, Adane, and Bhagwan Singh Chandravanshi. "Levels of essential and non-essential metals in the raw seeds and processed food (roasted seeds and bread) of maize/corn (*Zea mays* L.) cultivated in selected areas of Ethiopia." *Bull Chem Soc Ethiop* 31 (2017): 185-199.

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