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Assessment of selected minerals from avocado, mango and banana with their supporting soil samples cultivated in Yeki Worerda, Southwest Ethiopia

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ABSTRACT

This study focused on the quantitative determination of selected essential and heavy metals in avocado, banana and mango samples with their respective soil samples collected from Darimu, Yeki, Kura, Fide, Zinki, Bechi, Idris and Kubito kebeles.. The metals investigated were Ca, Cd, Cr, Cu, Ni, Pb and Zn. Acid digestion was used for sample preparation prior to injection. Finally, Flame Atomic Absorption Spectrometer (FAAS) was used to determine the concentration of metals. The result indicated that, Cd and Ni were not detected in all samples while Cr was not detected in avocado and mango fruit samples. Avocado fruit contains: 2.65% Ca, 1.98% Cu, 12.02% Pb and 8.17% Zn while its soil contains: 35.49% Ca, 62.08% Cr, 24.86% Cu, 20.91% Pb and 21.05% Zn. Banana fruit contains: 1.39% Ca, 2.75% Cr, 47.47% Cu, 14.18% Pb and 24.38% Zn while its soil contains: 39.85% Ca, 20.49% Cr, 11.86% Cu, 18.51% Pb and 17.31% Zn. Mango fruit contains: 3.09% Ca, 3.95% Cu, 12.98% Pb and 7.89% Zn while its soil contains: 17.53% Ca, 14.68% Cr, 9.60% Cu, 21.39% Pb and 21.19% Zn. Ca was highly up taken by mango while Cu, Pb and Zn were highly up taken by banana sample. On the other hand, Cr was up taken only by banana fruit sample.

Keywords: Major-essential metals, Minor-essential metals, Non-essential metals, Soil, Fruit

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INTRODUCTION

Back ground of the study

In Ethiopia 80% of the population is rural based and the rest is urban based. This 80% rural population follows the traditional agricultural ways of farming system, so out of this predominantly rural population is food insecure. Due to various factors such as the undeveloped farming style, insufficient and unseasonal rainfall and others, the Ethiopian farmers got insufficient crop from their farming. In relation to this the rural population uses different wild and cultivated plants as a source of food especially in the famine periods [1,2].

In Ethiopia different wild and cultivated plants have been used as a source of food, the mechanism chosen is a result of a progressive narrowing of options that leads from broad attempts to minimize risk in the long term through actions designed to limit damage caused by a crisis. For example, the Konso people in southern Ethiopia uses wild edible plants available in that area for three consecutive years (1996–1999) of drought seasons of crop failure. Different parts of these wild and cultivated plants have been used as a source of food such as leaf, steam, fruit and root. In all rural parts of the country consumption of these wild and cultivated food plants is a common phenomenon. These plants are important as food supplement and as means of survival during time of drought and famine. These wild and cultivated food plants are sources of vitamins, minerals, trace elements and protein. There by, these food plants contribute to improve local food security and people's income [3].

The southern part of Ethiopia especially the southwest is rich in biodiversity, in relation to this different wild and cultivated plants have been used as a source of food especially at the rular areas. Yeki woreda is among the most reach in biodiversity, different fruits are highly available. Avocado, mango and Banana are among the fruits which are widely consumed in the form of direct consumption and in the form of juice. Food chain contamination by heavy metals has become a burning issue in recent years because of their potential accumulation in biosystems through contaminated water, soil and air. Therefore Monitoring programs for residues and contaminants contribute to improving food safety, warn of actual and potential food scares and facilitate evaluation of possible health hazards by providing continuous information on levels of environmental pollution in this world. Generally, nutritional metals do occur naturally in fruits and vegetables as essential trace elements needed for good health, but they could be toxic when their concentrations exceed limits of safe exposure [4,5]. This study is aimed to analyze and determine the concentration of major, minor-essential and toxic metals in the fruits of avocado, mango and banana collected from Yeki woreda.

MATERIALS AND METHODS

MATERIALS AND METHODS

The study was conducted in Southern Nations Nationalities and Peoples (SNNP) Regional State in Sheka Zone, Yeki woreda. Yeki woreda is situated in the Southern part of Ethiopia and about 610 km South of Addis Ababa. Tepi town the city of the woreda has a latitude and longitude of 7°12′N 35°27′E with a mean elevation of 1,097 meters above sea level respectively. Yeki woreda has received an average annual rainfall ranging from 1801 to 2000 mm and an average annual temperature ranging from 21.5 to 27.14˚C [6,7].

Sample collection and preparation

Depending on the availability, fruit samples were collected from Darimu, Yeki, Kura, Fide, Zinki, Bechi, Idris and Kubito kebeles. For this purpose, 10 fruit of each of banana, mango and avocado samples were collected from specific site. The fruit samples were packed in to paper bags of card board container, labeled and transported to laboratory for analysis. After collecting and mixing, all the samples were thoroughly washed with tap water and detergent solution, then after rinsed with distilled water to remove surface contaminants and deionized water to remove any metal ion contamination. The fruit samples were peeled with a stainless steel knife and the pulp was mixed by a mixer, the resulting fruit juice was desiccated at 105˚C for 24 h and the dried sample was cracked on an analytical grinder and homogenized with blending device and stored in polyethylene bags until digestion. Soil samples were collected from the same sites of fruit samples. For this purpose, 3 kg of soil samples were collected from specific sites. Soil samples were collected from the soil at which the fruit plant grows. A sampling technique was designed for collecting soil samples. Accordingly a circle was made with radius of one meter at which the center of the circle is pointed at the base of the fruit plant. The samples were collected from all directions and then homogenized together to get about 3 kg of soil sample from each fruit plant. The soil samples were packaged into polyethylene plastic of card board container, labeled and transported to laboratory for analysis. After collecting and mixing, all the samples were dried in oven. Dried soil samples were gently homogenized followed by some form of pulverization. After the soil samples have been dried and sieved, representative subsamples of soil samples have been obtained for analysis. Because of the tendency of the bulk sample to fractionate by aggregate size, it was thoroughly homogenized and soil sample by some form of mixing before weighing or scooping the subsample. Finally, quantitative amount of the samples were subjected to acid digestion and the solution obtained from digestion was injected to flame atomic absorption spectrometer for determination of metals concentration level under investigation.

Sample Analysis

Physicochemical parameters analysis: The concentration of major and minor essential metals in soils and fruit samples depends on the different soil parameters. The pH and EC values (solid: deionized water=1:5) of soil and fruit samples were measured by a pH meter and an EC meter, respectively [8]. In addition to this, organic matter and moisture content were determined for both samples. Organic matter (content) was determined based on the mass loss principles in muffle furnace after ashing the fruit and soil samples at 500˚C for 4 hr.

$$\%OM = \frac{M_s}{M_b} X100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 1$$

Where,

M_s-Mass of the sample after ashing (g)

M_b-Mass of the sample before ashing (g)

OM=Organic Matter, %

On the other hand, moisture content was determined based on the mass loss after drying it in oven at 105°C for 24 hr.

$$\%M = \frac{M_s}{M_b} X100 \quad \text{..} \; 2$$

Where,

M_s-Mass of the sample after oven drying (g)

M_b-Mass of the sample before oven drying (g)

%M=Moisture content

Sample digestion: 0.5 g of fruit sample was digested by the mixture of HCl, HNO3 and H2O2 (3:1:2) at 90°C for 2 hrs. 0.5 g of soil samples were digested with the mixture of HNO_3 and $HClO_4$ (3:1 v/v) at 90°C for 2 hrs [9-11]. The samples were removed from heat source and cooled for 30 minutes. For both fruit and soil samples the blank sample was subjected to the same procedure. The solutions were filtered with whatmann filter paper and diluted to 50 ml. Finally, the solutions collected from digestion after filtration and dilution were analyzed for Ca, Cd, Cu, Cr, Ni, Pb and Zn levels by Flame Atomic Absorption Spectrometer (FAAS). All analysis was done in triplicate and the means were reported.

Transfer Factor (TF): The transfer factor is the ratio of the concentration of specific metals to the total metal concentration in the respective soil sample [12].

$$Transfer\ Factor(TF) = \frac{Metal\ concentration\ in\ fruit}{Metal\ concentration\ in\ soil}$$

RESULTS AND DISCUSSION

Physicochemical Parameters Analysis

Moisture (%): moisture content ranges from 38-57 for fruit and 66-71 for soil samples. In moisture content: mango>banana>avocado fruit samples while avocado soil>mango soil>banana soil samples.

Organic Matter (OM) (%): organic matter content indicated that high strength of the soil samples to retain more metals in to the soil particles. In retaining strength of metals for the soil samples: mango soil>banana soil>avocado soil samples. On the other hand the result confirmed that the higher metals concentration in the soil rather than in fruit samples which was in agreement with the metals concentration obtained after atomic absorption analysis.

Electrical Conductivity (EC): Electrical conductivities of the samples were ranges from 7.24-7.56 for fruit samples while that of soil samples was 0.33-0.51. In electrical conductivity values of the soil samples: mango, banana>avocado for fruit samples while banana soil>avocado soil>mango soil. Hence, banana and mango fruits as well as banana soil samples were found to be high in ionic concentration. Generally, electrical conductivities of soil samples were found to be higher than that of fruit samples.

pH: The pH values obtained ranges from 7.24-7.56 for fruit samples while it was 7.35-7.63 for soil samples. In pH: mango>banana>avocado from fruit samples while mango soil, banana soil>avocado soil samples. Hence, all most all samples were neutral and this shows that the fruit samples are suitable for consumption related to its pH. Because of the pH of the soil samples were above 5.6 all soil samples allow the transfer of metals from soil to plants [13]. On the other hand the pH conditions of the soil samples were suitable for plant growth (Table 1) [8].

Table 1. Determination of physicochemical parameters

Sample Code	Moisture (%)	OM (%)	EC (mS/cm)	pH
Avocado	38.50 ± 0.54	13.39 ± 1.23	0.06 ± 0.005	7.24 ± 0.01
Banana	52.40 ± 1.21	19.69 ± 0.56	0.08 ± 0.007	7.52 ± 0.09
Mango	57.74 ± 0.57	7.77 ± 0.54	0.08 ± 0.007	7.56 ± 0.05
Avocado soil	71.33 ± 2.05	79.72 ± 0.05	0.44 ± 0.02	7.35 ± 0.03
Banana soil	66.00 ± 0.83	80.63 ± 0.12	0.51 ± 0.003	7.63 ± 0.02
Mango soil	68.67 ± 0.47	85.00 ± 0.03	0.33 ± 0.03	7.63 ± 0.06

Determination of concentration of Metals

Calcium (Ca): Calcium is one of the essential minerals needed for building the bones and teeth of animals and humans. It plays a vital role in the functioning of nerves and muscles, and in the activations of a large number of enzymes. It is also needed for ensuring membrane permeability and immune defense. A deficiency of Ca can lead to disorders like rickets, osteoporosis, dentition, tachycardia, etc. Calcium is an important mineral required for bone formation and neurological function of the body. Recommended Dietary Allowance (RDA) for calcium is 800 mg for both adult and children (Table 2) [14].

Table 2. Determination of Calcium

Sample Code	Metal Mean Concentration (mg/kg) ± SD	SD	%RSD	TF
	Ca			
Avocado	91 ± 0.12	0.12	2.07	0.028
Banana	48 ± 0.01	0.01	2.25	0.015
Mango	106 ± 0.06	0.06	5.46	0.033
Avocado soil	1219 ± 0.26	0.26	2.15	-
Banana soil	1369 ± 0.08	0.08	0.57	-
Mango soil	602 ± 0.04	0.04	0.62	-

Calcium is one of the essential minerals needed for building the bones and teeth of animals and humans. It plays a vital role in the functioning of nerves and muscles, and in the activations of a large number of enzymes. It is also needed for ensuring membrane permeability and immune defense. A deficiency of Ca can lead to disorders like rickets, osteoporosis, dentition, tachycardia, etc. [14]. Calcium is an important mineral required for bone formation and neurological function of the body. Recommended Dietary Allowance (RDA) for calcium is 800 mg for both adult and children.

The result indicated that, Cu was detected in all samples. In Ca concentration: banana soil>avocado soil>mango soil>mango>avocado>banana. The Ca concentration was highest in banana soil while it was lowest in banana fruit sample. In transfer factor: mango>avocado>banana. Generally, the transfer factor of mango was found to be high for Ca while that of banana was found to be low. All fruit samples were below the RDA of Ca and hence, they were not rich enough in Ca.

Chromium (Cr): Chromium in contaminated soil is mainly present in two stable forms: trivalent, Cr (III) which is low toxic and hexavalent, Cr (VI) [15]. Cr (VI) is the more toxic form of chromium and is also more mobile. Cr(III) mobility is decreased by adsorption to clays and oxide minerals below pH 5 and low solubility above pH 5 due to the formation of Cr(OH)3 [16]. Cr (VI) is the product of oxidation of Cr (III) with atmospheric oxygen. The Cr (III) reactivity increase when the inert crystals and amorphous mineral are transformed in organic and hydroxide forms, smaller and more mobile. The equilibrium between the two chromium forms in soil depends upon soil physical and chemical characteristics. The oxidation process is only controlled by the reaction kinetics, due to Cr (III) species immobility and insolubility. Cr (III) tends to be strongly bound by soil humic acid polymers, and this affinity restricts the availability of Cr (III) to be oxidized and reduce the organic matter decomposition [15].

Chromium mobility depends on sorption characteristics of the soil, including clay content; iron oxide content and the amount of organic matter present. Cr (VI) is the more toxic form of chromium and is also more mobile. The equilibrium between the two chromium forms in soil depends upon soil physical and chemical characteristics (Table 3) [16].

Table 3. Determination of Chromium

Sample Code	Metal Mean Concentration (mg/kg) ± SD	SD	%RSD	TF
	Cr			
Avocado	ND	_	_	-
Banana	9 ± 0.004	0.004	4.9	0.028
Mango	ND	_	_	-
Avocado soil	203 ± 0.001	0.001	0.03	-
Banana soil	67 ± 0.01	0.01	1.68	-
Mango soil	48 ± 0.001	0.001	0.21	-

The result indicated that, Cr was detected in avocado soil, banana fruit, banana soil and mango soil samples. In Cr concentration level: avocado soil>mango soil>banana soil>banana fruit sample. Cr was not detected in avocado and mango fruit samples. Transfer factor was calculated only for banana fruit sample in which it was detected. The permissible limit of Cr in vegetable is 2.3 mg/kg and the obtained value for banana was above this limit and hence eating banana fruits may have the risk related to high concentration of Cr. But in case of avocado and mango they were free of Cr fate probability of high concentration.

Copper (Cu): Copper is an essential micronutrient required in the growth of both plants and animals. Copper is indeed essential, but in high doses it can cause anaemia, liver and kidney damage, and stomach and intestinal irritation. In fact, unlike some man-made materials, Cu is not magnified in the body or bio accumulated in the food chain. In the soil, Cu strongly complexes to the organic implying that only a small fraction of copper will be found in solution as ionic copper, Cu(II). The solubility of Cu is drastically increased at pH 5.5 [17]. The cupric ion, Cu^{2+}, and hydroxide complexes, $CuOH^+$ and $Cu(OH)_2$, are also commonly present. Copper forms strong solution complexes with humic acids. The affinity of Cu for humates increases as pH increases and ionic strength decreases. In anaerobic environments, when sulfur is present CuS will form. Solution and soil chemistry strongly influence the speciation of copper in groundwater systems. In aerobic, sufficiently alkaline systems, $CuCO_3$ is the dominant soluble copper species. Copper mobility is decreased by sorption to mineral surfaces. Cu^{2+} sorbs strongly to mineral surfaces over a wide range of pH values [16].

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Table 4. Determination of Copper

Sample Code	Metal Mean Concentration (mg/kg) ± SD	SD	%RSD	TF
	Cu			
Avocado	7 ± 0.01	0.01	10.62	0.043
Banana	42 ± 0.004	0.004	0.02	1.03
Mango	14 ± 0.0003	0.0003	0.21	0.085
Avocado soil	88 ± 0.0001	0.0001	0.008	-
Banana soil	169 ± 0.004	0.004	0.89	-
Mango soil	34 ± 0.0001	0.0001	0.04	-

Copper is an essential micronutrient required in the growth of both plants and animals [17]. Cu is constituent of several enzymes and is associated with the growth and formation of bones, absorption of iron during haemoglobin and myoglobin synthesis, and Fe utilization. Cu deficiency simultaneously leads to a decrease in Fe content in some tissues [14]. Copper is indeed essential, but in high doses it can cause anaemia, liver and kidney damage, and stomach and intestinal irritation. In fact, unlike some man-made materials, Cu is not magnified in the body or bioaccumulated in the food chain [17]. Copper is required in the body for enzyme production and biological electron transport. The recommended dietary allowance is 3 mg/day for adult and 2 mg/day for children.

The result indicated that, Cu was detected in all samples. In Cu concentration level: banana soil>avocado soil banana fruit>mango soil>mango fruit>avocado fruit sample. In transfer factor: banana>mango>avocado. Generally, the transfer factor of banana was found to be high for Cu while that of avocado was found to be low. The permissible limit of Cu in vegetable is 73.3 mg/kg and the concentration of Cu obtained in all fruit samples was below this limit and hence, all of these fruit samples were free from the fate related to high concentration of Cu.

Lead (Pb): Lead is a naturally occurring, bluish gray metal usually found as a mineral combined with other elements, such as sulphur (*i.e.* PbS, PbSO4), or oxygen ($PbCO_3$). The most stable forms of lead are Pb(II) and lead-hydroxy complexes. Lead (II) is the most common and reactive form of Pb, forming mononuclear and polynuclear oxides and hydroxides. Lead phosphates, lead carbonates and lead hydroxides insoluble compounds. Lead sulfide (PbS) is the most stable solid form within the soil matrix and forms under reducing conditions [17].

The primary industrial sources of lead contamination include metal smelting and processing, secondary metals production, lead battery manufacturing, pigment and chemical manufacturing, and lead-contaminated wastes. Lead released to groundwater, surface water and land is usually in the form of elemental lead, lead oxides and hydroxides, and lead-metal oxyanion complexes [16].

Inhalation and ingestion are the two routes of exposure, and the effects from both are the same. Pb accumulates in the body organs (*i.e.* brain), which may lead to poisoning (plumbism) or even death. The gastrointestinal tract, kidneys, and central nervous system are also affected by the presence of lead. Children exposed to lead are at risk for impaired development, lower IQ, shortened attention span, hyperactivity, and mental deterioration, with children under the age of six being at a more substantial risk. Adults usually experience decreased reaction time, loss of memory, nausea, insomnia, anorexia, and weakness of the joints when exposed to lead. Lead is not an essential element. It is well known to be toxic [17].

Most lead that is released to the environment is retained in the soil. The primary processes influencing the fate of lead in soil include adsorption, ion exchange, precipitation, and complexation with sorbed organic matter. These processes limit the amount of lead that can be transported into the surface water or groundwater. The relatively volatile organolead compound tetramethyl lead may form in anaerobic sediments as a result of alkyllation by microorganisms. The amount of dissolved lead in surface water and groundwater depends on pH and the concentration of dissolved salts and the types of mineral surfaces present. In surface water and ground-water systems, a significant fraction of lead is undissolved and occurs as precipitates ($PbCO_3$, Pb_2O, $Pb(OH)_2$, $PbSO_4$), sorbed ions or surface coatings on minerals or as suspended organic matter (Table 5) [16].

Table 5. Determination of Lead

Sample Code	Metal Mean Concentration (mg/kg) ± SD	SD	%RSD	TF
	Pb			
Avocado	50 ± 0.001	0.001	0.21	0.198
Banana	59 ± 0.0006	0.0006	0.09	0.233
Mango	54 ± 0.008	0.008	1.56	0.213
Avocado soil	87 ± 0.006	0.006	0.69	-
Banana soil	77 ± 0.002	0.002	0.22	-
Mango soil	89 ± 0.009	0.009	1.09	-

Pb may be commonly found in feldspars, micas and also in phosphate minerals, such as apatite and the plumb gummite group of minerals due to the isomorphous substitution of lead for K and Ba and sometimes Ca in the minerals. Lead addition to soils in agricultural herbicides/pesticides is significant [13].

Pb was detected in all samples. In Pb concentration level: mango soil>avocado soil>banana soil>banana fruit>mango fruit>avocado fruit samples. In transfer factor: banana>mango>avocado. Generally, the transfer factor of banana was found to be high for Pb while that of avocado was found to be low. The permissible limit of Pb in vegetables is 0.3 mg/kg and the value obtained for all of fruit samples under investigation were above this limit. On the other hand the concentration of Pb should not be tolerated because of health risk problem resulted from Pb even at low concentration level. Hence, eating of these fruits may not be safe because of high Pb concentration.

Zinc (Zn): Zinc occurs naturally in soil, but Zn concentrations are rising unnaturally, due to anthropogenic additions. Most Zn is added during industrial activities, such as mining, coal, and waste combustion and steel processing [17].

Zinc is one of the most mobile heavy metals in surface waters and groundwater because it is present as soluble compounds at neutral and acidic pH values. At higher pH values, zinc can form carbonate and hydroxide complexes which control zinc solubility. It readily precipitates under reducing conditions and in highly polluted systems when it is present at very high concentrations, and may coprecipitate with hydrous oxides of iron or manganese [16].

Zinc is essential for human growth and development. It is used in the synthesis of hormones, enzymes, proteins and other components that promote physical and mental growth. Zinc is required for immune system, tissue repair and wound healing, optimum insulin action, reproduction, vision, taste, and behavior. Amongst other disorders, Zn deficiency causes poor growth and retarded development. Zn is known for its catalytic function and structural role in enzyme reactions [14]. Zinc is an essential micronutrient associated with number of enzymes, especially those associated with synthesis of ribonucleic acid. Zinc deficiency limits the rate of recovery for protein energy in malnourished children. WHO recommended standard for zinc in adult and children are 15 mg/day and 10 mg/day respectively (Table 6) [18].

Table 6. Determination of Zinc

Sample Code	Metal Mean Concentration (mg/kg) ± SD	SD	%RSD	TF
	Zn			
Avocado	59 ± 0.007	0.007	1.3	0.137
Banana	125 ± 0.002	0.002	0.12	0.409
Mango	57 ± 0.006	0.006	0.98	0.133
Avocado soil	152 ± 0.001	0.001	0.05	-
Banana soil	176 ± 0.008	0.008	0.62	-
Mango soil	153 ± 0.004	0.004	0.28	-

Zn was detected in all samples. In Zn concentration: banana soil>mango soil>avocado soil>banana fruit>avocado fruit>mango fruit samples. In transfer factor: banana>avocado>mango. The permissible limit of Zn in vegetables is 9.4 mg/kg and the values obtained for all samples were above this limit. Hence, utilizing these fruits may be resulted in the fate health risk associated with high Zn concentration. On the other hand, the transfer factor of banana was found to be high for Zn while that of mango was found to be low.

CONCLUSION

The overall result indicated that, Cd and Ni were not detected in all samples. The concentration of minerals detected was higher in the soil samples when compared with their respective fruit samples. This shows that, the amount of minerals in the soil is higher and it is safe to produce these fruits on the area under investigation for the future time. Uptake of Ca mineral was found to be high for avocado and mango fruit samples. Uptake of Zn mineral was found to be high for banana fruit sample.

Mango fruit is rich in Ca mineral while banana fruit is rich in Cu, Pb and Zn. On the other hand, avocado fruit is the least rich in Ca, Cu, Pb and Zn. Ca was highly up taken by mango while Cu, Pb and Zn were highly up taken by banana sample. Cr was not detected in avocado and mango fruit samples.

In avocado soil: Ca, Pb and Zn were moderately mobile from soil to plants while Cu was less mobile. In banana soil: Ca, Cr, Cu, Pb and Zn were highly mobile from soil to plant. In mango soil: Pb was highly mobile, Zn was moderately mobile while Ca and Cu were less mobile from soil to plant. This transfer of metals from the soil to the plant is governed by soil properties like pH, electrical conductivity and soil organic matter.

The concentration of Ca was below RDA in all fruit samples hence, they were not rich enough in Ca mineral. On the other hand the concentration of Cu was below the permissible limit set for thus metal and hence, the fruit samples may not result in the problems related to high Cu concentration. The concentration of Cr, Pb and Zn obtained in avocado, banana and mango fruits under investigation were above permissible concentration of these metals in fruits. Therefore these fruits may affect the health of the society in relation to the health risk associated to high concentration of these metals.

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