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# Spectroscopic Determination of Some Major and Trace Elements in Tomato Cultivated in Selected Areas of Tigray: Northern Ethiopia

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# Abstract

The aim of this study was to determine the concentration of major and trace elements in tomato around selected areas of Tigray, Northern Ethiopia. The heavy metal analysis was done using Flame Atomic Absorption Spectroscopy (FAAS). The Mean concentration of metals (ppm) recorded for tomato found in the four sites: Shire Fe>Ca>Zn>Mn>K>Mg>Cu>Pb>Ni>Cd>Cr; Adwa Fe>Zn>Ca>Mn>Mg>K>Cu>Pb>Cr>Ni>Cd; Wukro Fe>Ca>Zn>K>Mn>Mg>Pb>Ni = Cu>Cr>Cd; and Alamata Fe>Ca>Zn>Mn>K>Mg>Cu>Ni>Cd>Cr; Pb. In all study areas; higher concentrations of Fe, Ca and Zn were recorded and concentration of Cd and Cr was found lower in the sites. The recorded metal concentration shows that except for Pb and Cd all values were found below the WHO permissible limits. The metal content of soil samples was also recorded in the four cites all values were under the permissible limits set for irrigation soil. The analyzed metal content in water samples was under WHO permissible limits used for irrigation purpose. Hence, Cd and Pb were above the maximum permissible limit by WHO. Pb and Cd concentrations might pose undesirable effect on the health of the community and they are toxic lesser naturally. So, this indicates the tomatoes grown in the areas need to get attention for the heavy metal risks.

Keywords: Atomic absorption • Spectroscopy • Metals • Tomato • Soil

# Introduction

In Ethiopia tomato is the most important and commonly grown vegetable crop, both during the rainy and dry seasons for its fruit by smallholder farmers, commercial state and private farms [1].

Tomato products are used as constituent in different conventional dishes because of the compatibility with other food ingredients, the concentration, availability of many nutrients in this products and their wide area consumption by human beings and animals. The consumption of tomato lowers the risk of cancer, heart disease, degenerative disease of the eye, osteoporosis and diabetes among other things. It also reduces the chances of asthma and lowers homocysteine levels [2].

Heavy metals can be the major contaminants for food and water bodies in our environment. Metals are non-biodegradable that can persist in the environment this can links to the tissue of vegetables. Vegetables can be contaminated with heavy metals during irrigation of water and different type of fertilizers, and industrial emission [3].

Different techniques can be used [4] for the determination of metals in tomato. Among these, Flame Atomic Absorption Spectroscopy (FAAS) the most frequently used since it is rapid and gives reproducible results for the determination of major, minor and trace elements. Therefore, the purpose of this study is to assess the levels of some major, minor and trace elements in tomato grown in different zones of Tigray, Ethiopia.

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# **Materials and Methods**

#### Sampling size and sampling method

A three stage random sampling procedure was used for the selection of the study area and sample respondents for the depth of the study. In the first stage, Tigray region has been selected purposively for the present study, because of the districts having more tomato cultivated area. The districts have more irrigation potential for cultivation of the tomato. Hence, these study areas was purposively selected for the present study. In the second stage, random sampling techniques were employed for the selection of study villages and sample respondents; out of seven predominant tomato cultivation zones, four zones were selected by using simple random sampling from different directions of the district. In the third stage, the list of tomato producers has been collected from Agricultural and Rural Development Office (ARDO) for the seven villages. Care was taken to cover all categories of the farmers. Altogether sixteen sample respondents were selected four zones. The sample respondents have been selected on probability proportionate to size.

#### Instruments

An Atomic absorption spectrometer (AA240FS, Varian, Australia) was used to analyze metallic elements. This AAS was equipped with standard hollow cathode lamps and an air-acetylene flame was used for determination of trace elements and heavy metals such as Ca, Ni, Mg, K, Fe, Cu, Cr, Ca, Pb,Mn, and Znin the tomato, soil and water samples. Other preliminary equipment like analytical balance (BA3100P, Sartorius, Australia Proprietary Ltd., Australia), Hot Plate (206HA Hot Plate, S.E.M. (SA) Proprietary. Ltd., South America), round bottom flasks, and refrigerator were used during the entire laboratory work.

### Collection and preparation of tomato samples

Mature and fresh tomato was collected randomly from different sites of the study area namely Site 1, Site 2, Site 3, and Site 4. The after the collected tomato samples was washes with distilled water to remove surface pollutants that adheres. Then sample was placed in a washed crucible and oven dried at 80 °C for 24h in an oven. Finally the dried tomato was grinded manually using mortal and pastel; then sieved using different size sieving mesh, homogenized in to fine powder and stored in polyethylene bags to avoid contamination.

## Collection and preparation of soil samples

About 1 kg of soil samples was collected from three sampling sites of each study area of the tomato samples grown around the riverside using stainless steel auger at 0-15 cm depths and stored in plastic bags. All the mixed soil samples were dried in an oven at 105 °C for 12 hrs until it weighs constant then the weighed was grinded and pass through 200 mesh (75µm) [5] sieve and stored and labeled for further analysis.

#### Collection and preparation of water samples

All water samples were collected from the river which is used for irrigation to grow the tomatousing polyethylene bottles, which were pre-washed with 10% nitric acid and de-ionized water [6]. Bottles were rinsed three times and immersed 20 cm below water surface for taking samples and brought to the lab. The samples were acidified using HNO<sub>3</sub> and stored in refrigerator at 4 °C for analysis.

#### Optimization of the digestion procedure

To prepare a clear colorless sample solution that is suitable for the analysis using FAAS different procedures for the digestion of soil and tomato samples were digested using  $HNO_3$ ,  $HCIO_4$  and  $H_2O_2$  mixtures by varying parameters such as the volume of the acid mixture, digestion time and digestion temperature. Examining the nature of the final digests obtained by varying the above parameters, the optimized procedure for each case was selected depending upon the clearness of the digest which was obtained with less digestion time, less reagent volume and simplicity the digestion procedure.

### **Treatment of water samples**

Triplicate of 50 mL water sample was transferred into three beakers (400 mL) and drops of concentrated HNO<sub>3</sub> were added to the beakers containing the water sample. Reagent blank was also prepared. Finally, the essential and non-essential metals were determined by FAAS [4].

### **Digestion of soil samples**

About 1.00 g of air-dried ground soil sample was transferred into 400 mL beaker and to this 6:1.5 ratios of Aqua- regia, and  $H_2O_2$  were added, respectively. The mixture was heated at 270 °C for 3 h. in fuming hood and then cooled to room temperature. Then, the mixture was transferred to a 250-mL volumetric flask filled with distilled water to the mark, let to settle for at least 15 h, filtered and analyzed the metals by FAAS [7].

The optimization of the acid mixture was found in the ratio of 6:1.5 of aquaregia and  $H_2O_2$  at the digestion time of 3 h. The optimum temperature was at 270 °C to digest 1.00 gram of soil and the optimal conditions are selected

based on clarity of the digested sample and minimal temperature consumption (Table 1).

## Digestion of tomato sample

1.00 g of each ground powder tomato sample was placed into 100 mL beaker and were digested using 8 ml of  $HNO_3$ ,  $HCIO_4$  mixture and,  $H_2O_2$  in the ratio of 5:2:1(v/v) at 270 °C for 3 hours in the hot plate. After cooling the solution was filtered using what No 42 filter paper and analysed using FAAS [7].

To prepare a clear colorless sample solution that is suitable for the analysis using FAAS, tomato digestion procedure were optimized using a mixture of different chemicals like  $HNO_3$ ,  $HCIO_4$  and  $H_2O_2$  by varying parameters such as volume of the acids digestion time and temperature. From the optimizationprocedures, the acid mixture of 5 ml of  $HNO_3$ , 2 ml of  $HCIO_4$ , and 1 ml of  $H_2O_2$  digestion time of 3 h. and digestion temperature of 270 °C was found in the optimalcondition for 1 g tomato sample. Thus, this optimal condition was used for the tomato sample (Table 2).

#### **Method validation**

The accuracy of the digestion procedure and efficiency of the FAAS instrument for tomato, soil and water were checked by a spiking sample with known concentration. Spiked samples were prepared by adding a small known quantity of metal standard solutions to three sub-samples of a water sample and soil sample by applying a similar digestion procedure and analyzing for the levels of metals and calculating the recovery percent [8]. Tomato samples were digested using HNO<sub>3</sub>, HClO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub> mixtures by varying parameters such as the volume of the acid mixture, digestion time and digestion temperature.

Soil recovery study was carried out using standard reference materials obtained from Ezana Mining PLC, Mekelle, Tigray, Ethiopia for some metals in the soil sample.

 $Percent \ Recovery = \frac{(Amount \ After \ Spiking - Amount \ Before \ Spiking)}{(Amount \ Added)} \times 100\%$ 

# **Results and Discussion**

### Calibration curve of standards

The calibration curve for each metal was drawn to determine the concentration of metal in the sample solutions. The working standard concentration vs. their corresponding absorbance value and correlation coefficients was plotted and summarized (Table 3). The quantity r is linear correlation The range of values for the correlation coefficient are as showed in table 3 which shows strong relationship.

Table 1. Optimization of digestion for soil sample.

No	Reagent (s)	Volume reagent (ml)	Tem (°C)	Digestion time(h)	Results
1	Aqua-regia :H <sub>2</sub> O <sub>2</sub>	06:01	300	03:00	Deep yellow
2	Aqua-regia:H <sub>2</sub> O <sub>2</sub>	05:02.5	290	03:00	Yellow with suspension
3	Aqua-regia:H <sub>2</sub> O <sub>2</sub>	05:01.5	270	03:00	Light yellow no suspension
4	Aqua-regia:H <sub>2</sub> O <sub>2</sub>	06:01.5	270	03:00	light yellow
5	Aqua-regia:H <sub>2</sub> O <sub>2</sub>	05:02	270	03:00	Deep yellow no suspension
6	Aqua-regia:H <sub>2</sub> O <sub>2</sub>	05:03	250	02:00	Clear light yellow with suspension

Trial No.	Reagent(s)	Volume (ml)	Temp (°C)	Digestion time(h)	Result
1	HNO3:HCIO4:H2O2	3:3:2	300	3:00	Deep yellow
2	HNO3:HCIO4:H2O2	4:3:2	290	3:00	Yellow
3	HNO3:HCIO4:H2O2	5:2:1	270	3:00	Clear and color less
4	HNO3:HCIO4:H2O2	5:2:1	300	2:30	Clear and yellow
5	HNO <sub>3</sub> :HClO <sub>4</sub> :H <sub>2</sub> O <sub>2</sub>	6:2:1	270	3:00	Clear and yellowish
6	HNO3:HCIO4:H2O2	5:2:1	250	2:00	Clear light yellow

#### **Recovery test**

The efficiency and accuracy of the optimized were evaluated by analyzing the spiked sample in tomato and water. Determination was carried out triplicate to ensure precision of measurements. Samples recovery ranges from 84.73% to 99.93% (Table 4) which is acceptable range [8].

The percentage recoveries of metals in the spiked samples ranged from 92.33% to 99.93% for tomato and 92% Cd, 96% Mn for water with Relative Standard Deviation below 10% which shows the efficiency of the method (Table 4).

## Levels of some major, minor and trace elements in the tomato samples

The levels of concentration of some essential and non-essential metals (Pb, Cr, Cu, Cd, Zn, Fe, Mn, Ni, Ca, Mg, and K) determined in the samples of tomato were reported for each metal as the mean of four measurements along with the corresponding total standard deviation for the given sample. The results obtained are summarized in (Table 5).

The results showed that the levels of Pb in all sites ranged between 0.52 (site 1) to 2.72 (site 2) ppm. But in all sites, the concentration of lead was above the WHO permissible limit. Similar results were communicated by Demirbas A [9]. The highest and the lowest Pb content was 2.72 and 0.52 ppm in the tomatoes, respectively. The highest concentration of Pb may be due to the human activities, vehicles, and fuel composition. Therefore, the consumption of this vegetable would result from health problems (Table 5).

The Cd content ranged from 0.96 to 1.36 ppm. As it is compared with WHO permissible limit Cd concentration found in tomato fruit was above the limit. Highest concentration of Cd was recorded in the four sites this might be as a result of application of pesticides. In relation to this study Cdis used in chemical industries in the manufacturing of pesticides and herbicides used in agriculture [10]. Therefore the tomato grown in all sites of the study needs more treatment (Table 5).

The highest level of K and Ca in the sample of tomato are probably due metallic elements are highly mobile in plant tissue and can be translocated from old plat tissue to new. The other reason can be due to the presence of fertilized soil with mature and organic residues (Table 5). Similar results were done by Demirbas A [9] where the highest and the lowest K contents are 18.27 and 10.16 ppm in the tomatoes, respectively. The highest calcium and magnesium contents were 85.02 and 11.67 ppm, respectively. The mineral matter composition of vegetables characterizes their nutrition conditions and indicates the yield potentials. Excessive amounts of K and Mg in tomato inhibits the Ca uptake and blossom-end rot, which is a result of Ca deficiency [11]. In the case of Ca deficiency in the growth substrate, the Ca and P levels in tomato plants have decreased [12].

The Cu concentration in tomato ranged between 2.64 to 8.38 ppm. The highest concentration of Cu was found inshire site. All the tomato samples were below standard (10 ppm) similar results were communicated in other studies [13] in which copper content differs according to the pollution source and soil type. Consumption of this vegetable will not result from Cu related health problems (Table 5). The concentration of Cr in the tomato sample ranges between 0.86 to 2.54 ppm which beyond the permissible limit of WHO result. This higher concentration of Cr can be due to industrial emissions specially leather industry which uses Cr which enters in to water bodies it is not also an essential for plant growth [14]. The concentration of Ni in tomato in all sites ranged between 2.36 to 4.46 ppm which is below the permissible limit of WHO. So sample tomatoes found in all sites are free out of nickel pollution [15]. Zn concentration ranged between 35.96 to 38.72 ppm and it is below the permissible limit of WHO results but these concentrations can be releases as a result of number of tracks and emission [16].

# Levels of some major, minor and trace elements in water samples

The levels of heavy metals recorded in water samples are summarized and except Cr (Shire), Cd (the Shire and Wukro), and Cu (Shire) all are below the WHO permissible limit for irrigation water. Therefore the concentration of

Table 3. Concentrations of working standard solutions and correlation coefficients of the calibration curves for the studied metals in tomato soil and water.

Metal Analyzed	Concentrations of the Working standard Solutions (mg/L)	Correlation Coefficient ( R)	Regression Equation
Pb	0,5,10, 25, 50	0.99689	y=0.00395x-0.00525
Cr	0,5, 10, 25,50	0.99613	y= 0.00438x+0.0314
Cu	0,5, 10,25,50	0.93744	y= 0.01795x-0.12038
Cd	0,5, 10 ,25, 50	0.92785	y= 0.01396x+0.14332
Zn	0,5, 10 ,25, 50	0.92149	y= 0.01288x+0.19406
Fe	0,5, 10 ,25, 50	0.98933	y= 0.01289x+0.17587
Mn	0,5, 10 ,25, 50	0.98843	y= 0.00936x+0.0852
Ni	0,5, 10 ,25, 50	1.0000	y= 0.00802x+0.0027
Са	0,5, 10,25, 50	0.91602	y=0.00253x+0.1831
Mg	0,5, 10 ,25, 50	0.9933	y= 0.01352x+0.0207
К	0,5, 10,25, 50	0.96286	y= 0.00023x+0.00093

Table 4. Recovery test results for metals determination in tomato and water samples using spiking method.

% Recovery							
Metal	Mean Tomato	Mean Soil	Mean Water	Spiking Concentration of Tomato	Spiking Concentration for Water	Tomato	Water
Pb	2.28	-	BDL	6.96	0.45	93.67 ± 0.03	-
Cr	0.86	89.34	BDL	5.48	1.99	92.33 ± 0.31	-
Cd	1.36	BDL	0.02	6.22	0.48	97.13 ± 0.05	92 ± 0.4
Cu	7.44	71.09	BDL	12.44	0.49	99.93 ± 0.17	-
Zn	38.72	89.01	BDL	43.42	0.51	94.00 ± 0.06	-
Fe	108.34	375.88	BDL	112.98	2.09	92.80 ± 0.26	-
Mn	17.91	102.85	0.02	22.58	1.94	93.33 ± 0.4	96 ± 0.2
Ni	2.62	22.52	BDL	7.43	0.57	96.13 ± 0.07	-

metals in water has been found with less contribution to the concentration of metals found in tomato fruit (Table 6). The levels of concentration of all the selected metals in water are below the detection limit.

### Levels of some major, minor and trace elements in the soil samples

Soil samples collected from different areas of Ttigray, Ethiopia were found to contain detectable metal contents of K, Mg, Ca, Fe Mn, Cr and Ni in the soil sample (Table 7). Plants can absorb and can accumulate in their roots other parts of it which can transferred in our food chains. Therefore the presence of these analyzed metals in the tomato samples might be due to the high content of metals present in the soil.

The concentration of metals found in soil from the given data except for Cd all the other metals have a high contribution to the metal concentration of tomato measured in the Shire. But Cd has the smallest contribution due to the small amount of concentration recorded in soil (Table 7).

Concentrations of metals found in soil at the site of Adwa was found highest except Pb and Cd and have high contribution for the increment of the concentration of metals in the tomato (Table 7). The Concentrations of metals found in the soil at the site of Wukro have high contribution for the concentration of tomato except Pb, Cd and Zn metals. But the concentrations of Pb, Cd and, Zn have less contribution, due to the smallest recorded concentration in soil. The concentration of metals found in soil around Alamata has a high contribution to the metal concentration of tomato, except Cd, due to the lowest concentration recorded (Table 7).

### **Transfer factor**

As the vegetables are the source of human consumption, the soil-toplant transfer quotient is the main source of human exposure. The transfer factor calculated in this study was based on the total metal content in tomato vegetables. Transfer factor expresses the bioavailability of a metal at a particular position on a species of plant. This depends on different factors such as the soil pH and the nature of the plant itself [17].

Transer Factor (TF) =  $\frac{(Concentration of metal in Tomato)}{C}$ (Concentration of metal in Soil)

The transfer factor of metals from soil and water to the tomato samples were summarized (Table 8).

Mn and Cu at the site of Adwa had greater soil plat transfer rate

able 5. The levels of concentration of metal	s (Mean ± SD) in the tomato sam	ples and it's WHO tolerance limit (N=9).
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Name of Metals	Shire	Adwa	Wukro	Alamata	Ewers, 1991
Pb	5.63 ± 0.21	1.45 ± 0.07	1.69 ± 0.09	2.27 ± 0.15	100
Cr	14.50 ± 0.72	21.00 ± 0.71	17.20 ± 0.36	89.34 ± 0.47	100
Cd	BDL	BDL	BDL	BDL	3
Cu	26.18 ± 0.31	$14.92 \pm 0.45$	13.11 ± 0.97	71.09 ± 0.45	100
Zn	94.13 ± 0.98	$58.40 \pm 0.85$	15.92 ± 0.21	89.01 ± 0.22	300
Fe	841.20 ± 0.51	512.98 ± 0.63	157.05 ± 0.53	375.88 ± 0.89	5000
Mn	128.19 ± 0.70	415.90 ± 0.57	223.58 ± 0.86	102.85 ± 0.65	2000
Ni	22.77 ± 0.59	$16.20 \pm 0.42$	10.56 ± 0.82	22.52 ± 0.65	50
Са	1210.70 ± 0.57	750.00 ± 0.00	510.83 ± 0.80	2229.97 ± 0.79	-
Mg	1059.18 ± 0.32	389.65 ± 0.49	2129.74 ± 0.76	1499.59 ± 0.47	-
К	291.47 ± 0.74	500.59 ± 0.86	247.35 ± 0.57	461.47 ± 0.46	-

Table 6. Levels of the concentration of metals in (ppm) of water samples around the selected Areas of Tigray.

No	Metals	Pb	Cr	Cd	Cu	Zn	Fe	Mn	Ni	Ca	Mg	к
1	Shire	*	0.05 ± 0.003	0.01 ± 0.001	0.01 ± 0.002	*	*	*	*	109.2 ± 0.5	13.65 ± 0.02	1.01 ± 0.3
2	Adwa	*	*	0.001 ± 0.0003	*	*	*	0.03 ±	*	105.1 ± 0.6	13.65 ± 0.4	1.1 ± 0.02
3	Wukro	*	*	0.02 ± 0.0006	*	*	*	0.02 ± 0.005	*	157.05 ± 0.03	13.65 ± 0.8	1.07 ± 0.03
4	Alamata	*	0.02 ± 0.003	0.01 ± 0.0004	*	*	*	*	0.02	111.08 ± 0.2	12.96 ± 0.6	0.98 ± 0.1
5	FAO	5	0.1	0.01	0.2	2	5	0.2	0.2			
*- indiantas	holow dotaction	limit										

Table 7. Levels of the concentration of metals in soil found at different sites.

Name of Metals	Shire	Adwa	Wukro	Alamata	Ewers, 1991
Pb	5.63 ± 0.21	1.45 ± 0.07	1.69 ± 0.09	2.27 ± 0.15	100
Cr	14.50 ± 0.72	21.00 ± 0.71	17.20 ± 0.36	89.34 ± 0.47	100
Cd	BDL	BDL	BDL	BDL	3
Cu	26.18 ± 0.31	14.92 ± 0.45	13.11 ± 0.97	71.09 ± 0.45	100
Zn	94.13 ± 0.98	58.40 ± 0.85	15.92 ± 0.21	89.01 ± 0.22	300
Fe	841.20 ± 0.51	512.98 ± 0.63	157.05 ± 0.53	375.88 ± 0.89	5000
Mn	128.19 ± 0.70	415.90 ± 0.57	223.58 ± 0.86	102.85 ± 0.65	2000
Ni	22.77 ± 0.59	16.20 ± 0.42	10.56 ± 0.82	22.52 ± 0.65	50
Ca	1210.70 ± 0.57	750.00 ± 0.00	510.83 ± 0.80	2229.97 ± 0.79	-
Mg	1059.18 ± 0.32	389.65 ± 0.49	2129.74 ± 0.76	1499.59 ± 0.47	-
K	291.47 ± 0.74	500.59 ± 0.86	247.35 ± 0.57	461.47 ± 0.46	-

#### Table 8. Soil to tomato transfer factor.

Transfer Factor From Soil to Tomato concentration in (ppm)							
Elements	Shire	Adwa	Wukro	Alamata			
Pb	0.40	0.12	1.61	0.23			
Cr	0.06	0.12	0.06	0.01			
Cu	0.05	0.56	0.20	0.11			
Cd	-	-	-	-			
Zn	0.41	0.0007	2.26	0.41			
Fe	0.001	0.21	0.006	0.003			
Mn	0.01	0.86	0.07	0.023			
Ni	0.11	0.003	0.25	0.02			
Са	0.07	0.08	0.11	0.03			
Mg	0.01	0.02	0.004	0.01			
К	0.03	0.02	0.07	0.03			

concentration to the tomato than from the rest sites (Table 8). The higher transfer quotient of the selected metals indicates stronger accumulation of the respective metal by the vegetables.

# Conclusion

Tomato is one of an economically important and widely grown vegetable and has the capability of absorb metal concentrations which can damage human beings this study aims to determine the level of metals in different selected areas of Tigray Ethiopia.

Samples were selected in diferrent four ares of Ttigray (Shire, Alamata, Adwa and Wukro) and the level of metal concentrations was determined using FAAS. The result indicates that the metal concentration (Mean ± SD, ppm, in dry weight) recorded for tomato found in Shire Fe>Ca>Zn>Mn>K>Mg>C u>Pb>Ni>Mn>Mg>K>Cu>Pb>Cr>Ni>Cd, Adwa Fe>Zn>Ca>Mn>Mg>K>Cu>Pb>Cr>Ni>CdWukro Fe>Ca>Zn>Kn>Mg>Cu>Ni>CdAwa Fe>Zn>Ca>Mn>K>Mg>Cu>Ni>Cd>Ca>Zn>Mn>K>Mg>Cu>Ni>Cd>Cr>Pb. Optimum recovery results ranged from 92.33% to 99.93%for tomato and 92% to 96% for water with RSD below 10% which shows high efficiency of the method used. In the studied sites all concentrations are below the level of WHO permissible limit except Pb and Cd.

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# **Conflict of Interest**

None.

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