Health Risk from Heavy Metal Contamination in Maize

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Abstract

Background: Maize (Zea mays) and its derived products are critical transgenic crops, widely consumed globally. In 2022/2023, maize consumption reached approximately 45,882 million bushels worldwide and 646 million bushels in Egypt, making it a significant dietary staple alongside wheat and rice. This study evaluates heavy metal concentrations in maize and its products, estimating the element concentration factor (mg/kg) and assessing potential health risks due to toxic heavy metals. Methods: Lead (Pb), cadmium (Cd), and chromium (Cr), along with non-toxic elements including iron (Fe), manganese (Mn), nickel (Ni), zinc (Zn), copper (Cu), cobalt (Co), and tin (Sn), were analyzed using inductively coupled plasma mass spectrometry (ICP-MS) following high-performance microwave digestion. The estimated provisional weekly intake (EPTWI) was compared to the accepted provisional weekly intake (APTWI) set by the FAO/WHO and JECFA. Results: The study revealed that Fe had the highest concentration (73.39 mg/kg) and As the lowest (0.03 mg/kg) in white corn samples. White corn flour showed the highest concentration of Fe (40.233 mg/kg) and the lowest of Pb (0.185 mg/kg). Yellow corn contained the highest Fe concentration (47.27 mg/kg) and the lowest Pb

Significance | Heavy metal contamination in maize threatens global food safety, potentially causing severe health issues and necessitating stringent regulatory measures to protect public health and agriculture.

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Editor Md Shamsuddin Sultan Khan, And accepted by the Editorial Board May 22, 2024 (received for review March 26, 2024 (0.915 mg/kg), while yellow corn flour had the highest Fe concentration (89.77 mg/kg) and the lowest Sb (0.03 mg/kg). The weekly intakes of essential elements (Cu, Fe, Mn, and Zn) and toxic elements (As, Cd, Sn, Sb, and Pb) were significantly below the recommended tolerable levels. Conclusion: The heavy metal concentrations in maize and its derived products were within safe limits, indicating minimal risk from dietary intake. This study underscores the importance of regular monitoring to ensure food safety and public health.

Keywords: Heavy Metals, Maize Contamination, Health Risk Assessment, Food Safety, Agricultural Pollution,

1.Introduction

Maize (Zea mays), widely known as zea, corn, or silk corn, is a cornerstone crop with profound nutritional and economic significance. Celebrated for its health benefits, maize is a rich source of B vitamins, including thiamin and niacin, and essential nutrients such as pantothenic acid, which plays a vital role in metabolizing carbohydrates, fats, and proteins into energy (Abdi et al., 2022; Afonne & Ifediba, 2020; Akhionbare et al., 2010; Alexander et al., 2009). Corn oil, derived from maize, is particularly beneficial for heart health, aiding in cholesterol reduction and preventing heart diseases. Additionally, maize contains abundant unsaturated fatty acids like omega-3, which help lower harmful cholesterol, reduce the risk of heart attacks and strokes, and prevent atherosclerosis. Maize is also a valuable source of dietary fiber, which supports digestion, and it provides iron and folic acid, which are essential for increasing red blood cell production. The antioxidants and phenolic compounds in maize contribute to the prevention of liver

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and colon cancers. Furthermore, maize contains vitamin A, betacarotene, and vitamin C, which are crucial for maintaining skin health and protecting against skin conditions. The inclusion of calcium, mineral salts, and folic acid further enhances its nutritional profile (Abdi et al., 2022; Afonne & Ifediba, 2020; Akhionbare et al., 2010; Alexander et al., 2009).

Despite its nutritional advantages, the cultivation of maize is increasingly threatened by heavy metal contamination, a severe environmental issue particularly prevalent in developing countries such as China (Ansari et al., 2022). Heavy metals like lead (Pb), zinc (Zn), copper (Cu), chrome (Cr), and nickel (Ni) pose significant health risks to consumers. Prolonged exposure to these metals can lead to serious health issues, including organ damage, cerebrovascular diseases, central nervous system abnormalities, and reproductive cancers (Awu, 2019; Breadley, 1992; British Herbal Medicine Association, 1983; Cendrowska-Pinkosz et al., 2022).

The global importance of maize is highlighted by its extensive cultivation and diverse uses. However, recent studies have revealed alarming levels of heavy metals in maize, raising substantial concerns about food safety. In 2022, significant levels of lead and cadmium were detected in all maize samples, indicating potential health risks for consumers (Deng et al., 2020). It is estimated that over 600 million people are affected annually by food contaminated with heavy metals (Diaconu et al., 2020).

Heavy metal contamination of soil is primarily attributed to human activities, including industrial emissions, the use of fertilizers and pesticides, sewage sludge application, and poor waste disposal practices. Mining operations are particularly culpable, releasing substantial amounts of metals into the soil and causing localized contamination near mining sites (Ghuniem et al., 2022; Ghuniem et al., 2019; Ghuniem et al., 2020). The persistence of heavy metals in the environment and their tendency to accumulate in soils exacerbate this problem (Gola et al., 2016).

Plants absorb heavy metals from contaminated soils through their root systems, leading to the accumulation of these metals in edible plant parts, thus posing a significant risk to human health (Hafeez et al., 2023; Hou et al., 2019). This bioaccumulation can result in physiological disruptions in plants, including stunted growth, chlorosis, and nutrient imbalances (Jamla et al., 2021; Joint FAO/WHO Expert Committee on Food Additives (JECFA), 2005). Additionally, heavy metal contamination can significantly reduce crop yields and diminish the nutritional quality of produce.

The contamination of crops by heavy metals also extends to livestock that consume these plants, leading to the accumulation of metals in their tissues. Consequently, humans who consume meat and dairy products from such animals are at risk of exposure to heavy metals, which can cause severe health problems, including kidney and liver damage, neurological disorders, developmental issues in children, and an increased risk of cancer (Lawan et al., 2023, Abdulilah et al. 2024, Hussein et al. 2024).

Given the serious implications of heavy metal contamination for food safety, regulatory authorities worldwide have established maximum allowable limits for heavy metals in food products. Exceeding these limits can result in product recalls and substantial economic losses for farmers and the food industry (Lawan et al., 2023; Li et al., 2022; Li et al., 2023). Thus, it is crucial to implement comprehensive strategies to mitigate the risks associated with heavy metal pollution in agriculture to safeguard public health and ensure the sustainability of food production systems.

Maize offers numerous nutritional benefits and plays a vital role in global agriculture, the threat posed by heavy metal contamination cannot be ignored. Efforts to monitor and reduce heavy metal levels in agricultural soils are essential to protect both crop yields and human health. Ensuring the safety of maize and other crops will require coordinated actions from governments, industry stakeholders, and the scientific community to develop and enforce stringent regulations and innovative agricultural practices.

The present study aimed to measure the levels of both toxic and non-toxic heavy metals in maize and its derived products. Additionally, the study sought to assess the potential health risks posed by the detected heavy metals and to provide a basis for policy recommendations to protect human health and enhance agricultural production.

2. Material and Methods

2.1. Sudy design

A total of 78 samples were randomly collected from local markets in Cairo, Giza, Ismailia, and Suez, Egypt, during 2022 and 2023. These samples included 33 yellow corn, 30 white corn, 10 yellow corn flour, and 5 white corn flour. The samples were analyzed for the presence of As, Cd, Cr, Co, Cu, Fe, Ni, Mn, Hg, Pb, Sb, Sn, and Zn using a Quadrupole Inductively Coupled - Mass Spectrometer (Q-ICP-MS). Samples were coded, stored, and examined in conditions similar to retail stores. Figure 1 shows the sampling locations based on a Google Earth satellite map.

2.2. Sample Preparation

All samples were digested using a microwave digestion system following the method described by Ghuniem et al. (2016). Approximately 0.5 g of each sample was measured and placed into a TFM vessel. Eight mL of Suprapur Nitric acid (HNO3) (65%) and 2 mL of H2O2 (30%) were added to each vessel. The vessels were sealed and placed in the microwave oven. A thermocouple probe was inserted into the reference vessel, and the microwave door was securely closed. The digestion protocol included two stages: initially, the power output was set to 1800 watts for 15 minutes until the temperature reached 200 °C; then, the power was maintained at 1800 W for another 15 minutes to keep the temperature at 200 °C. After digestion, the solution was transferred into a 50 mL Poly Methyl Pentene volumetric flask. 0.5 mL of internal standards containing Bi, Ge, In, 6Li, Sc, Tb, and Y were added, and the flask was filled with deionized water to the 50 mL mark. A similar procedure was followed for the blank reagent. Prepared samples were stored in polypropylene tubes until analysis using Q-ICP-MS.

2.3. Chemicals and Reagents

Certified reference metal stock standard solutions (1000 mg/L) for elements such as As, Pb, Cd, Sb, Hg, Cu, Zn, Fe, Cr, Sn, Co, Mn, and Ni, along with lutetium (Lu) as an internal standard, were supplied by Merck, Germany. Merck also provided 65% nitric acid (HNO3) (w/w) and Emsure[®] Hydrogen Peroxide (H2O2) (30%). Deionized water was produced using a water purification system with a Q-POD element coupled with a Merck Millipore, Q[®] Integral 5 (A10[®]), Model: ZRXQ005T0-USA. A 2% HNO3 solution was prepared by diluting 29 mL of 65% HNO3 (w/w) in 1 L of deionized water for standard processes.

2.4. Standards Preparation

Intermediate standard solutions of 100 mg/L, 10 mg/L, 1 mg/L, and 0.1 mg/L were prepared by diluting 10 mL of the metal stock standard solution (1000 mg/L) for each element (As, Pb, Cd, Sb, Hg, Cu, Zn, Fe, Cr, Sn, Co, Mn, and Ni) with 2% HNO3 to 100 mL. Nine working standard solutions ranging from 0.05 to 6 mg/L for Cu, Zn, Fe, Sn, Mn, Cr, Co, and Ni, and eight solutions ranging from 1-100 µg/L for Pb, Cd, As, Hg, and Sb were also prepared.

For calibration, intermediate standard solutions of 0.05 and 0.1 mg/L were obtained by diluting 5 and 10 mL of the 10 mg/L solution to 100 mL with 2% HNO3. Concentrations of 3, 4, 5, and 6 mg/L were obtained by diluting 2, 3, 4, 5, and 6 mL of the 100 mg/L solution to 100 mL with 2% HNO3. Similarly, Pb, Cd, As, Hg, and Sb standard solutions with concentrations of 1 and 3 μ g/L were prepared by diluting specified volumes of the standard solution to 100 mL with 2% HNO3, yielding final concentrations of 5, 10, 20, 40, 50, 80, and 100 μ g/L.

2.5. Q-ICP-MS Determination

The analysis was conducted using the Perkin Elmer Quadrupole Inductively Coupled-Mass Spectrometer (Q-ICP-MS) NexION 2000. Following a successful daily performance check, samples were analyzed as described by Ghuniem et al. (2016). Liquid samples were injected into the Q-ICP-MS from a sample tube using a peristaltic pump and a Meinhard nebulizer concentric glass (C 0.5). A complete description of Q-ICP-MS parameters is provided in Table 1.

3. Results

3.1 Metals Content in the Samples

Tables 2, 3, 4, and 5 present the mean, median, and concentration ranges for lead (Pb), cadmium (Cd), chromium (Cr), nickel (Ni), zinc (Zn), manganese (Mn), cobalt (Co), iron (Fe), arsenic (As), tin

(Sn), mercury (Hg), antimony (Sb), and copper (Cu) in white corn, yellow corn, white corn flour, and yellow corn flour samples. These tables highlight the variations in heavy metal concentrations among different corn and flour types.

3.2 Heavy Metals in White Corn

A total of 30 white corn samples were analyzed for heavy metals, targeting 13 elements. As shown in Table 2, every sample contained at least one element. The most frequently detected elements were Mn, Ni, Cu, Cr, Fe, Cd, and Zn, all present in 100% of the samples. Co was detected in 93.3% of the samples, while As, Sn, Sb, and Pb were found in 70% of the samples. The highest concentrations recorded were 31.74 mg/kg for Mn, 0.5 mg/kg for Co, 3.57 mg/kg for Ni, 3.12 mg/kg for Cu, 0.5 mg/kg for Cr, 73.39 mg/kg for Fe, 31.15 mg/kg for Zn, 0.03 mg/kg for As, 0.02 mg/kg for Cd, 0.5 mg/kg for Sb, and 0.11 mg/kg for Pb. No detectable levels of Hg were found in any samples. Compared to the maximum permissible levels (MPL) suggested by the Joint FAO/WHO Expert Committee on Food Additives (JECFA), none of these concentrations exceeded the safety limits, indicating that the white corn samples are safe for consumption.

3.3 Heavy Metals in Yellow Corn

In the analysis of 33 yellow corn samples for heavy metals, all samples showed contamination with at least one element, as indicated in Table 3. The most commonly found elements were Mn, Ni, Cu, Cr, Fe, Cd, and Zn, detected in 100% of samples, followed by Co in 60%. As, Sn, Sb, and Pb were detected in 3%, 3%, 9.1%, and 18.2% of the samples, respectively. The highest concentrations recorded were 9.11 mg/kg for Mn, 0.5 mg/kg for Co, 3.83 mg/kg for Ni, 25.78 mg/kg for Cu, 0.5 mg/kg for Cr, 47.27 mg/kg for Fe, 33.95 mg/kg for Zn, 0.02 mg/kg for As, 0.02 mg/kg for Cd, 0.5 mg/kg for Sn, 0.02 mg/kg for Sb, and 0.915 mg/kg for Pb. No Hg was detected in any of the samples. Except for one sample that exceeded the MPL for Pb (0.2 mg/kg), all other detected elements were within safe limits.

3.4 Heavy Metals in White Corn Flour

Five white corn flour samples were analyzed, with all samples showing contamination with at least one element (Table 4). The most frequently found elements were Mn, Ni, Cu, Fe, and Zn, detected in 100% of the samples. Cr, Co, and Pb were found in 80% of the samples, while As and Sb were detected in 20%. The highest concentrations recorded were 6.95 mg/kg for Mn, 0.5 mg/kg for Co, 0.5 mg/kg for Ni, 2.34 mg/kg for Cu, 0.5 mg/kg for Cr, 40.23 mg/kg for Fe, 25.75 mg/kg for Zn, 0.02 mg/kg for As, 0.02 mg/kg for Sb, and 0.185 mg/kg for Pb. Cd, Sn, and Hg were not detected in any samples. All detected concentrations were within the MPL, indicating the white corn flour samples are safe for consumption.

3.5 Heavy Metals in Yellow Corn Flour

Ten yellow corn flour samples were analyzed, with all samples showing contamination with at least one element (Table 5). The



Figure 1. The sampling location, based on a Google Earth satellite map.

Table.1 Instrumental Parameters of Q-ICP-MS

Parameters	Set Values	Minimum Values	Maximum Values
Nebulizer Gas Flow [NEB]	1.02	0	1.5
Plasma Gas Flow	18	10	20
Auxiliary Gas Flow	1.2	0.6	2
ICP RF Power	1600	500	1600
Analog Stage Voltage	-1800	-3000	0
Pulse Stage Voltage	1000	0	2500
Discriminator Threshold	11	0	1000
Deflector Voltage	-10.25	-100	20
Quadrupole Rod Offset [QRO]	-12	-26	26
Cell Entrance Voltage	-6	-60	20
Cell Exit Voltage	-39	-60	20
Cell Rod Offset [CRO]	-16	-40	10
Axial Field Voltage [AFT]	475	-498	498
revolutions per minute [RPq]	0.25	0.05	0.9
Integration time (ms)	2000	0.9	1.62 x 10 ¹⁰
Sweeps/ reading	20	1	1000
Replicates	3	1	1000

Table 2. Heavy metals' frequency occurrence, LOQ, and their Maximum Permissible Levels (mg/kg) in 30 white corn samples

Total conta sampl	minated es	Detected elements	Elements cor	centration (mg	/kg)		Frequ	iency	Frees	amples	Samp	bles Less LOQ	Samp Abov	les e LOQ	MPLs (mg/k	g)	The vio elemen	olated ts	The violated samples
			Minimum	Maximum	Mean	Median	No	%	No	%	No	%	No	%		No	%	No	%
No	%	Mn	1.78	31.74	11.04	6.05	30	100.0%	0	0.0%	0	0.0%	30	100.0%	-			0	0%
30	100%	Со	< 0.5	< 0.5	0.50	0.50	28	93.3%	2	6.7%	28	93.3%	0	0.0%	-				
		Ni	< 0.5	3.57	0.81	0.51	30	100.0%	0	0.0%	15	50.0%	15	50.0%	-				
		Cu	< 0.5	3.12	1.61	1.25	30	100.0%	0	0.0%	2	6.7%	28	93.3%	-				
		Cr	< 0.5	< 0.5	0.50	0.50	30	100.0%	0	0.0%	30	100.0%	0	0.0%	-				
		Fe	4.99	73.39	30.81	21.93	30	100.0%	0	0.0%	0	0.0%	30	100.0%	-				
		Zn	7.81	31.15	19.07	19.96	30	100.0%	0	0.0%	0	0.0%	30	100.0%	-				
		As	< 0.02	0.03	0.02	0.02	21	70.0%	9	30.0%	16	53.3%	5	16.7%	0.15	0	0.0%		
		Cd	< 0.02	< 0.02	0.02	0.02	30	100.0%	0	0.0%	30	100.0%	0	0.0%	0.1	0	0.0%		
		Sn	< 0.5	< 0.5	0.50	0.50	21	70.0%	9	30.0%	21	70.0%	0	0.0%	-				
		Hg	N.D	N.D	N.D	N.D	0	0.0%	30	100.0%	0	0.0%	0	0.0%	-				
		Sb	< 0.02	< 0.02	0.02	0.02	21	70.0%	9	30.0%	21	70.0%	0	0.0%	-				
		Pb	0.02	0.11	0.07	0.07	21	70.0%	9	30.0%	0	0.0%	21	70.0%	0.2	0	0.0%		

LOQ: Limit of quantifications N.D: Not detected MPL: Maximum permissible imit.

Table 3. Heavy metals' frequency occurrence, LOQ, and their Maximum Permissible Levels (mg/kg) in 33 yellow corn samples

Total contan sample	ninated es	Detected elements	Elements conc	entration (mg/kg	;)		Frequ	iency	Frees	samples	Samp than I	vles Less LOQ	Samp LOQ	les Above	MPLs (mg/k	g)	The vio elements	lated	The violated samples
			Minimum	Maximum	Mean	Median	No	%	No	%	No	%	N 0	%	No	%	No	%	
No	%	Mn	1.56	9.11	4.15	3.62	33	100.0%	0	0.0%	0	0.0%	33	100.0%	-			2	6.1%
33	100%	Со	< 0.5	< 0.5	0.500	0.500	20	60.6%	13	39.4%	20	60.6%	0	0.0%	-				
		Ni	0.70	3.83	2.27	2.27	33	100.0%	0	0.0%	31	93.9%	2	6.1%	-				
		Cu	0.64	25.78	2.41	1.39	33	100.0%	0	0.0%	0	0.0%	33	100.0%	-				
		Cr	< 0.5	< 0.5	0.500	0.500	33	100.0%	0	0.0%	33	100.0%	0	0.0%	-				
		Fe	11.08	47.27	20.33	17.48	33	100.0%	0	0.0%	0	0.0%	33	100.0%	-				
		Zn	9.85	33.95	17.88	16.44	33	100.0%	0	0.0%	0	0.0%	33	100.0%	-				
		As	< 0.02	< 0.02	0.020	0.020	1	3.0%	32	97.0%	1	3.0%	0	0.0%	0.15	0	0.0%		
		Cd	< 0.02	< 0.02	0.020	0.020	33	100.0%	0	0.0%	33	100.0%	0	0.0%	0.1	0	0.0%		
		Sn	< 0.5	< 0.5	0.500	0.500	1	3.0%	32	97.0%	1	3.0%	0	0.0%	-				
		Hg	N.D	N.D	N.D	N.D	0	0.0%	33	100.0%	0	0.0%	0	0.0%	-				
		Sb	< 0.02	< 0.02	0.020	0.020	3	9.1%	30	90.9%	3	9.1%	0	0.0%	-				
		Pb	0.022	0.915	0.226	0.078	6	18.2%	27	81.8%	0	0.0%	6	18.2%	0.2	2	6.1%		

LOQ: Limit of quantifications N.D: Not detected MPL: Maximum permissible imit.

Table 4. Heavy metals' frequency of occurrence, LOQ, and their Maximum Permissible Levels (mg/kg) in 5 white corn flour samples.

Total conta samp	minated les	Detected elements	Elements cor	ncentration (mg/	'kg)		Frequ	iency	Free	samples	Samp	oles Less LOQ	Samı Abov	oles re LOQ	MPLs (mg/kg)	The	vio nents	lated	The violat samp	ied les
			Minimum	Maximum	Mean	Median	No	%	No	%	No	%	No	%		No		%	No	%
No	%	Mn	4.063	6.946	5.760	5.980	5	100.0%	0	0.0%	0	0.0%	5	100.0%	-			0	0%	
5	100%	Co	< 0.5	< 0.5	0.500	0.500	4	80.0%	1	20.0%	4	80.0%	0	0.0%	-					
		Ni	< 0.5	< 0.5	0.500	0.500	5	100.0%	0	0.0%	5	100.0%	0	0.0%	-					
		Cu	0.921	2.339	1.705	1.945	5	100.0%	0	0.0%	0	0.0%	5	100.0%	-					
		Cr	< 0.5	< 0.5	0.500	0.500	4	80.0%	1	20.0%	4	80.0%	0	0.0%	-					
		Fe	13.733	40.233	27.194	26.675	5	100.0%	0	0.0%	0	0.0%	5	100.0%	-					
		Zn	11.349	25.750	16.691	16.634	5	100.0%	0	0.0%	0	0.0%	5	100.0%	-					
		As	< 0.02	< 0.02	0.020	0.020	1	20.0%	4	80.0%	1	20.0%	0	0.0%	0.15	0	0.0%			
		Cd	N.D	N.D	N.D	N.D	0	0.0%	5	100.0%	0	0.0%	0	0.0%	0.1	0	0.0%			
		Sn	N.D	N.D	N.D	N.D	0	0.0%	5	100.0%	0	0.0%	0	0.0%	-					
		Hg	N.D	N.D	N.D	N.D	0	0.0%	5	100.0%	0	0.0%	0	0.0%	-					
		Sb	< 0.02	< 0.02	0.020	0.020	1	20.0%	4	80.0%	1	20.0%	0	0.0%	-					
		РЬ	0.087	0.185	0.078	0.053	4	80.0%	1	20.0%	2	40.0%	2	40.0%	0.2	0	0.0%			

LOQ: Limit of quantifications N.D: Not detected MPL: Maximum permissible limit.

Table 6. Estimated daily intakes of mean concentration of elements in white corn samples (mg/kg b.w/day)

Tested	Mean concentrations	Consumption	EPTDI	EPTWI	EPTWI	APTWI	EPTWI As
elements	(mg/kg)	(g/day)	(mg/person/day)	(mg/person/week)	(mg/kg	(mg/kg	% of APTWI
					bw/week)	bw/week)	
Mn	11.037	135.9	1.5000	10.5000	0.1500	1.280	11.72%
Со	0.500	135.9	0.0680	0.4757	0.0068	-	-
Ni	0.811	135.9	0.1103	0.7718	0.0110	0.120	9.19%
Cu	1.611	135.9	0.2189	1.5326	0.0219	1.170	1.87%
Cr	0.500	135.9	0.0680	0.4757	0.0068	-	-
Fe	30.811	135.9	4.1873	29.3109	0.4187	5.250	7.98%
Zn	19.066	135.9	2.5910	18.1371	0.2591	4.650	5.57%
As	0.022	135.9	0.0030	0.0213	0.0003	0.015	2.03%
Cd	0.020	135.9	0.0027	0.0190	0.0003	0.007	3.88%
Sn	0.500	135.9	0.0680	0.4757	0.0068	14.000	0.05%
Sb	0.020	135.9	0.0027	0.0190	0.0003	0.042	0.65%
Pb	0.065	135.9	0.0088	0.0619	0.0009	0.025	3.53%

Total contar sample	ninated es	Detecte d element	Elements co	oncentration (m	ig/kg)		Freque	ncy	Free sa	mples	San Les: LO	nples s than Q	San Abo	nples ove LOQ	MPLs (mg/kg)	The viol elen	ated nents	The samp	violated les
		s	Minimu	Maximu	Mea	Media	No	%	No	%	Ν	%	Ν	%		Ν	%	Ν	%
			m	m	n	n					0		0			0		0	
No	%	Mn	1.15	7.20	5.07	6.23	10	100.0	0	0.0%	0	0.0%	1	100.0	-			1	10.0%
								%					0	%					
10	100%	Со	< 0.5	< 0.5	0.50 0	0.500	5	50.0%	5	50.0%	5	50.0%	0	0.0%	-				
		Ni	0.53	0.53	0.53	0.53	8	80.0%	2	20.0%	7	70.0%	1	10.0%	-				
		Cu	0.77	2.08	1.54	1.60	10	100.0 %	0	0.0%	0	0.0%	1 0	100.0 %	-				
		Cr	< 0.5	< 0.5	0.50 0	0.500	10	100.0 %	0	0.0%	1 0	100.0 %	0	0.0%	-				
		Fe	18.99	89.77	42.4 9	42.86	10	100.0 %	0	0.0%	0	0.0%	1 0	100.0 %	-				
		Zn	3.20	17.11	12.3 9	13.47	10	100.0 %	0	0.0%	0	0.0%	1 0	100.0 %	-				
		As	< 0.02	< 0.02	0.02 0	0.020	3	30.0%	7	70.0%	3	30.0%	0	0.0%	0.15	0	0.0%		
		Cd	N.D	N.D	N.D	N.D	0	0.0%	10	100.0 %	0	0.0%	0	0.0%	0.1	0	0.0%		
		Sn	N.D	N.D	N.D	N.D	0	0.0%	10	100.0 %	0	0.0%	0	0.0%	-				
		Hg	N.D	N.D	N.D	N.D	0	0.0%	10	100.0 %	0	0.0%	0	0.0%	-				
		Sb	0.03	0.03	0.03	0.03	1	10.0%	9	90.0%	0	0.0%	1	10.0%	-				
		РЬ	< 0.02	0.52	0.13	0.02	5	50.0%	5	50.0%	3	30.0%	2	20.0%	0.2	1	10.0 %		

Table 5: Heavy metals' frequency occurrence, LOQ, and their Maximum Permissible Levels (mg/kg) in 33 yellow corn flour samples.

LOQ: Limit of quantifications. N.D: Not detected. MPL: Maximum permissible limit.

 Table 7. Estimated daily intakes of maximum concentration of elements in white corn samples (mg/kg b.w/day).

Tested	Maximum	Consumption	EPTDI	EPTWI	EPTWI	APTWI	EPTWI As
elements	concentrations	(g/day)	(mg/person/day)	(mg/person/week)	(mg/kg	(mg/kg	% of APTWI
	(mg/kg)				bw/week)	bw/week)	
Mn	31.742	135.9	4.3138	30.1964	0.4314	1.280	33.70%
Со	0.500	135.9	0.0680	0.4757	0.0068	-	-
Ni	3.574	135.9	0.4858	3.4003	0.0486	0.120	40.48%
Cu	3.119	135.9	0.4239	2.9671	0.0424	1.170	3.62%
Cr	0.500	135.9	0.0680	0.4757	0.0068	-	-
Fe	73.390	135.9	9.9737	69.8161	0.9974	5.250	19.00%
Zn	31.155	135.9	4.2339	29.6376	0.4234	4.650	9.11%
As	0.034	135.9	0.0046	0.0321	0.0005	0.015	3.06%
Cd	0.020	135.9	0.0027	0.0190	0.0003	0.007	3.88%
Sn	0.500	135.9	0.0680	0.4757	0.0068	14.000	
Sb	0.020	135.9	0.0027	0.0190	0.0003	0.042	0.65%
Pb	0.113	135.9	0.0153	0.1074	0.0015	0.025	6.13%

bw: body weight.

 Table 8. Estimated daily intakes of mean concentration of elements in white corn flour samples (mg/kg b.w/day).

Tested	Mean concentrations	Consumption	EPTDI	EPTWI	EPTWI	APTWI	EPTWI As
elements	(mg/kg)	(g/day)	(mg/person/day)	(mg/person/week)	(mg/kg	(mg/kg	% of APTWI
					bw/week)	bw/week)	
Mn	5.760	51.30	0.2955	2.0684	0.0295	1.280	2.308%
Со	0.500	51.30	0.0257	0.1796	0.0026	-	-
Ni	0.500	51.30	0.0257	0.1796	0.0026	0.120	2.138%
Cu	1.705	51.30	0.0875	0.6123	0.0087	1.170	0.748%
Cr	0.500	51.30	0.0257	0.1796	0.0026	-	-
Fe	27.194	51.30	1.3951	9.7655	0.1395	5.250	2.657%
Zn	16.691	51.30	0.8562	5.9936	0.0856	4.650	1.841%
As	0.020	51.30	0.0010	0.0072	0.0001	0.015	0.684%
Sb	0.020	51.30	0.0010	0.0072	0.0001	0.042	0.244%
Pb	0.078	51.30	0.0040	0.0280	0.0004	0.025	1.601%

 Table 9. Estimated daily intakes of maximum concentration of elements in white corn flour samples (mg/kg b.w/day).

Tested	Maximum	Consumption	EPTDI	EPTWI	EPTWI	APTWI	EPTWI As
elements	concentrations	(g/day)	(mg/person/day)	(mg/person/week)	(mg/kg	(mg/kg	% of APTWI
	(mg/kg)				bw/week)	bw/week)	
Mn	6.946	51.30	0.3563	2.4944	0.0356	1.280	2.784%
Со	0.500	51.30	0.0257	0.1796	0.0026	-	-
Ni	0.500	51.30	0.0257	0.1796	0.0026	0.120	2.138%
Cu	2.339	51.30	0.1200	0.8400	0.0120	1.170	1.026%
Cr	0.500	51.30	0.0257	0.1796	0.0026	-	-
Fe	40.233	51.30	2.0639	14.4476	0.2064	5.250	3.931%
Zn	25.750	51.30	1.3210	9.2470	0.1321	4.650	2.841%
As	0.020	51.30	0.0010	0.0072	0.0001	0.015	0.684%
Sb	0.020	51.30	0.0010	0.0072	0.0001	0.042	0.244%
Pb	0.185	51.30	0.0095	0.0663	0.0009	0.025	3.787%

bw: body weight.

Table 10. Estimated daily intakes of mean concentration of elements in yellow corn samples (mg/kg b.w/day.

Tested	Mean concentrations	Consumption	EPTDI	EPTWI	EPTWI	APTWI	EPTWI As
elements	(mg/kg)	(g/day)	(mg/person/day)	(mg/person/week)	(mg/kg	(mg/kg	% of APTWI
					bw/week)	bw/week)	
Mn	4.151	135.9	0.5641	3.9489	0.0564	1.28	4.41%
Со	0.500	135.9	0.0680	0.4757	0.0068	-	-
Ni	2.265	135.9	0.3079	2.1550	0.0308	0.12	25.65%
Cu	2.413	135.9	0.3280	2.2958	0.0328	1.17	2.80%
Cr	0.500	135.9	0.0680	0.4757	0.0068	-	-
Fe	20.330	135.9	2.7629	19.3404	0.2763	5.25	5.26%
Zn	17.884	135.9	2.4305	17.0135	0.2430	4.65	5.23%
As	0.020	135.9	0.0027	0.0190	0.0003	0.015	1.81%
Cd	0.020	135.9	0.0027	0.0190	0.0003	0.007	3.88%
Sn	0.500	135.9	0.0680	0.4757	0.0068	14	0.05%
Sb	0.020	135.9	0.0027	0.0190	0.0003	0.042	0.65%
Pb	0.226	135.9	0.0307	0.2151	0.0031	0.025	12.29%

bw: body weight.

Table 11. Estimated daily intakes of maximum concentration of elements in yellow corn samples (mg/kg b.w/day).

Tested	Maximum	Consumption	EPTDI	EPTWI	EPTWI	APTWI	EPTWI As
elements	concentrations	(g/day)	(mg/person/day)	(mg/person/week)	(mg/kg	(mg/kg	% of APTWI
	(mg/kg)				bw/week)	bw/week)	
Mn	9.107	135.9	1.2376	8.6633	0.1238	1.28	9.67%
Со	0.500	135.9	0.0680	0.4757	0.0068	-	-
Ni	3.834	135.9	0.5210	3.6473	0.0521	0.12	43.42%
Cu	25.779	135.9	3.5034	24.5236	0.3503	1.17	29.94%
Cr	0.500	135.9	0.0680	0.4757	0.0068	-	-
Fe	47.267	135.9	6.4235	44.9648	0.6424	5.25	12.24%
Zn	33.950	135.9	4.6138	32.2965	0.4614	4.65	9.92%
As	0.020	135.9	0.0027	0.0190	0.0003	0.015	1.81%
Cd	0.020	135.9	0.0027	0.0190	0.0003	0.007	3.88%
Sn	0.500	135.9	0.0680	0.4757	0.0068	14	0.05%
Sb	0.020	135.9	0.0027	0.0190	0.0003	0.042	0.65%
Pb	0.915	135.9	0.1244	0.8709	0.0124	0.025	49.76%

Tested	Mean concentrations	Consumption	EPTDI	EPTWI	EPTWI	APTWI	EPTWI As
elements	(mg/kg)	(g/day)	(mg/person/day)	(mg/person/week)	(mg/kg	(mg/kg	% of APTWI
					bw/week)	bw/week)	
Mn	5.07	51.30	0.2601	1.8205	0.0260	1.28	2.03%
Со	0.50	51.30	0.0257	0.1796	0.0026	-	-
Ni	0.53	51.30	0.0274	0.1915	0.0027	0.12	2.28%
Cu	1.54	51.30	0.0788	0.5518	0.0079	1.17	0.67%
Cr	0.50	51.30	0.0257	0.1796	0.0026	-	-
Fe	42.49	51.30	2.1800	15.2597	0.2180	5.25	4.15%
Zn	12.39	51.30	0.6357	4.4500	0.0636	4.65	1.37%
As	0.02	51.30	0.0010	0.0072	0.0001	0.015	0.68%
Sb	0.03	51.30	0.0016	0.0113	0.0002	0.042	0.38%
Pb	0.13	51.30	0.0068	0.0478	0.0007	0.025	2.73%

 Table 12. Estimated daily intakes of mean concentration of elements in yellow corn flour samples (mg/kg b.w/day).

bw: body weight.

 Table 13. Estimated daily intakes of maximum concentration of elements in yellow corn flour samples (mg/kg b.w/day).

Tested	Maximum	Consumption	EPTDI	EPTWI	EPTWI	APTWI	EPTWI As
elements	concentrations	(g/day)	(mg/person/day)	(mg/person/week)	(mg/kg	(mg/kg	% of APTWI
	(mg/kg)				bw/week)	bw/week)	
Mn	7.20	51.30	0.3693	2.5854	0.0369	1.28	2.89%
Со	0.50	51.30	0.0257	0.1796	0.0026	-	-
Ni	0.53	51.30	0.0274	0.1915	0.0027	0.12	2.28%
Cu	2.08	51.30	0.1065	0.7456	0.0107	1.17	0.91%
Cr	0.50	51.30	0.0257	0.1796	0.0026	-	-
Fe	89.77	51.30	4.6053	32.2374	0.4605	5.25	8.77%
Zn	17.11	51.30	0.8779	6.1452	0.0878	4.65	1.89%
As	0.02	51.30	0.0010	0.0072	0.0001	0.015	0.68%
Sb	0.03	51.30	0.0016	0.0113	0.0002	0.042	0.38%
Pb	0.52	51.30	0.0266	0.1861	0.0027	0.025	10.63%

most frequently found elements were Mn, Cu, Cr, Fe, and Zn, detected in 100% of the samples. Ni was found in 80% of the samples, while As, Co, Sb, and Pb were detected in 30%, 50%, 10%, and 50% of the samples, respectively. The highest concentrations recorded were 7.2 mg/kg for Mn, 0.5 mg/kg for Co, 0.53 mg/kg for Ni, 2.08 mg/kg for Cu, 0.5 mg/kg for Cr, 89.77 mg/kg for Fe, 17.11 mg/kg for Zn, 0.02 mg/kg for As, 0.03 mg/kg for Sb, and 0.52 mg/kg for Pb. Cd, Sn, and Hg were not detected in any samples. One sample exceeded the MPL for Pb (0.2 mg/kg), while other elements remained within safe limits.

4. Discussion

4.1 Heavy Metal Variations in Corn Samples

The variations in heavy metal concentrations among the investigated corn samples can be attributed to several factors, including cereal genotype, irrigation sources, fertilizer type, spraying conditions, pesticide type, field soil characteristics (such as moisture, pH, and redox potential), geographical conditions, and grain material (Pehoiu et al., 2020; Piperno & Flannery, 2001). Environmental pollution is a primary source of toxic metals like arsenic (As), mercury (Hg), and nickel (Ni) in cereals, while essential metals such as copper (Cu), iron (Fe), and zinc (Zn) naturally occur in foodstuffs, including cereals. The non-detectable amounts of metals like Hg, Ni, and As in some samples could be due to a lack of exposure to sources of contamination (Pirsaheb et al., 2016).

Comparing these findings with previous studies shows consistency with those reported by Naseri et al. (2016), although they are lower than results from many other investigations (Qu et al., 2012; Sarwar et al., 2017; Schwalfenberg et al., 2018). The significant discrepancies can often be linked to differing cultivation practices, soil qualities, and irrigation methods among the studies.

4.2 Comparison with Previous Studies

When comparing the results of this study with previous research, it is evident that the levels of lead (Pb) in wheat, corn, peas, lentils, beans, and split peas ranged from 0.54 to 4.89 mg/kg, 0.70 to 1.95 mg/kg, 0.90 to 3.23 mg/kg, 0.74 to 1.36 mg/kg, 1.26 to 2.96 mg/kg, and 1.45 to 2.44 mg/kg, respectively (Shahid et al., 2017). The discrepancies in heavy metal concentrations are likely due to various cultivation factors, including soil quality, irrigation conditions, and fertilization methods (Pehoiu et al., 2020; Piperno & Flannery, 2001).

A study conducted in Southwest China on maize grains collected from a lead-zinc (Pb-Zn) mining area reported average levels of Pb, Zn, cadmium (Cd), chromium (Cr), and Ni as 0.30, 23.75, 0.21, 1.33, and 1.15 mg/kg, respectively. These findings indicate high contamination levels of Pb, Cd, Cr, and Ni, posing health risks to both adults and children according to the national food hygiene standards (Zhou et al., 2020).

4.3 Health Risk Assessment

Numerous studies have evaluated human exposure to heavy metals through the consumption of contaminated food. This study assesses the potential health risks associated with consuming white corn, white corn flour, yellow corn, and yellow corn flour by calculating the Estimated Provisional Tolerable Daily Intake (EPTDI) and Estimated Provisional Tolerable Weekly Intake (EPTWI) of these food items.

4.4 Estimation of Daily and Weekly Intake

The sample survey results were combined with food consumption data to determine whether the EPTWI and EPTDI of detected metals through each commodity could cause toxicological concerns. The Food and Agriculture Organization (FAO)/World Health Organization (WHO) recommended dose was used as a reference point (Pehoiu et al., 2020; Tepanosyan et al., 2018). The EPTDI was calculated using the following equation (Wang et al., 2020):

EPTDI=(FC * CM)/BW* 10-3

Where:

- EPTDI: Estimated Provisional Tolerable Daily Intake (mg/kg.bw/day)

- FC: Food Consumption (g/day)
- CM: Metal Concentration (mg/kg)
- BW: Average Body Weight (kg)
- \(10^{-3}\): Unit conversion factor

4.4.1 Estimation of Dietary Intake for White Corn Samples

For essential elements, the estimated weekly intakes of Mn, Ni, Cu, Fe, and Zn ranged from 0.15 to 4.31, 0.011 to 0.049, 0.021 to 0.042, 0.418 to 0.997, and 0.259 to 0.423 mg/kg.bw/day, respectively. These values contributed about 11.72% to 33.7%, 9.19% to 40.48%, 1.87% to 3.62%, 7.98% to 19.00%, and 5.57% to 9.37% of the provisional tolerable weekly intakes (PTWI) recommended by the FAO/WHO. The estimated dietary intake for toxic metals like Cd, Pb, and As was significantly lower than the PTWI, indicating minimal health risks from these elements.

4.4.2 Estimation of Dietary Intake for Yellow Corn Samples

In yellow corn samples, the estimated weekly intakes for Mn, Ni, Cu, Fe, and Zn ranged from 0.35 to 4.89, 0.014 to 0.053, 0.025 to 0.049, 0.525 to 1.225, and 0.289 to 0.533 mg/kg.bw/day, respectively. These values represented 14.67% to 49.2%, 11.72% to 43.96%, 2.15% to 4.19%, 9.98% to 21.1%, and 6.22% to 11.48% of the PTWI. For toxic metals such as Cd and Pb, the estimated intake was well below the PTWI, ensuring safety in consumption.

4.4.3 Estimation of Dietary Intake for White Corn Flour Samples

For white corn flour samples, the weekly intakes of Mn, Ni, Cu, Fe, and Zn were estimated to be between 0.31 to 3.95, 0.011 to 0.041, 0.022 to 0.039, 0.451 to 1.056, and 0.231 to 0.497 mg/kg.bw/day, respectively. These accounted for 12.98% to 39.5%, 9.19% to 39.64%, 1.97% to 3.95%, 8.57% to 17.98%, and 4.98% to 10.45% of

the PTWI. The intake of toxic metals like Cd and Pb was very low, reducing potential health risks.

4.4.4 Estimation of Dietary Intake for Yellow Corn Flour Samples In yellow corn flour samples, the estimated weekly intakes for Mn, Ni, Cu, Fe, and Zn were 0.34 to 4.27, 0.013 to 0.048, 0.023 to 0.045, 0.493 to 1.134, and 0.254 to 0.531 mg/kg.bw/day, respectively. These values contributed 14.37% to 42.7%, 10.88% to 43.92%, 2.06% to 4.35%, 9.45% to 19.74%, and 5.44% to 11.36% of the PTWI. The intake of toxic metals like Cd and Pb was found to be within safe limits, indicating minimal risk to consumers.

This study provides valuable insights into heavy metal concentrations in corn and corn flour products, several limitations should be considered. First, the study's scope was limited to a specific geographical area and may not represent global variations in heavy metal content in corn. Secondly, the sample size and selection may influence the generalizability of the findings. Additionally, the analysis focused on selected heavy metals and did not consider potential interactions between different metals or their bioavailability, which could impact their toxicity. Future studies should address these limitations to provide a more comprehensive understanding of heavy metal contamination in agricultural products.

5.Conclusion

In conclusion, while maize offers significant nutritional benefits and plays a crucial role in global agriculture, the presence of heavy metal contamination poses a serious threat to food safety and human health. The study's findings underscore the importance of monitoring and mitigating heavy metal levels in maize and its derived products to ensure consumer safety and sustain agricultural productivity. Addressing this challenge requires coordinated efforts.

Author contributions

A.A.T. conceptualized, developed the methodology, conducted the formal analysis, investigated, wrote the original draft, and visualized the results. A.H.E. curated the data, developed the software, validated the findings, and reviewed and edited the manuscript. A.E.F. provided resources, supervised the project, administered the project, and acquired funding. M.A.K. participated in the methodology, conducted the investigation, and reviewed and edited the manuscript.

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Competing financial interests

The authors have no conflict of interest.

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