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Quantitative Toxicological Risk Profiling of Carcinogenic Heavy Metal Contaminants in Agricultural Products: A Focused Geo- Environmental Study in Tanore Upazila, Rajshahi District, Bangladesh

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ABSTRACT
This study evaluates the contamination of agricultural crops with carcinogenic heavy metals in Tanore Upazila, Rajshahi District which is a well-known area for its important contribution to agriculture production. This study explores six frequently consumed plants- Green chili, coriander seed, potato tubers Brinjal fruit (whole), Onion bulb and Turmeric rhizomes. With the growing worldwide apprehension about heavy metal accumulation in food crops, particularly within developing nations, this research purposes to estimate the cadmium (Cd), lead (Pb), arsenic (As) and chromium(Cr) levels of these plants and evaluate health risk. Raw samples were obtained from the local fields and then they underwent strict cleaning & preparation protocols to give accurate results in the analysis. This was followed by quantification of heavy metals concentration using Atomic Absorption Spectrophotometry (AAS). E.D.I., T.H.Q. and H.I. were calculated to assess non-carcinogenic health risks. The final obtained results are for green chili, E.D.I. and T.H.Q. are respectively 0.000199 and 0.1993 for Cd, 0.000665 and 2.2167 for As, 0.000183 and 0.0458 for Pb, 0.000120 and 0.040 for Cr and H.I. is 2.5018. For coriander, E.D.I. and T.H.Q. are respectively 0.000031 and 0.0314 for Cd, 0.000055 and 0.1834 for As, 0.000283 and 0.0707 for Pb, 0.000133 and 0.0443 for Cr and H.I. is 0.3298. For potato, E.D.I. and T.H.Q. are respectively 0.000010 and 0.0097 for Cd, 0.000017 and 0.0554 for As, 0.000012 and 0.0029 for Pb, 0.000015 and 0.0050 for Cr and H.I. is 0.0730. For brinjal, E.D.I. and T.H.Q. are respectively 0.000005 and 0.0097 for Cd, 0.000007 and 0.0246 for As, 0.000011 and 0.0029 for Pb, 0.000010 and 0.0033 for Cr and H.I. is 0.0360. For onion, E.D.I. and T.H.Q. are respectively 0.000036 and 0.0361 for Cd, 0.000032 and 0.1068 for As, 0.000242 and 0.0606 for Pb, 0.000116 and 0.0387 for Cr and H.I. is 0.2422. For turmeric, E.D.I. and T.H.Q. are respectively 0.000022 and 0.1392 for Cd, 0.000042 and 0.1392 for As, 0.000241 and 0.0603 for Pb, 0.000118 and 0.0393 for Cr and H.I. is 0.2608.

Keywords: Heavy Metals, Agricultural Contamination, Health Risks, Cadmium, Food Safety

1. Introduction

The accumulation of toxic elements in food crops is among the growing global issues, mostly associated with developing countries due to various factors including industrial activities; poor waste disposal and contaminated irrigation water that make agricultural produce contamination by carcinogenic heavy metals. Heavy metals such as cadmium (Cd), lead (Pb), arsenic (As) and chromium Cr have the capability to get into soil, water thus food-chain. These hard metals may lead to severe lifetime health hazards like cancer, developmental defects in children and other serious leading chronic diseases even when consumed at minimal levels with an extended period[1].As Bangladesh is a country that is mainly dependent on agriculture, therefore there are of course huge challenges also faced, like heavy metal contamination in crops. Moreover, places that are famous for the cultivation of vegetables (e.g., potato and brinjal), spices (coriander, onion, and green chili), and tuber seed crops like turmeric face additional risks due to a lot of practices often rooted in traditional knowledge about health—poor agricultural conditions create high vulnerability indices. Identifying these toxic metals in agricultural produce is key to understanding the potential health risks because food consumption, including dietary intake, represents their main exposure pathway for humans. This study aims to conduct a comprehensive risk assessment through toxicological testing for heavy metals (carcinogenic) in Tanore Upazila agricultural products. This study focuses on the geo-environmental factors that lead to this contamination, and it may or will relate influence in public health such as food safety[2].

2. Description of study area

As the maximum supply of vegetables in Rajshahi city market comes from Tanore upazila, we have decided to select Tanore as the study area as most of the people consume vegetables from the mentioned area. Tanore Upazila (rajshahi district) area 295.40 sq km, located in between 24°29' and 24°43' north latitudes and in between 88°24' and 88°38' east longitudes. It is bounded by Nachole and Niamatpur upazilas on the north, Paba and Godagari upazilas on the south, Mohanpur and Manda upazilas on the east, Nachole, Nawabganj Sadar and Godagari upazilas on the west.

Fig 1. Tanor Upazilla, Rajshahi

3. Collection and preparation of spices samples

Table 1. Local names, English names, scientific names and family of analyzed spice samples

Local name (Bangla)	English name	Scientific name	Family
Kacha Morich	Green Chili	*Capsicum annum*	Solanaceae
Peyaj	Onion	*Allium cepa*	Amaryllidacea e
Holuud	Turmeric	*Curcuma longa*	Zingiberaceae
Beguun	Brinjal	*Solanum melongena*	Solanaceae
Aloo	Potato	*Solanum tuberosum*	Solanaceae
Dhoniya	Coriander	*Coriandrum sativum*	Apiaceae

The field near the Tanore upazila area (Figure 1) was selected, where samples from six (6) different agricultural products were collected. Table 1 provides a detailed description of the products, including their English names, scientific names, and local names, along with their varieties. The samples were rinsed well under running water to remove any mud, silt, and what we empirically hoped might be parasitic eggs. The samples were then rinsed again with deionized water in order to ensure that the cross sections are free from other particles. The non-edible parts were separated and the edible ones cut in small pieces under laboratory conditions. To minimize contamination, the chopped samples were air-dried in situ at room temperature on a clean bench top. Subsequently, the samples were dried in a laboratory oven at 1000°C until a constant weight was achieved. The dried samples were ground in the machine to ensure that particles had a fine consistency and sieved with an 80-mesh sieve. Samples were homogenized by repeated grinding and placed in airtight containers within desiccators at low moisture conditions to avoid liquid-solid phase change during storage. The analysis was conducted within the same week to ensure sample freshness [3].

4. Spices sample Analysis

The amounts of hazardous heavy metals in various rainfall samples are examined using the Atomic Absorption Spectrophotometric (AAS) technique. One gram of dried powdered material was added to the appropriate digestion containers for each digestion. In 250 ml digestion vessels, the sample was mixed with 10 ml of 69% w/w HNO_3 and 2 ml of 30% w/w H_2O_2. The samples were then heated continuously, progressively raising the temperature to 80–100 °C until a clear solution was achieved. Whatman No. 42 filter paper was used to filter the digest solution after it had cooled and been centrifuged for two minutes at 30 rpm. Double-distilled water was used to get the final volume in a 50 ml volumetric flask. Finally, an atomic absorption spectrophotometer (AAS) was used to analyze the treated materials. Atomic absorption spectrophotometry was used to determine the levels of Pb, Cd, Cr, and As in the filtrate of digested spice samples (GTA 120-AA240Z and Spectra 220 AAS, Varian, Australia). The gadget came with a unique lightbulb made of a particular metal. Using manually made standard solutions of the pertinent heavy metals and drift blanks, the instrument was calibrated. [4]

Table 2. List of necessary chemicals

Name of Chemicals	Property
Nitric Acid (HNO_3)	Colorless to Yellow Liquid, 1.51g/cm^3 density at 20^{0}C, 83^{0}C Boiling Point
Hydrogen Peroxide (H_2O_2)	Colorless, 1.45 g/cm^3 density, 150^{0}C Boiling Point

5. Data analysis

5.1 Metal pollution index:

Based on the overall concentration of heavy metals found in all tested samples, the MPI (metal pollution index) was determined. By taking the geometric mean of all the metal concentrations in the samples, this index was computed [5].

$$M.P.I. = (Cf_1 \times Cf_2 \times \ldots\ldots \times Cf_n)^{1/n} \qquad (i)$$

Where, Cf_n = concentration of metal in the spice samples.

Consumption of the products and potential health hazards: The estimated daily intake (EDI), The target hazard ratio (THQ) and the Hazard Index (HI) were used to evaluate the possible health risks associated with heavy metal consumption through the use of the products. Body weight, daily consumption, and the element concentrations in the samples all contribute to the EDI value. Equation (2) was used to estimate the EDI values of the metals under analysis [6].

$$E.D.I. = \frac{C_{metal} \times IR}{BW} \qquad (ii)$$

where BW is the average body weight (kg), IR (ingestion rate) is the average daily consumption of spices (grams per day per individual), and C_{metal} (mg/kg) is the average weighted heavy metal content in spices. [7]. The study found that the average adult consumes 10 g of spices per day per person of dry weight. The average weight of an adult was 60.0 kg [8]. The non-carcinogenic dangers of prolonged exposure to contaminants in vegetables are determined using THQ.; Eq (3) was used for the calculations.

$$T.H.Q. = \frac{EDI}{Rf_D} \qquad (iii)$$

where Rf_D represents each metal of interest's reference dosage levels (mg/kg day_1). Pb, Cd, Cr, and As had Rf_D values of 0.004, 0.001, 0.003, and 0.0003 mg/kg daily, respectively [9–10].
The H.I.'s objective is to determine the overall non-carcinogenic risk to human health posed by exposure to several contaminants. As shown in Eq. (4), H.I. is the sum of all the heavy metal hazard quotients in spices.

$$H.I. = T.H.Q.(Pb) + T.H.Q.(Cd) + T.H.Q.(Cr) + T.H.Q.(As) \qquad (iv)$$

The population may have potential negative health consequences if THQ/HI values ≥ 1, while there is less chance of clear negative effects if THQ/HI values < 1 [11-13].

6. Result and Discussion

The concentrations are provided in Table 3 following the analysis of the samples.

Table 3. Heavy metal concentration in samples

Sample ID	Concentration of Heavy Metals (mg/kg)			
	Cd	As	Pb	Cr
Green Chili	1.1958	3.9901	1.0996	0.7214
Coriander	0.1882	0.3302	1.6974	0.7997
Potato	0.0582	0.0997	0.0703	0.0922
Brinjal	0.0311	0.0443	0.0688	0.0589
Onion	0.2166	0.1922	1.4534	0.6947
Turmeric	0.1320	0.2506	1.4465	0.7103

6.1 Metal concentration

6.1.1 Cadmium (Cd):

Cadmium is harmful to human health, as it accumulates in the kidneys and leads to renal failure and bone demineralization. It is also associated with lung cancer and cardiovascular issues. Endocrine processes and reproductive health are influenced by even the smallest concentrations [14-16]. The concentration of Cadmium (Cd) in Table 2 ranged from 0.0311 mg/kg to 1.1958 mg/kg. The green chili sample in this study is the most cadmium-contaminated, with a concentration of 1.1958 mg/kg, as observed in table 3. The sequence can be expressed as green chili>onion>coriander>potato>brinjal in order to represent a cadmium-contaminated sample. The permissible limit for cadmium consumption in food products is 6 mg/kg (dry weight basis) [17]. Therefore, each sample is deemed to be safe in this investigation.

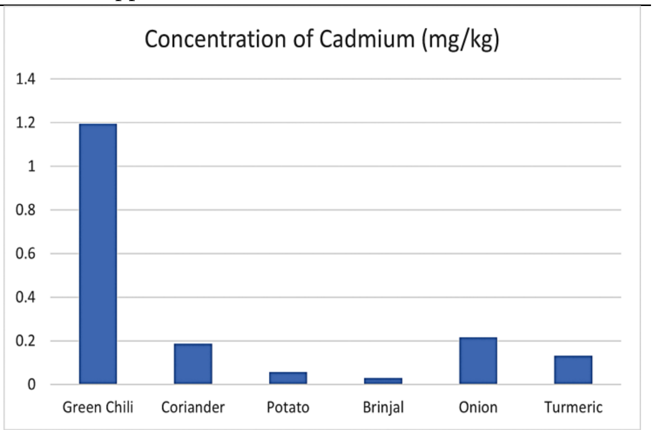

Fig 2. Concentration of Cadmium in different spices and vegetables

6.1.2Arsenic (As):

Arsenic is a poisonous material that mostly harms the skin, liver, kidneys, and respiratory organs of humans. Chronic exposure to this substance is correlated with the development of malignancies in these organs. It also results in neurotoxicity, heart diseases, and suppression of the immune response. Arsenic, even in the low dose, causes reproductive and developmental issues [18–19]. The concentration of arsenic varied from 0.0443 mg/kg to 3.9901 mg/kg. Arsenic (As) contamination is highest in the green chili sample. To represent an Arsenic (As) contaminated sample, the sequence can be expressed as green chili>coriander>turmeric>onion>potato>brinjal. In foodstuffs, the permissible limit of As is 1 mg/kg (dry weight basis) [20]. Table 3 indicates that the permissible limit of As in green chili has been exceeded.

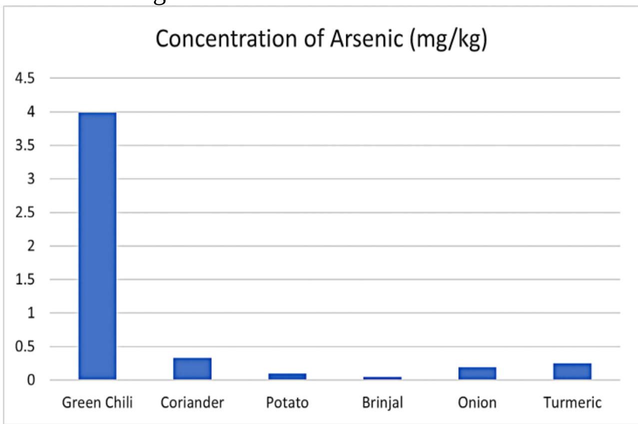

Fig 3. Concentration of Arsenic in different spices and vegetables

6.1.3 Lead (Pb):

Lead is an extremely poisonous heavy metal that causes various harmful effects on many different organs and tissues in the body, particularly with regard to its impact on the nervous system. In kids, this can affect brain functioning and behavior as well, leading to a lower IQ. After continued exposure, it results in heart disease, anemia, and kidney injury. In vulnerable groups like infants and expecting mothers, minimal exposure to lead can impair neurological as well as developmental processes [21-22]. The highest Pb was detected in a sample and ranged from 0.0688 to 1.6974 mg/kg. The Coriander example has the highest level of contamination. The following expression can be written as coriander>onion>turmeric>green chili>potato>brinjal (Lead contamination sequence). Lead in foods is regulated at all levels, with the permissible level limit of 7.2 mg/kg (dry weight.) [22]. As a result, it can be said that the entire samples (100%) taken from Tanore upazila in Rajshahi are safe for human consumption.

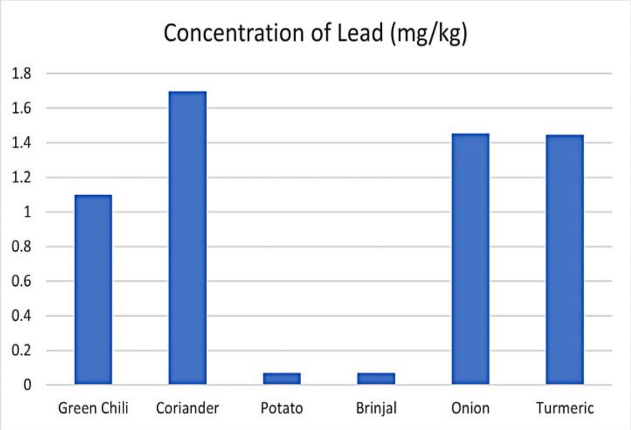

Fig 4. Concentration of Lead in different spices and vegetables

6.1.4 Chromium (Cr):

One of the most toxic and carcinogenic species is chromium, particularly in its hexavalent form (Cr(VI)), which causes lung cancer by inhalation. Exposure over a longer period of time can also cause skin irritation, ulcers, and dermatitis. Furthermore, it is able to cause genotoxic damages such as damage to the DNA and an increase in cancer risk and genetic mutations [24–26]. The level of Chromium (Cr) obtained from Table 2 was between 0.0589 mg/kg to 0.7997 mg/kg Contamination levels are highest in samples of coriander. The order of the Chromium level is: coriander>green chili>turmeric>onion> potato > brinjal. Chromium The maximum level of chromium intake approved for the human organism is 1 mg/kg [27]. Hence, it can be concluded that the entire samples collected from Rajshahi zone in Tanore upazilla are safe for human consumption.

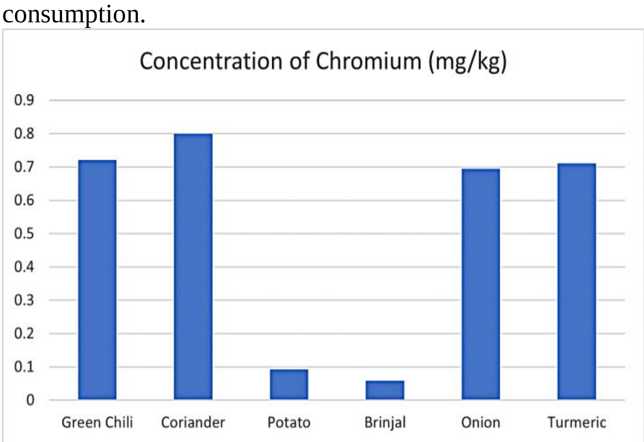

Fig 5. Concentration of Chromium in different spices and vegetables

6.1.5 Metal pollution index (MPI):

Figure 6 illustrates the methodology used to construct the metal pollution index (MPI). The process is: Brinjal(0.0486)<Potato (0.0783)<Turmeric (0.4294)<Onion (0.4528)<Coriander (0.5389)<Green Chili (1.3948). The Metal Pollution Index (MPI) indicates significant variances in possible health concerns by assessing heavy metal contamination in diverse spices and vegetables. Green chili had the highest MPI value of 1.3948 mg/kg, indicating potentially significant levels of heavy metal contamination, such as arsenic (As). Because of the contamination, using it on a frequent basis may be dangerous. Turmeric and coriander, on the other hand, had moderate MPIs of 0.4294 mg/kg and 0.5389 mg/kg, respectively, indicating that they were moderately polluted, particularly with cadmium (Cd) and arsenic. The least contaminated with heavy metals among examined materials were brinjal and potatoes, which had MPI values of 0.0486 mg/kg and 0.0783 mg/kg, respectively. These findings indicate that potatoes and brinjal are superior alternatives to other spices and vegetables in terms of the health risks associated with heavy metal consumption. Nevertheless, the MPI results suggest that the elevated accumulation of heavy metals in these samples may pose a health risk to humans.

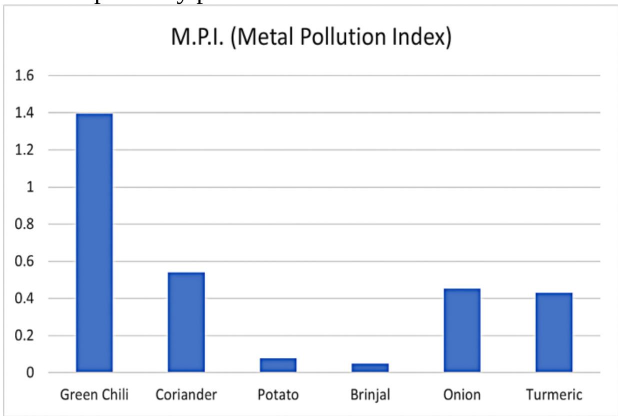

Fig 6. Metal pollution index of spices and vegetables samples from Tanore Upazila

6.1.6 Evaluation of health risks:

The health risk evaluation of heavy metals found in many spices and vegetables such as green chili, coriander, potatoes, brinjal, onions, and turmeric. The primary parameters for heavy metals like Cd, As, and Pb are Estimated Daily Intake (E.D.I.), Target Hazard Quotients (T.H.Q.), and Hazard Index (H.I.). Table 3 shows that the determined EDI values for Cd, As, Pb, and Cr were 0.000005 to 0.000199, 0.000007 to 0.000665, 0.000011 to 0.000283, and 0.000010 to 0.000133. Cr, Cu, and Zn had E.D.I. values ranging from 0.0002-0.0041, 0.0018-0.0270, and 0.0018-0.0090.The T.H.Q. values were varied from 0.0052 to 0.1993 for Cd, 0.0246 to 2.2167 for As, 0.0029 to 0.0707 for Pb and 0.0033 to 0.0443 for Cr. For Cr, Cu and Zn, the T.H.Q. values were varied from 0.008 to 1.3805, 0.0499 to 0.1453,0.0062 to 0.0301 respectively. The greatest risk for arsenic was 2.2167(T.H.Q. value), while the H.I. value for green chili was 2.5018. Therefore, the regular consumption of green chili could put us at excess of arsenic levels, which might not be good for our health. Furthermore, the values of Cr and other metals were 0.3298 and 0.2608, and they were lower, but emphasized by the level of arsenic for coriander and turmeric. In terms of heavy metal concentration, potatoes and brinjal are the safest choices because their HI values are far below the risk threshold (0.0730 for potatoes and 0.0360 for brinjal). Despite the fact that Lead and arsenic are significant factors, onions also exhibit a comparatively low risk, with an HI of 0.2422.

Our research shows that certain foods shows a little amount of risks but others mainly Green Chili contains As at an amount which might cause dangers to the consumers. To minimize the health hazards the regular assessment of the daily consuming products are essential. .

Table 4. Values of E.D.I., T.H.Q. and H.I.

Sample Name	Cd		As		Pb		Cr		H.I.
	E.D.I.	T.H.Q.	E.D.I.	T.H.Q.	E.D.I.	T.H.Q.	E.D.I.	T.H.Q.	
Green Chilli	0.000199	0.1993	0.000665	2.2167	0.000183	0.0458	0.000120	0.040	2.5018
Coriander	0.000031	0.0314	0.000055	0.1834	0.000283	0.0707	0.000133	0.0443	0.3298
Potato	0.000010	0.0097	0.000017	0.0554	0.000012	0.0029	0.000015	0.0050	0.0730
Brinjal	0.000005	0.0052	0.000007	0.0246	0.000011	0.0029	0.000010	0.0033	0.0360
Onion	0.000036	0.0361	0.000032	0.1068	0.000242	0.0606	0.000116	0.0387	0.2422
Turmeric	0.000022	0.0220	0.000042	0.1392	0.000241	0.0603	0.000118	0.0393	0.2608

7.Conclusion

This result reveals how monitoring and management are immediately required for the contamination of toxic metals in food crops, particularly vegetables and spices, which are crucial constituents of local economies as well as communities' consumption at Tanore Upazila, Rajshahi District. If regularly consumed over a long time, these food sources (which are high in carcinogenic heavy metals like Cadmium, Lead, Arsenic and Chromium) can cause great health dangers for the consumer. The research provides crucial implications for quantifying the extent of the problem and highlights that sustainable land management and waste removal, followed by monitoring frequency, are needed to mitigate all these risks. Profiling toxicological risk assessment as well as spotting out key geo-environmental factors underlying contamination. Ensuring food safety and reducing the hazards to public health caused by heavy metal contamination must be the top concern for both local and national policymakers.

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NOMENCLATURE

E.D.I. : the estimated daily intake
T.H.Q.: the target hazard ratio
H.I. : hazard index
M.P.I. : metal pollution index
Cf_n : concentration of metal in the spice samples
C_{metal} : average weighted heavy metal content in spices(mg/kg)
I.R. : ingestion rate, (gram/day individual)
B.W. : average body weight (kg)
Rf_D : reference dosage values (mg/kg day1)