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Human health risk assessment of heavy metals in agricultural soil and food crops (Wheat and Rice)

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Abstract: Atomic absorption spectroscopy (AAS) was used in this work to assess the heavy metal content of 80 samples of crops (wheat and rice) and 20 samples of soil. The findings demonstrated that agricultural soil had mean heavy metal concentrations that were below the recommended limit. The mean concentrations of heavy metals in the wheat crop were Ni (0.86 ± 0.016) > Pb (0.329 ± 0.21) > Co (0.251 ± 0.007) > Cd (0.016 ± 0.0032) > Cr (0.00) mg/kg fresh weight, respectively. And in rice the mean concentration was Pb (0.051±0.013) > Ni (0.046±0.012) > Co (0.057±0.009) > Cd (0.030±0.007) > Cr (0.00). In conclusion, the current findings provide some fundamental knowledge concerning the risks to human health in the study area and heavy metal pollution of crops.

Keywords: Atomic absorption spectroscopy, Heavy metals, Concentration, Wheat and Rice.

Introduction: Globally, heavy metal contamination has spread widely, disrupting the environment and creating major health problems to people. Most experts agree that the main reasons of this issue are the increasing speed of urbanisation, changes in land usage, and industrialization, particularly in developing nations with exceptionally high populations, like India and China [1]. The variety of environmental pollutants has grown enormously since the industrial revolution and economic globalisation, with innumerable anthropogenic origins. As a result, there is now a global concern over the various and rising concerns related to food security, notably their close connection to human health [2]-[5]. As, Pb, Cd, and Hg are just a few dangerous metalloids and heavy metals that aren't necessary for metabolism or other biological processes. These metals are harmful in a number of ways [6], and the US Environmental Protection Agency and the Agency for Toxic compounds and Disease Registry (ATSDR) have listed them among the top 20 most dangerous compounds [7-9].

The metabolic functioning of biota is closely connected to the presence of certain heavy metals, including chromes and enzymes, such as Cu, Fe, and Zn (and even Cr (III)) [10]. Although it poses dangers to human health at high doses, nickel is a necessary component of urease [11]. Soil-food crop and vegetable systems are a common example of abiotic-biotic interactions in the environment. Heavy metals have negative effects on soil biota through microbial activities and interactions between soil-microbes, in addition to their effects on human health [12]-[14].

Beneficial soil insects, invertebrates, and small and large mammals are all impacted, particularly in agriculture [15]. For instance, as the Chinese medicinal herb Feng dan (Paeonia ostii) has shown, heavy metal contamination should be checked on plants used for conventional human health care to prevent negative consequences [16]. When planted close to smelting or other industrial regions, many medicinal plants have been proven to bioaccumulate different metals (such as Cd, As, Cr, Cd, Cu, Pb, and Fe) [17]-[20]. Compared to vegetables grown outdoors, greenhouse vegetables are also significantly more contaminated with heavy metals as Cu, Zn, Mn, Pb, and Cd (but not Fe) [21].

This is presumably because greenhouse veggies receive less light. The development of efficient remediation systems requires a deeper understanding of the mechanisms governing the transport of nutrients from soil to food crops. In order to achieve this goal, this paper first discusses various heavy metal contamination sources in soil systems, their significance to dangers to human health, the fundamental mechanisms driving such pollution, and the ensuing dietary consumption of contaminated crops. It's interesting that this review tries to give a broad overview of the geographical distribution of heavy metal sources in agro-ecosystems in relation to anthropogenic variables and processes. Information on heavy metal pollution in soil-food crop subsystems throughout all inhabited continents is also included in this regard. To further clarify the physiological/molecular mechanisms involved in the uptake of metallic pollutants into food crops, the ramifications of those subsystems for the environment and human health are thoroughly examined. In order to effectively manage heavy metals in the environment, the paper also examines cutting-edge remediation techniques, such as eco-remediation and the use of chemicals, biochar, and nanoparticles. By preventing or reducing the transfer of metallic pollutants from soil to food crops (soil-crop systems), these management techniques are intrinsically linked with the welfare of human

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health.

Material and methodology

Study area

In the current investigation, soil and plant samples from Haryana, India, were gathered. In India's northwest is the state of Haryana. Despite being in the subtropical area, Haryana has an arid to semiarid climate.

A field is chosen from the Bhiwani district for the soil and crop sample process. The district receives 420 mm of rainfall on average per year. One of the 21 districts in India's Haryana State is the Bhiwani District. Bhiwani serves as the administrative centre for the Bhiwani District. It is situated 261 kilometres north of Chandigarh, the state capital. The population of Bhiwani District is 1629109. By population, it is the third-largest District in the State. There are 491 villages and 10 Tehsils in the Bhiwani District. With 84926 residents, Siwani Tehsil is the smallest Tehsil in terms of population. With 474873 residents, Bhiwani Tehsil is the largest Tehsil in terms of population. In the district of Bhiwani, 317 villages exist. The village chosen for sampling is not in a heavy metal-prone area, but a large portion of the study will focus on the uptake of heavy metals by crops from normal soil and the influence of soil parameters.

The primary industries of the local inhabitants are agriculture and animal husbandry. The two main grains grown in the region during the Rabi and Kharif seasons are Oryza sativa (rice) and Triticum aestivum (wheat). Fields are prepared for Kharif crops between April and May, seeds are sown at the start of the rainy season in June, and Rabi crops are sown between the end of October and the beginning of November and are always harvested between March and April. Wheat, rice, and agricultural soil samples were taken from the study region in April - May and October - November of 2021, respectively.

Sample collection

Agricultural samples of crops (Wheat and Rice) were collected during the period of April-May and Oct-Nov, 2021. In order to evaluate the transfer and translocation factor of heavy metals in food crops and corresponding soils were collected in their respective harvesting seasons. The details of the samples collected are given below:

1. Wheat (Triticum spp.): Samples of wheat crop from identified sampling stations were collected during harvesting season (April-May) for the year (2021). About 20 samples were

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collected each weighing 500 - 1000g. After removal of extraneous matter like soil pebbles, stones and other debris the samples were sealed in plastic containers, taken to the laboratory and stored till further analysis.

2. Rice (Oryza sativa): Samples of rice crop were collected during its harvesting season (November- December) for the year (2021). A total of 20 samples were collected each weighing 500 - 1000g. The collected samples were cleaned, sealed and stored as discussed above.

3. Soil sample: In order to evaluate transfer and translocation factor of heavy metals from soil to above collected different environmental matrices, corresponding sub surface soil samples from rooting zone were also collected. About 20 soil samples were collected during different sampling seasons. From a depth of 5-10 cm, four sub-samples of soil from rectangular grid of 0.5 m2 area were collected and then mixed together to obtain a representative sample. The soil samples each weighing 500g were collected using non metallic spade so as to get rid of the metal contamination. Samples were sealed in clean plastic bags after removing foreign bodies. Soil samples were air dried, grounded and then passed through a 2.0 mm sieve and stored in air tight containers till further analysis.

Sample processing

Soil Samples Processing

- Soil samples were air dried, grounded and stored in air-tight plastic containers for further use for physico-chemical analysis. After removal of extraneous matter like pebbles and plant roots etc. Soil samples were oven-dried at a temperature of 110°C until a constant weight of the sample was achieved. Then the samples were ground in grinder with care to avoid cross contamination. After milling, the whole samples were sieved using 2.0 mm sieve.

- For heavy metals analysis, processed samples were stored in air tight plastic containers to have moisture free conditions till further analysis.

Agricultural Sample Processing

Wheat and Rice Samples Processing

- The fresh weight of the samples was recorded just after collection.

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- Different parts (roots, shoots and grains) of wheat and rice crop were dried in drying oven at 110°C temperature until a constant weight of the sample was achieved.

- After drying, the dry weight of the sample was recorded and about 100 g dry subsamples were ashed in a muffle furnace at 350-400°C till the ash became white.

- The ashed samples were then stored in moisture free conditions till further analysis

Sample analysis

The details of various methods used to analyze physico-chemical characteristics of soil and naturally occurring heavy metals, soil physico-chemical characteristics and heavy metals in different agricultural crops and soil samples are given below.

Heavy Metals Analysis

Sample Digestion

Atomic Absorption Spectrophotometer (SenSAAGBC, Australia) was used to assess the total Cd, Ni, Cr, Co, and Pb contents of agricultural crops and soil samples. Concentrations were then represented in mg kg-1 on a dry weight basis. Each sample of agricultural crop ash weighed 0.2 g, and 5.0 ml of a 9:1 (v/v) diacid (HNO3 and HClO4) mixture was added to it. Similarly, 5.0 ml of a diacid combination was combined with 0.5g of each soil sample. After taking the sample mixture in clean Teflon containers, it was digested on a hot plate the following day while it was left open at room temperature. When digestion was finished, the containers were quantitatively transferred into glass beakers and chilled to room temperature. Then the digests were evaporated to dryness on hot plate at a temperature of 130-150°C and residue was dissolved in double distilled water to make desired volume (50 ml). Extracted solutions were transferred to polypropylene bottles and refrigerated until analysis.

To create all of the working standards for analysis, approved standard solutions containing 1000 mg/L were diluted. Atomic Absorption Spectrophotometer (AAS) employed air as support and acetylene gas as fuel. With the exception of chromium, which was quantified using a reducing nitrous oxide flame, every case used an oxidising flame. Using an Atomic Absorption Spectrophotometer (SenSAAGBC, Australia), the extracts were examined for the presence of eight heavy metals, including Cd, Ni, Cr, Co, and Pb. Quality assurance and control procedures were used during the processing and analysis of the samples to guarantee the validity of the findings. Double distilled water was used to prepare standards, prepare samples, and rinse glassware in order to prevent sample contamination. To eliminate analytical bias, reagent blanks were examined, and the data were then corrected for blanks. Relative standard deviations (RSDs) of replicate measurements were 0.999. To ensure the reliability of results, standards of respective metals were run after every 10 samples analyzed.

Water samples were run directly on AAS for heavy metals (Cd, Ni, Cr, Co, and Pb) quantification. Prior to analysis the waters samples were filtered through 0.45-µm Whatsmann filter paper. Filtered samples were analyzed for heavy metals by directly running into AAS with 48h after receiving in the laboratory.

Health Risk Assessment from Consuming Food Grains Crops (Wheat and Rice)Chronic Daily Intake

CDI is the exposure to the population expressed as the mass of a substance per unit body weight per unit time, averaged over a long period of time (a lifetime).

Chronic Daily Intake of heavy metals through grains (wheat and rice) ingestion was calculated according to formula given by (USEPA, 2010).

$$\text{CDI (Ingestion)} = \frac{Cm * Fir * Ef * Ed}{WAB * TA}$$

Where, CM is the concentration of a heavy metal in grains (Wheat and Rice) (mg kg^{-1} DW) FIR is the ingestion rate (0.147 kg day^{-1} for wheat grains, 0.178 kg day^{-1} for rice) for an adult person living in the study area (FAO, 2014)

EF is the exposure frequency (365 days $year^{-1}$) ED is the exposure duration (70 years for adults)

WAB is the average body weight (60 kg for Indian adults) (NNMB, 2002)
TA is the average exposure time for non-carcinogenic effects (ED × 365 days $year^{-1}$).

Total Hazard Quotient

THQ has been calculated as the ratio between the estimated dose of a contaminant and the dose level below which there will not be any appreciable risk, i.e. the Reference Oral Dose. Where RfDo is the oral reference dose (mg kg^{-1} day^{-1}) and is an estimation of the daily exposure to which human population is likely to be exposed without any appreciable risk of deleterious effects during a lifetime (USEPA, 2010). The RfDo values used were 1.0×10^{-3} , 4.0×10^{-2} , 2.0×10^{-2} , 7.0×10^{-1} , 3.0×10^{-1} , 4.0×10^{-3} , 1.5 and 0.0003 mg kg^{-1} day^{-1} for

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Cd, Cu, Ni, Fe, Zn, Pb Cr and As respectively (USEPA, 2010). If THQ exceeds unity, potential non-cancer effects may be of concern (USEPA, 2010).

$$THQ = \frac{CDI}{RfDo}$$

Where CDI stands for chronic daily intake

RfDo stands for oral refrence doses

Results and discussion:

Heavy metal content in agricultural soil

Wheat (Triticum aestivum L.) with a global production of 659.1 million tonnes in 2012-2013, is the most important crop worldwide in basic food commodities followed by coarse grains and rice (FAO, 2013). Rice is a staple for nearly half of the world's 7 billion people and more than 90% of this is consumed in Asia. About 55% of the total rice production is accounted by China, Taiwan and India alone (IRRI, 2013). The range of studied heavy metal content in soil collected in April-May, Oct-Nov 2021 was as follows; Ni) 8 - 9 mg kg-1 , (Pb) 8 - 9 mg kg-1 , (Co) 6 - 7 mg kg-1 , (Cr) 0.1 - 0.2 mg kg-1 and (Cd) 3.0 – 4.5 mg kg-1 (Table 1) with mean value of heavy metal content (mg kg-1) was in the following order: Ni (9.34 ± 0.348) > Pb (8.50 ± 0.42) > Co (7.43 ± 0.28) > Cd (4.07 ± 0.186) > Cr (0.135 ± 0.028) (Table 1). The results of the present study showed that agricultural soil had highest content of Ni and lowest content of Cr. Moreover, all the studied heavy metals were within permissible limits of Indian standards (Awashthi, 2000).

Table 1: Range and mean of heavy metals in agricultural soil

Statistics	**Metals**				
	Ni	Pb	Cd	Cr	Co
Min.	8.900	8.017	3.821	0.109	7.971
Max.	8.937	8.992	4.414	0.120	6.102
Mean ± SD	9.349±0.348	8.507±0.420	4.078±0.186	0.135±0.028	7.437±0.286

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Heavy metal content in wheat grains

Wheat grain samples from ten sampling stations from the study area were collected during wheat harvesting season. All the collected samples were analyzed for Pb, Ni, Cd, Cr and Co content. Heavy metals in the samples of wheat grains collected during April - May, 2021 was: (Pb)0.011-0.083 mg kg-1,(Ni) 0.0650.097 mg kg-1,(Cd) 0.010 - 0.019 mg k(Co) 0.011 0.034 mg kg-1 and Cr was not measurable. Mean value of heavy metal content (mg kg-1) in wheat grains collected was in the following order: Ni (0.86 ± 0.016) > Pb (0.329 ± 0.21) > Co (0.251 ± 0.007) > Cd (0.016 ± 0.0032) > Cr (0.00) (Table 2). It is clear from the results that the content of Ni was highest and content of Cr was lowest in the studied wheat grain samples.

Table 2: Concentration of heavy metals in fruit of *Triticum aestivum*

S. No.	Heavy Metals	Mean
1	Ni	0.086±0.016
2	Pb	0.032±0.021
3	Cd	0.016±0.003
4	Cr	00
5	Co	0.025±0.007

Heavy metal content in rice grains

The range ofstudiedheavy metal content in rice grains collected during Oct – Nov, 2021 was as follows: (Co) 0.006 - 0.012 mgkg-1 , (Cd) 0.001 - 0.008 mg kg-1, (Pb) 0.009 – 0.027 mg kg-1 , (Ni) 0.014 - 0.075 mg kg-1, and (Cr) was unpredictable with mean value of heavy metal content (mg kg-1) in the ricegrains was in the following order: Ni (0.05 ± 0.01) > Pb (0.01 ± 0.00) > Co (0.009 ± 0.001) > Cd (0.00 3± 0.001) > Cr (0.00± 0.00) (Table 3)

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Table 3: Concentration of heavy metals in fruit of *Oryza sativa*

S. No.	Heavy Metals	Mean
1	Ni	0.057±0.017
2	Pb	0.018±0.006
3	Co	0.009±0.001
4	Cr	00
5	Cd	0.003±0.002

Chronic Daily Intake (CDI) of heavy metals via wheat grain ingestion

Estimation of the exposure level and tracing the routes of contaminants to the target organisms are of great importance for observing the underlying health risks. By consuming wheat grains (2021) grown at studied sampling locations in the study area an adult will intake 0.0003282 – 0.0006211 mg kg^{-1} day^{-1} of Ni, 0.00005555 – 0.0004191 mg kg-^{1} day^{-1} of Pb, 0.0000505 – 0.0001060 mg kg^{-1} day^{-1} of Cd, 0.00005555 – 0.0001717 mg kg-^{1} day^{-1} of Co and Cr value was nil and with mean CDI (mg kg^{-1} day^{-1}) of heavy metal via wheat fruit (2021) ingestion was in order: Co (0.0008229) > Ni (0.0004357) > Pb (0.0001661)> Cd (0.00012672) (table 4). Maximum permissible limits (mg kg^{-1} day^{-1}) of Cd, Pb, Ni, Co and Cr through ingestion of crops are 0.2, 0.3, 67.9, 50 and 0.1 respectively. Results of the present study revealed that mean CDI of metals through ingestion was lower than the threshold CDI values.

Table 4. Chronic daily intake (mg kg-1 day-1) of heavy metals via ingestion of wheat grain

Statistics	Metals				
	Ni	Pb	Cd	Cr	Co
Min.	0.0003282	0.0000555	0.0000505	0	0.0000555
Max.	0.0006211	0.0004191	0.0001717	0	0.0001717
Mean	0.0004357	0.0001661	0.0001267	0	0.0008229

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Chronic Daily Intake (CDI) of heavy metals via rice grain ingestion

Estimation of the exposure level and tracing the routes of contaminants to the target organisms are of great importance for observing the underlying health risks. By consuming rice grain (2021) grown at studied sampling locations in the study area an adult will intake 0.0000707 – 0.0003787 mg kg^{-1} day^{-1} of Ni, 0.00004545 – 0.0001363 mg kg^{-1} day^{-1} of Pb, 0.00000505 – 0.0000252 mg kg^{-1} day^{-1} of Cd, 0.0000303 – 0.0000606 mg kg^{-1} day^{-1} of Co and no value was observed in Cr with mean CDI (mg kg^{-1} day^{-1}) of heavy metal via rice grain(2021) ingestion was in order: Pb (0.000933) > Ni (0.000290) > Cd (0.0000161) > Co (0.0000133) (Table.5). Maximum permissible limits (mg kg^{-1} day^{-1}) of Cd, Pb, Ni, Co and Cr through ingestion of vegetables are 0.2, 0.3, 67.9, 50 and 0.1 respectively. Results of the present study revealed that mean CDI of metals through ingestion was lower than the threshold CDI values.

Table 5. Chronic daily intake (mg kg-1 day-1) of heavy metals via ingestion of rice grain

Statistics	Metals				
	Ni	Pb	Cd	Cr	Co
Min.	0.0000707	0.0000454	0.0000050	0	0.0000303
Max.	0.0003787	0.0001363	0.0000252	0	0.0000606
Mean	0.000290	0.000933	0.0000161	0	0.0000133

Total Hazard Quotient (THQ) of heavy metals via ingestion of wheat grain

The THQ of individual heavy metal to the target population via ingestion of wheat grain (2021) was in the range of 0.01641- 0.03105 (Ni), 0.01587– 0.1197 (Pb), 0.01683 – 0.03535 (Cd) and 0.1851 – 0.5723 (Co)). The mean value of overall THQ of individual heavy metal to the target population via ingestion of wheat grain (2021) was in the order: Co(0.42248) > Pb (0.04746) > Cd (0.0274) > Ni (0.02178) and Cr value was nil (Table 6). The THQ of studied heavy metals was less than unity thus their daily intake via ingestion of wheat grain is unlikely to cause adverse health effects to target population.

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Table 6 Total hazard quotient of heavy metals via ingestion of wheat grain

	Ni	Pb	Cd	Cr	Co
Min.	0.01641	0.01587	0.01683	0	0.1851
Max.	0.03105	0.1197	0.03535	0	0.5723
Mean ± SD	0.02178	0.04746	0.0274	0	0.4224

Total Hazard Quotient (THQ) of heavy metals via ingestion of rice grain

The THQ of individual heavy metal to the target population via ingestion of rice grain (2021) was in the range of 0.003535- 0.018938 (Ni), 0.0129– 0.0389 (Pb), 0.00168 – 0.0134 (Cd) and 0.101 – 0.185 (Co)). The mean value of overall THQ of individual heavy metal to the target population via ingestion of wheat grain (2021) was in the order: Co (0.1565) > Pb (0.026688) > Cd (0.0054) > Ni (0.01451) and Cr value was nil (Table 7). The THQ of studied heavy metals was less than unity thus their daily intake via ingestion of rice grain is unlikely to cause adverse health effects to target population.

Table 7: Total hazard quotient of heavy metals via ingestion of rice grain

Statistics	**Metals**				
	Ni	Pb	Cd	Cr	Co
Min.	0.003535	0.0129	0.00168	0	0.1010
Max.	0.01893	0.0389	0.0134	0	0.1850
Mean ± SD	0.01451	0.02668	0.0054	0	0.1565

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