Heavy Metals in Agricultural Soils and Level of Contamination with Crop Production

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Abstract
Heavy metals (HM) can be defined as metallic elements that are greater than 40 in atomic weight and above 5 g/cm^3 in specific gravity and cause abnormal effects on the biota at low concentrations. This study aimed to assess the levels of HM contamination in soils and unpolished rice grains (*Oryza sativa*) at three separated paddy cultivation fields in Anuradhapura, Gampaha, and Jaffna over one consecutive season. The concentrations of arsenic (As), cadmium (Cd), and lead (Pb) were detected using inductively coupled plasma mass spectrometry (ICP-MS). According to the results, HM concentrations of As and Pb in the soil for all studied fields were below the maximum permissible limits (MPL) set by the World Health Organization/Food and Agriculture Organization (WHO/FAO). However, Pb content in rice grains was high in all stations relative to the MPL for crops given by WHO/FAO. The results revealed that Cd has exceeded MPL of both soil and grains in the Jaffna paddy field according to the WHO/FAO guidelines and Cd has a high transfer factor (TF>0.27) from soil to grain among all concerned agricultural lands. Other heavy metals have lower TF values (0.001 to 0.131). Regarding the contamination factor, As, Cd and Pb showed a moderate level of contamination severity over three regions.

Keywords: Agricultural soil, Contamination factor, Heavy metal, Rice grain, Transfer factor

1 Introduction

Heavy metals (HMs) refer to metallic chemical elements with high density, which can be hazardous and toxic even at low concentrations [1]. Human populations face potential risks of exposure to heavy metals through various pathways, including the consumption of rice, vegetables, and water, as well as inhalation of airborne particles containing these toxic elements [2]. Due to their high atomic weights and densities, these toxic elements can persist in the environment for extended periods, adversely affecting soil quality, agricultural productivity, and ultimately human health [3].

The exposure of individuals to heavy metals through agricultural foods is influenced by various factors, including food preparation, processing, and consumption practices specific to different cultural contexts. While heavy metals can naturally occur in soil and water, they can also be introduced through agricultural practices involving fertilizers, pesticides, and other chemicals. Deep well water in Sri Lanka is generally known to be free from heavy metal contamination [4]. Nevertheless, the presence of heavy metals in food remains a potential contributing factor to the prevalence of chronic kidney disease of unknown etiology (CKDu) among the population in Sri Lanka [2].

Table 1: MPL of heavy metals in soil and rice (WHO (1996)) [5] (mg/kg)

Heavy metals	**As**	**Cr**	**Cd**	**Pb**	**Cu**	**Co**	**Ni**
Soil	20	100	0.8	85	36	10	35
Rice	0.2	1.3	0.4	0.3	20	0.01	0.1

2 Methodology

2.1 Study Area

For this research, three distinct paddy-cultivating fields were selected as the study area for sampling. Each of these areas possesses unique geological and climatic formations, contributing to the diversity of the research findings (Fig. 1).

Figure 1: Landsat / Copernicus satellite images of the study areas

1. Paddy field in Jaffna (P^J): This zone is a flat terrain that belongs to the dry zone in Sri Lanka, characterized by Grumusol cover which is a saline alkaline soil (pH>7.5). Ca^{2+} is the dominant cation in this soil. There is a very low saturated hydraulic conductivity. Grumusol has been recognized as the highest clay mineral contained soil class according to the soil classification in Sri Lanka [6].

2. Paddy field in Anuradhapura (P^A): The landscape condition of this area is an undulating terrain which is comprised of reddish-brown earth in upper crests and low humic gley soils in lower valleys [7]. This region is in the dry zone of the country, known for its distinct climatic conditions characterized by low rainfall and high evaporation rates.

3. Paddy field in Gampaha (P^G): Situated in the wet zone of the country and experiences high levels of rainfall and approximately room temperatures. The soil class of the specific site can be categorized into the alluvial soil class which has been subjected to flood within the past decade.

All the above paddy fields receive irrigated water and rainwater but the common source of irrigated water for the dry zone are large water tanks while the wet zone is rivers, canals, and sub-water streams.

2.2 Sample collection

It involves gathering soil and rice grain samples from selected study areas.

Two sets of samples were collected during the research. The first set comprised 18 soil samples taken before cultivation from a depth of 0-15 cm in the selected study areas. The second set included 18 soil and 18 rice grain samples (approximately 25 g) collected after harvesting from the same depth for each District. Two sets of samples were taken to find out whether there had been an accumulation of heavy metals in the soil due to fertilizers and insecticides applied during that time.

2.3 Preprocessing of soil samples

2.3.1 Drying the soil samples

Upon collecting the soil samples, the first step in the sample preparation process was drying them to remove any moisture that could potentially affect the accuracy of subsequent analyses.

2.3.2 Size reduction

Soil: The soil sample analysis commenced with an initial size reduction, breaking down larger chunks using a hammer. Subsequently, meticulous mixing ensured uniformity among smaller soil particles. Employing the coning and quartering method, the mixed soil formed a conical pile divided into four equal portions, one of which, precisely 200 grams, underwent grinding in a TEMA mill at 1000 rpm for 60 seconds. After grinding, 180 g of the sample was measured and sieved through a standard 63 µm sieve using an electrical sieve shaker for 2 minutes, effectively separating finer from coarser particles. The fine fraction, which passed through the sieve, was collected for further analysis.

Grain (rice): Initially, rice ears were threshed meticulously to remove the husk, leaving behind only the unpolished rice grains. Subsequently, these unpolished grains underwent air drying to eliminate excess moisture, a critical step to maintain the integrity of the analysis. Once dried, the rice grains were carefully milled, transforming them into powdered rice, a suitable form for subsequent analysis. To ensure consistency in particle size and uniformity within the sample, the powdered rice was then passed through a handheld flour sifter. Finally, the rice sample that successfully passed through the screening process was collected for further analysis.

2.4 Digestion

The digestion process involved breaking down the samples using chemicals to ensure the metals of interest were in a soluble and measurable form. Aqua regia, a powerful combination of acids (3 ml conc. HCl, 1 ml conc. HNO_3, and 1 ml conc. H_2O_2), was used as the digestion solution.

2.5 Sample analysing

The diluted samples were injected into the ICP–MS through an autosampler unit for testing metal content in the samples by using the EPA method 6020B.

3 Results and analysis

3.1 Heavy metal concentrations in soil samples

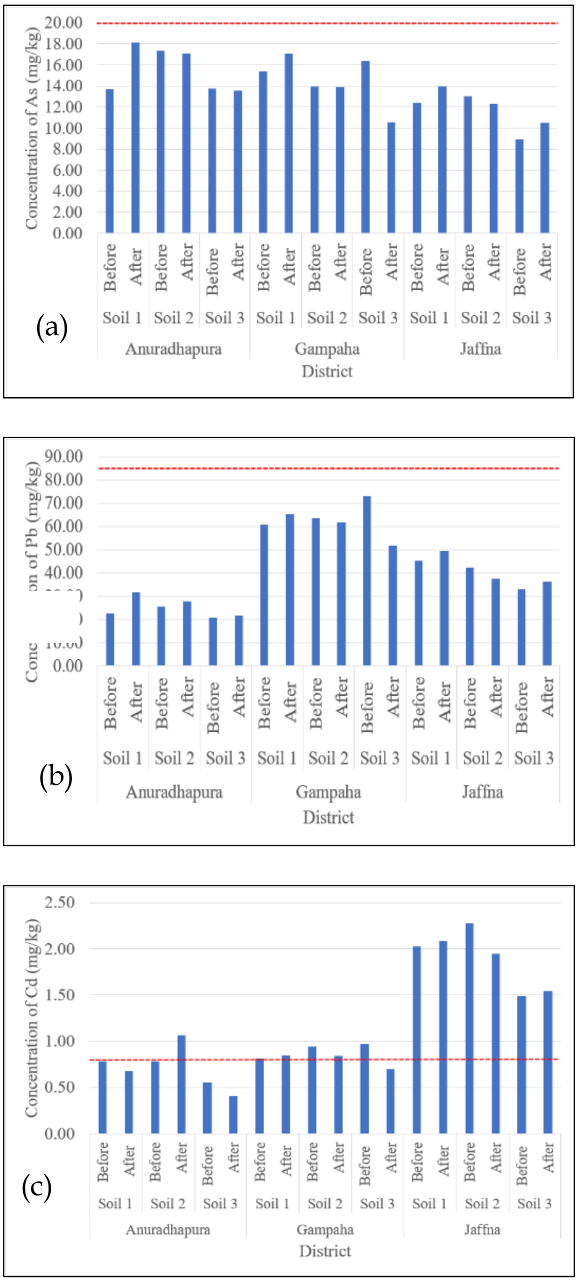


Figure 2: Total concentrations of As (a), Pb (b), and Cd (c) in soil [Red dotted lines; maximum permissible limits]

3.2 *Heavy metal concentration in rice grain samples*

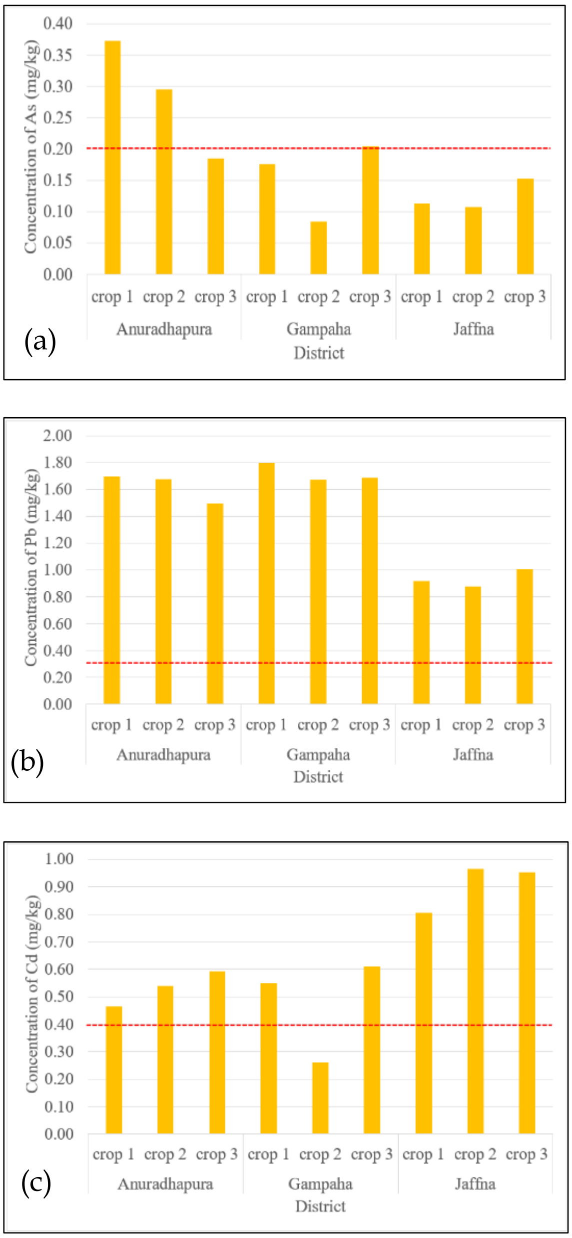


Figure 3: Total concentrations in rice grains for As (a), Pb (b) and Cd (c). [Red dotted lines; maximum permissible limits.]

3.3 Transfer factor (TF) [8] for the studied heavy metals

$$TF = \frac{\text{[Heavy metals] rice grains (mg/kg)}}{\text{[Heavy metal] soil (After) (mg/kg)}} \tag{1}$$

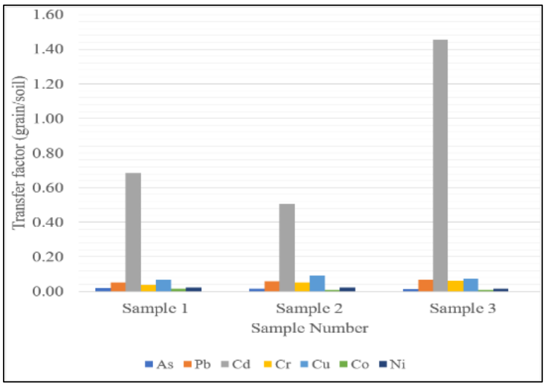


Figure 4: Transfer factor for Anuradhapura District samples

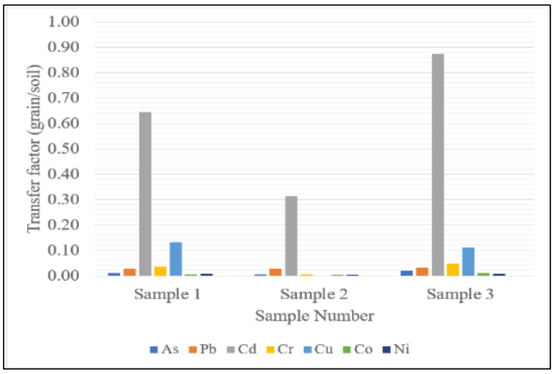


Figure 5: Transfer factor for Gampaha District samples

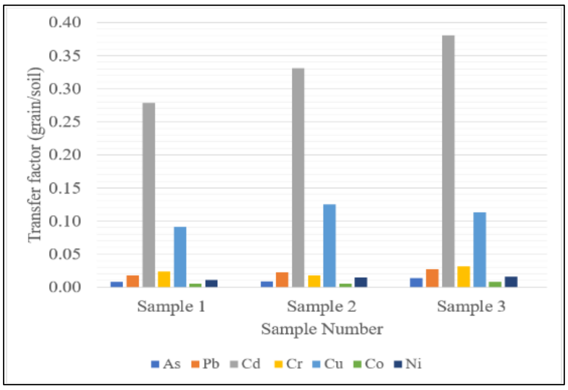


Figure 6: Transfer factor for Jaffna District samples

3.4 Contamination factor (CF)

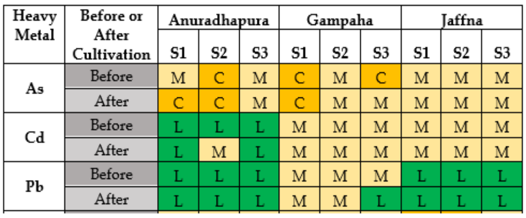
$$CF = \frac{Cm\ (sample)(\text{mg/kg})}{\text{Cm (background) (mg/kg)}} \tag{2}$$

Table 2: The four categories of contamination of CF [14]

Range	**Severity**
CF< 1	Low
1 < CF < 3	Moderate

3 < CF < 6	Considerable
CF > 6	High

Table 3: Severity results in soils



Heavy Metal	Before or After Cultivation	Anuradhapura			Gampaha			Jaffna		
		S1	S2	S3	S1	S2	S3	S1	S2	S3
As	Before	M	C	M	C	M	C	M	M	M
	After	C	C	M	C	M	M	M	M	M
Cd	Before	L	L	L	M	M	M	M	M	M
	After	L	M	L	M	M	M	M	M	M
Pb	Before	L	L	L	M	M	M	L	L	L
	After	L	L	L	M	M	L	L	L	L

L–Low, M–Moderate, C– Considerable
S1, S2 and S3 - Sample no. 1, 2 and 3.

4 Discussion

The results of the study indicate that there are significant abnormal site-specific contamination levels of As, Cd, and Pb in both soils and rice grains. As per WHO/FAO limits concentrations in soils of three locations are below the maximum permissible limit (MPL) (20 mg/kg). However, the threshold limit for agricultural soil which has been established by Finland based on European and Indian studies is 5 mg/kg for As [4]. This margin is critically lower compared to the obtained average As concentrations in soils before and after cultivation in Anuradhapura (P^A), Gampaha (P^G) and Jaffna (P^J) which are (14.91, 16.24), (15.24, 13.86) and (11.45, 12.23) in mg/kg respectively. Also, these values have significantly reached the MPL. There is an increment of As contamination in the soil after cultivation than before cultivation in (P^A), and (P^J) while there is a close gap between the two stages of soil in (P^G). Therefore, it seems to be a positive trend pattern of the As content in paddy soil versus time within a duration from growing to harvesting (fact [I]). As well as concentrations are approaching the MPLs for three soil types regarding the As (fact [II]). According to facts [I] and [II] it can be existed a common external source of As contains a significant concentration that accumulates with time in the soil.

In addition, the average concentration of As in P^A (0.28 mg/kg) in rice grain has exceeded the MPL (>0.2 mg/kg). P^A consists of low humic gley soils and no yield response of rice (*Oryza sativa*) to the added phosphorous (P) fertilizers at low humic gley soils in the dry zone of Sri Lanka and there is enough soil P available for a minimum of 11.5 years [9]. It may be a cause for an intensive application of (P) fertilizers. There are two main inorganic formations of As in soils such as arsenate [AsO_4^{3-}] and arenite [AsO_3^{3-}]. Arsenate is dominant in aerobic conditions while arenite [As^{3+}] is predominant compared to the arsenate [As^{5+}] in anaerobic conditions. Also, arenite is more toxic and mobile than Arsenate [10,11]. Rice is cultivated in anaerobic conditions in the paddy fields by letting them flood with irrigated water. Therefore, at low humic conditions mobility of ions can be increased and because of that [AsO_3^{3-}] can be transferred into the rice plant with a high amount under existing high As content in the soil at P^A.

Notably, average concentrations of Cd were higher than the MPLs [>0.8(soil), >0.4(grains)] (mg/kg) in (P^J) compared to the other two sites in soils at two occasions and rice grains. Those were 2.05 (before cultivation), 1.95 (after cultivation) in the soil, and 1.04 (rice grains) in mg/kg respectively. The selected site was in Jaffna and should most probably be Grumusol because this is the major soil type for irrigated rice in Jaffna and Mannar Districts and collected samples were dark greyish brown [7]. As per the key attributes of this soil type, saline and alkaline conditions (pH>7.5) in the soil may prevail during the cultivation period. Cd mobility is boosted at an acidic medium where pH is around 4.5 while mobility of As is increased at an alkaline medium [10]. Therefore, Cd which is added via external sources can be immobilized and retained in P^J with time relative to P^A and P^G (fact [III]). Also, Grumusols are in with a low saturated hydraulic conductivity (K_s) due to their high clay minerals ratio (fact [IV]). Along with that Ca^{2+} is dominant in this soil type (fact

[V]) [6]. If there is a high Ca^{2+} content in the soil, it can compete for adsorption sites [fact VI] [12]. Hence facts [III], [IV], [V] and [VI], it is probable that immobilized Cd compounds in Jaffna soil can be released into the soil solution as Cd^{2+} by Ca^{2+} cations at that alkaline medium and ultimately bioavailability of Cd can be increased of the rice plant.

Moreover, in situ, chemical compounds that contribute to increased soil salinity at P^J may represent high chloride ion (Cl^-) content. If there is a Cl^-based salinity in the soil the intake and upward transfer of Cd by rice can be boosted [12]. Also, Potassium (K) fertilizers such as KCl encourage further elevation of the Cl^- concentration in the paddy soil. Therefore, the high amount of Cd in rice grains at P^J may be a result of the intensive application of Cl^- containing amendments into the soil.

Pb concentrations in rice grains have been extremely exceeded the WHO limits in all three regions. There are many sources for Pb impurities which can come into the soil compared to the As and Cd such as from pesticides, soil enhancers, and combustion of fossil fuels by vehicles used for agricultural purposes [13]. Although there are numerous Pb-containing commodities available such as lead-acid batteries, and pesticides which are used abundantly, still there is no proper regulation for disposal. Also, the mean Pb competent in TSP is 252.5 mg/kg [11]. Therefore, a significant risk exists for Pb pollution in agricultural fields.

In Sri Lanka, excessive use of agrochemicals, including phosphate fertilizers, pesticides, fungicides, and organic manures, at rates higher than recommended by the Department of Agriculture, has been observed. This excessive agrochemical use may be responsible for the observed increase in Cd levels in certain fields [1].

5 Conclusions

The findings of this study indicate that the agricultural soils in selected sites are contaminated with heavy metals. As a result, it is crucial to implement measures to mitigate this contamination vital to safeguard soil health and protect human well-being. Mitigating heavy metal contamination in agricultural soils is vital for ensuring food safety and sustainable agricultural practices.

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