Exposure and Health (2023) 15:133–144
https://doi.org/10.1007/s12403-022-00481-5

ORIGINAL PAPER

Trace Elements and Arsenic Speciation of Field and Market Rice Samples in contrasting Agro-climatic Zones in Sri Lanka

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Received: 17 November 2021 / Revised: 23 February 2022 / Accepted: 12 April 2022 / Published online: 10 May 2022

Abstract

Rice is a major source for micro-elements for the Sri Lankan population, across all agro-climatic zones. This current study was conducted to investigate the variation of the metal(loid)s and As speciation in rice grains collected from wet, intermediate and dry zones of Sri Lanka. Field rice (brown rice) and market rice (polished rice) samples were analysed for total elemental profile and As speciation using ICP-MS and IC-ICP-MS, respectively. As, Cd, Co, Fe, Mn, Mo, Rb, Se, Sr and Zn in field grain samples varied across climatic zones. Highest median Cd, Cu, Mo, P, Rb, Se and Zn from wet zone; Co, Fe, Mn from intermediate zone; and As and Sr from dry zone were reported. Field rice (As, 0.3%; Cd, 1%) and market rice (As, 0%; Cd, 3%) samples exceeded maximum permissible levels of As and Cd. However, higher concentrations of both fields, 18% samples for As and 21% samples for Cd, and market, 7% samples for As and 38% samples for Cd, rice exceeded the recommended permissible levels of As and Cd in infant food according to EU regulations. The high per capita consumption and the chronic exposure to As and Cd through rice may cause adverse effects on Sri Lankan children and adults.

Keywords Rice · Sri Lanka · Climatic zones

Introduction

Sri Lanka is a tropical island located in the Indian Ocean and offers diverse agronomic growing conditions due to its geographical and climatic variability. The island is characterized by a flat coastal belt and an elevated central mountain tract. The mountainous centre acts as a barrier to the monsoon winds that brings the rain. Two monsoon seasons, the south-western and north-eastern, occur between May–October and December–March, respectively. The island is divided into three distinct climatic zones namely, wet, intermediate and dry zones (Alahacoon and Edirisinghe 2021; Jayawardane and Weerasena 2001). The boundaries of these climatic zones are demarcated not only by considering not only the rainfall distribution, but also the agricultural land use, distribution of forest species, topography and soil profile (Panabokke 1996).

Rice is the staple food of Sri Lankans, with an average per capita consumption across the entire population of ~ 300 g/day (Hu et al. 2016). Paddy rice is cultivated throughout the country under very contrasting environmental and soil conditions (Wickremasinghe and Wijewardena 2000), in two production seasons: Yala, and Maha (Panabokke et al. 2002). In the wet zone, paddy cultivation mainly depends on rainwater, whereas in the dry and intermediate zones, it depends on both rainwater and irrigated water from man-made reservoirs. Irrigation relies on both small and large irrigation systems, i.e. those constructed by the local farmers to tap nearby water resources and regional government larger irrigation systems (Panabokke et al. 2002; Mahatantila et al. 2008). The soil chemistries differ greatly between zones, with dry zone soils being of higher pH and elevated in salts, and wet zone soils with lower in pH and leached with respect to base cations (Sanjeevani et al. 2013; Rathnayake et al. 2015; Rubasinghe and Gunatilake 2016).

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Grain crops in general, and including rice, can be elevated in the renal toxicant and carcinogen Cd (Aoshima 2016; Shi et al. 2020), while rice is specifically elevated in As, a carcinogen (Williams et al. 2007). Cd is mobile under aerobic soil conditions and is elevated in rice during grain fill when paddies are allowed to dry out in the preparation for harvesting (Hussain et al. 2021; Yan et al. 2021). Contrastingly, As is mobilized under reduced conditions in soil and, hence, paddy rice is specifically elevated in this element (Arao et al. 2011; Hussain et al. 2021). There are two dominant arsenic species in grain, inorganic As (the sum of arsenate and arsenite) and dimethylarsinic acid (DMA), and these vary in rice grain globally (Carey et al. 2019). It is for inorganic As that rice is regulated as it is considered the primary concern, being a carcinogen (WHO 2014; Tchounwou et al. 2019). DMA is produced by soil microbes, and its presence in rice grain is stimulated by the organic matter content of soil, drives the reducing conditions of soil and subsequent stimulation of methylating bacteria (Hossain et al. 2021). Rice grain also contains elements essential to plants and to humans (Sha et al. 2017; TatahMentan et al. 2020). Metal(loid) profiles and As speciation of Sri Lankan field and market rice samples in different agro-climatic zones under different soil characteristics have not been extensively studied before. However, different research groups have studied certain elements (i.e. As, Cd, Pb and Hg) in Sri Lankan rice, relating their abundance and ingestion through rice to possible chronic diseases or paddy management systems (Fernando et al. 2020; Herath et al. 2018; Liu et al. 2020; Navarathna et al. 2021).

We hypothesise that the different agronomic zones of Sri Lanka may lead to contrasting mineral nutrition due to different cultivation techniques and soil chemistry should lead to different grain nutrition, particularly for As speciation and Cd. The objective of this study was to investigate the variation of the element distribution and the As speciation in field and market rice grains collected from different climatic zones in Sri Lanka.

Materials and Methods

Collection of Rice Samples and Preparation

Field grain samples ($n = 292$) were collected from paddy fields across Sri Lanka, representing climatic zones: dry ($n = 132$), intermediate ($n = 85$) and wet ($n = 75$). Sampling locations and different climatic zones are given in Fig. 1. Grains were removed from three panicles from three different plants separated 5 m apart by length, from the centre of each field of the same sapling location. Samples were bulked and transferred into brown paper bags and stored at room temperature until further processing. Collected samples were catalogued and a unique sample code was assigned for each sample. The location of the paddy field and relevant information were recorded. Once the samples were transferred into the laboratory, they were stored at room temperature. Market rice samples, designated for human consumption, were collected from multiple areas covering the whole island. Location, rice type according to local market descriptions, was recorded. Samples were catalogued and stored at room temperature. Field collected rice grain samples were manually de-husked. Prior to chemical analysis, samples were freeze dried using a freeze dryer (Christ Alpha 1-4 LD Plus). Dried samples were milled for 3 min at 500 rpm (Retch PM100 rotary ceramic ball mill).

Elemental Quantification

Powdered sample (~ 100 mg) was weighed out into 50 ml polypropylene centrifuge tubes and the weight was recorded to four significant figures. Nitric acid (2 ml, 69% (V/V), VWR Aristar) was added to each centrifuge tube. The same volume of nitric acid was added to three tubes, each designated as blanks and for appropriate certified reference materials (CRM), NIST 1568b. Tubes were vortexed briefly and left overnight to soak, and hydrogen peroxide (2 ml, 30% (V/V), VWR Analar Normapur) was added to each centrifuge tube following day. Samples were digested using microwave digester (CEM Mars 6 1800 W) for 30 min at 95 °C. The selected programme heated the samples up to 95 °C gradually through a two-stage process, digesting/extracting at 95 °C for 30 min. Heat from ambient to 55 °C in 5 min, hold for 10 min, heat to 75 °C, hold for 10 min, heat to 95 °C in 5 min, hold for 30 min. The digestate on cooling, internal standard (Fluka Analytical Rhodium internal ICP-MS standard) was added, and accurately volumed up to 30 ml with deionized water.

Eight standards, including a blank, were made up in the range 0–100 µg/l using Multi-Element 2 (SPEX CLMS-2 Multi-Element Solution 2, matrix: 5% HNO_3) and Multi-Element 4 (SPEX CLMS-4 Multi-Element Solution 4, matrix: water/Tr-HF). The standard tubes were made up to their final volume (50 ml) with HNO_3 (1% (V/V)). Rhodium was used as the internal standard (Fluka Analytical Rh internal ICP-MS standard) and was present in all standards and samples at 10 µg/l. From the extracts, 10 ml was poured into 15 ml polypropylene tubes to be placed into the autosampler (Cetac ASX-520 Auto-Sampler) in a predetermined random order. Analysis of the samples was carried out using ICP-MS (Thermo Scientific iCap Q ICP-MS). The ICP-MS operating conditions were forward RF power 1550 W, nebulizer gas flow was ~ 1 L/min and the nebulizer liquid sample flow rate was ~ 0.35 ml/min. Helium was used as the collision gas at a flow rate of ~ 4.0 ml/min. A full scan of 30 elements was conducted, using three replicates per sample,

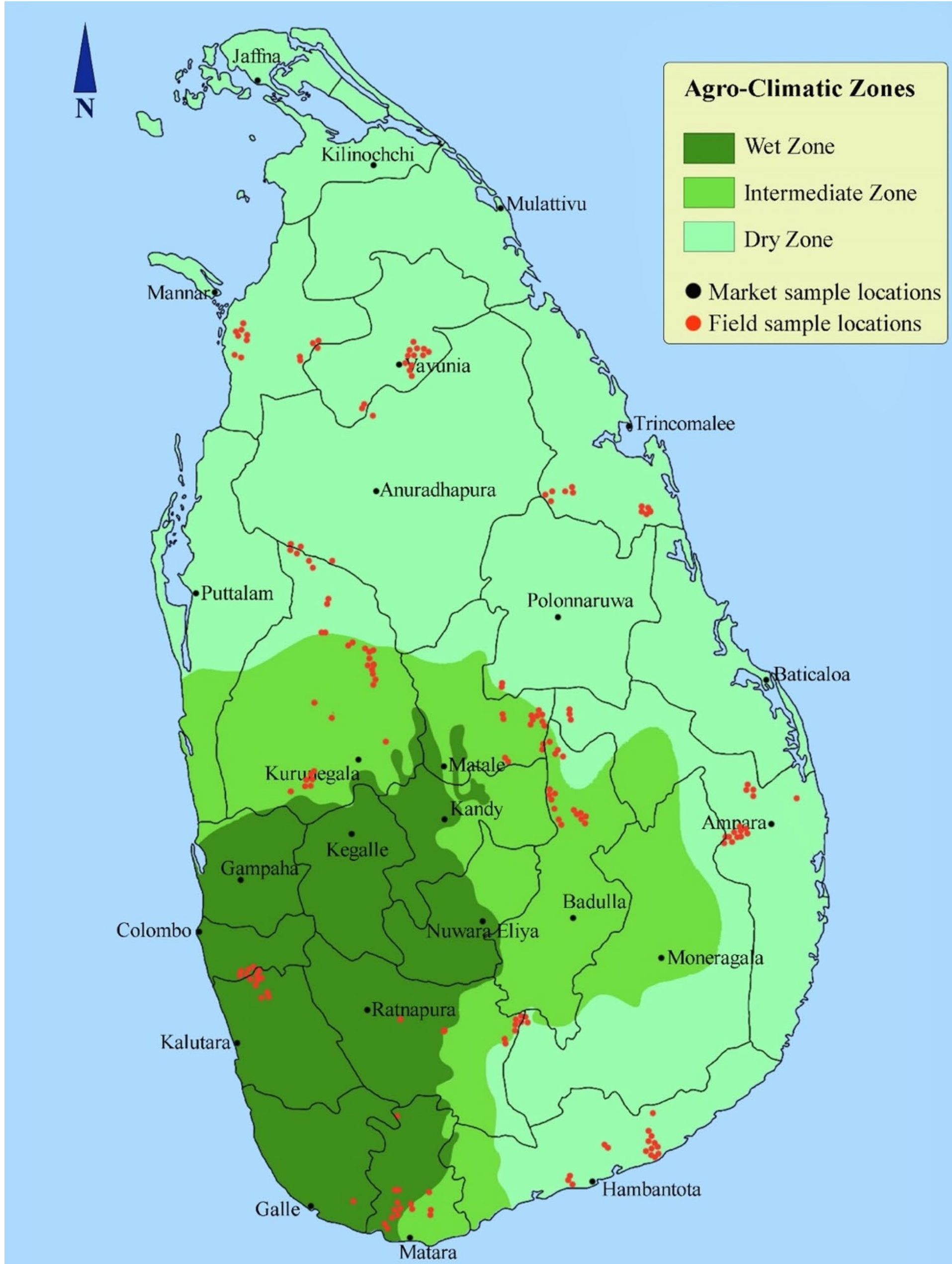

Fig. 1 Sampling locations for field and market rice. The map was prepared by the authors using data from the Department of Meteorology, Sri Lanka

giving a total analysis run time of approximately 4.5 min per sample. Samples were analysed by comparison to the standards previously mentioned. Only those elements giving a suitably precise calibration and an acceptable CRM recovery were reported (Table 1).

As Speciation Quantification

Powdered sample, (~ 100 mg) was weighed out into 50 ml polypropylene centrifuge tubes and the weight was recorded to four significant figures. Three additional tubes were used as blanks and three for CRMs. For As speciation NIST SRM 1568b rice flour was used. Nitric acid (1% (V/V), 10 mls) was pipetted into each tube and the tubes were swirled briefly. Centrifuge tubes were then placed into the carrousel for the microwave digester (CEM Mars 6 1800 W) and the appropriate digestion programme was selected. Samples were heated up to 95 °C gradually through a two-stage process, digesting/extracting at 95 °C for 30 min: heat from ambient to 55 °C in 5 min, hold for 10 min, heat to 75 °C, hold for 10 min, heat to 95 °C in 5 min, hold for 30 min. After cooling, each tube was made up to the final weight (10 g) with 1% (V/V) nitric acid. The precise weight of this was recorded. Tubes were

Table 1 Rice flour CRM (NIST 1568b) recovery and LoD (mg/kg) for each element/species ($n = 29$)

Element	Field rice survey LoD (mg/kg)	Market rice survey LoD (mg/kg)	% CRM recovery
As	0.0179	0.0132	81
Cd	0.0064	0.0098	78
Co	0.0131	0.0131	88
Cu	0.169	0.645	85
Fe	8.44	2.11	103
Mn	0.923	0.280	91
Mo	0.0939	0.0645	107
P	20	28.1	76
Rb	0.0715	0.0715	96
Se	0.00481	0.0207	61
Sr	0.125	0.129	
Zn	2.37	1.68	66
As species analysis			
DMA	0.000374	0.000556	103
MMA			104
As (V)			109
Sum of species			107

centrifuged at 4500 rpm for 20 min at 20 °C, using Sorvall Legend RT centrifuge.

Digested sample (700 μl) was transferred to a 2 ml polypropylene vial and finally hydrogen peroxide (7 μl, 30% (V/V), VWR Anaar Normapur) was added. The vial contents were thoroughly mixed and arranged into trays according to predetermined random run order and placed in the auto-sampler. A Thermo Dionex IC5000 Ion Chromatograph system with Dionex IonPac AS7 RFIC analytical column (2 × 250 mm) and Dionex AG7 guard column was used for the analysis. Mobile phase A consisted of 20 mM ammonium carbonate in deionized water and the mobile phase B consisted of 200 mM ammonium carbonate in deionized water. The flow rate was 0.3 ml/min using 100% mobile phase A when time = 0 min, followed by a linear change to 100% mobile phase B when time = 15 min, and finally followed by a linear change to 100% mobile phase A when time = 15.5 min. A DMA dilution series was used to calibrate the arsenic species quantification.

Statistics

All statistical analyses were performed using SPSS ver. 26.0 (IBM Inc., USA). The Kruskal–Wallis test was used to compare the medians between sample groups. Graphs were made using Prism GraphPad version 9.2.0 for Windows, GraphPad Software, San Diego, California USA.

Results

Analytical performance was evaluated by analysing the percentage recovery values of certified material for each element. The CRM (NIST 1568b) recoveries are shown in (Table 1). Selenium gave the poorest recovery (61%), followed by Zn (66%) but the results were included considering its importance to the diet, but the Se and Zn data must be interpreted with caution due to the low recovery. Strontium was reported even though absent in the CRM as it was diagnostic of the agroeconomic zones, and like Se and Zn, its absolute concentration must be treated with caution.

Metal(loid)s concentrations in field rice samples across climatic zones are given in Fig. 2. Highest median grain Cd (0.359 mg/kg), Cu (2.46 mg/kg), Mo (0.633 mg/kg), P (1961 mg/kg), Rb (13.3 mg/kg), Se (0.0372 mg/kg) and Zn (13.6 mg/kg) were detected in wet zone samples while lowest median Co (0.0358 mg/kg), Fe (11.4 mg/kg), Mn (16.9 mg/kg) and Sr (0.301 mg/kg) were found in the samples collected from the same zone. Intermediate zone samples showed the highest median Co (0.0842 mg/kg), Fe (13.4 mg/kg), Mn (20.5 mg/kg) and lowest median As (0.0473 mg/kg), Mo (0.442 mg/kg) and P (1873 mg/kg). Dry zone samples showed the highest median As (0.0717 mg/kg) and Sr (0.571 mg/kg) and lowest Cd (0.0125 mg/kg), Rb (4.96 mg/kg), Se (0.0166 mg/kg) and Zn (11.3 mg/kg). All metal(loid)s significantly differed across climatic zones, ($p < 0.001$), except Cu ($p = 0.385$) and P ($p = 0.512$) (Table 2). Inorganic As (As_i) was detected as the major As species in all field collected samples and DMA was detected as the major organic As species such as monomethyl arsenic acid (MMA) and tretramethylarsonium (Tetra) which were detected below LoD in all rice samples. DMA was found below LoD in 5% of the analysed rice samples. Median As_i concentrations were in wet zone (0.0588 mg/kg), intermediate zone (0.0438 mg/kg) and dry zone (0.0667 mg/kg), respectively (Fig. 3). Grain As_i concentrations vary across climatic zones ($p < 0.001$). Pairwise comparison showed that grain As_i varied significantly between wet-intermediate ($p = 0.028$) and intermediate-dry ($p < 0.001$) zones. Median DMA concentrations in wet zone, intermediate zone and dry zone were 0.00207 mg/kg, 0.00274 mg/kg and 0.00336 mg/kg, respectively. The distribution of DMA ($p = 0.002$) was significantly varied across agro-climatic zones. Pairwise statistical comparison (Table 2) showed that grain DMA content was significantly varied between wet–dry ($p = 0.016$) and intermediate-dry zones ($p = 0.001$).

Figure 4 shows Cd, Fe, Se, Zn and As speciation (As_i and DMA) in market rice (polished rice) samples in

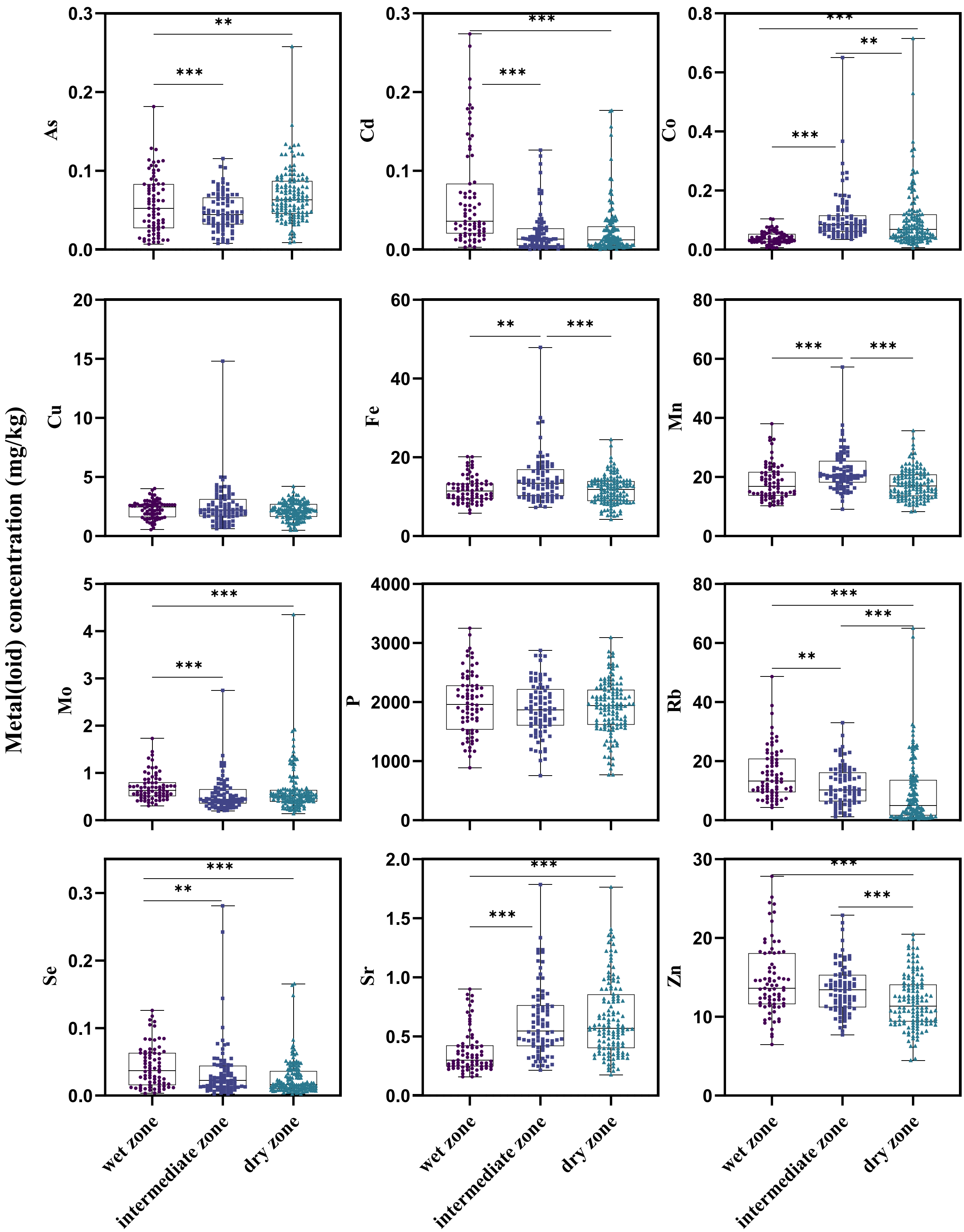

Fig. 2 Median concentrations of field rice grain metal(loid)s across different climatic zones. Bars represent the 25th and 75th percentiles. Differences between medians are shown by $p \leq 0.05$*, $p \leq 0.01$**, $p \leq 0.001$***

Table 2 Summary of Kruskal–Wallis test for the rice samples of different agro-climatic zones

Element	Overall analysis probality	Pairwise comparison probabilities between agro-climatic zones		
		Wet-intermediate	Intermediate-dry	Wet–dry
DMA	0.002	0.399	0.016	0.001
As_i	< 0.001	0.028	< 0.001	0.051
Sum of As species	< 0.001	0.092	< 0.001	0.025
Cd	< 0.001	< 0.001	0.972	< 0.001
Co	< 0.001	< 0.001	0.004	< 0.001
Cu	0.385			
Fe	0.001	0.002	< 0.001	0.926
Mn	< 0.001	< 0.001	< 0.001	0.605
Mo	< 0.001	< 0.001	0.098	< 0.001
P	0.512			
Rb	< 0.001	0.012	< 0.001	< 0.001
Se	< 0.001	0.01	0.091	< 0.001
Sr	< 0.001	< 0.001	0.601	< 0.001
Zn	< 0.001	0.314	< 0.001	< 0.001

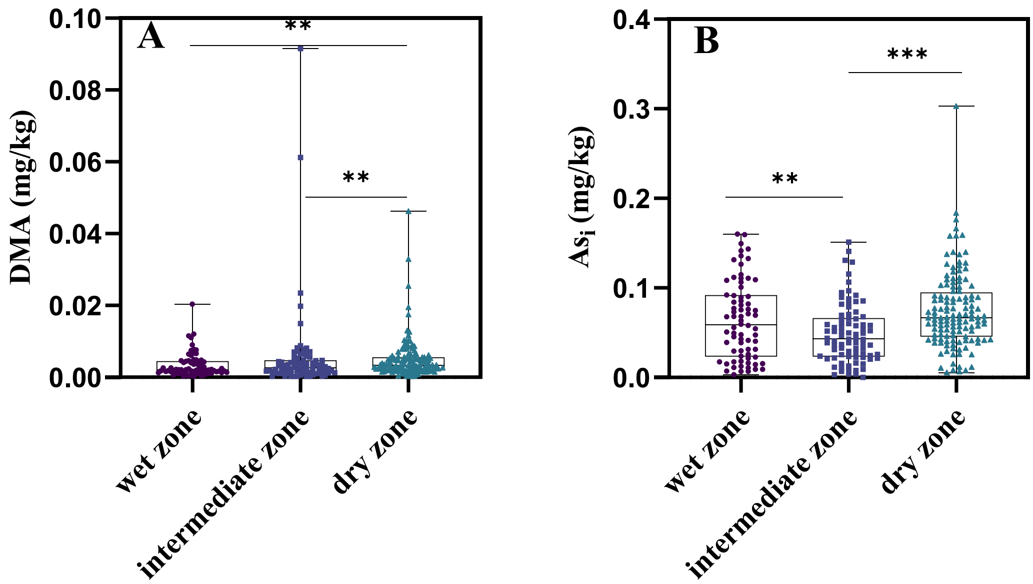

Fig. 3 Median concentrations of inorganic (**A**) and organic As (**B**) concentrations in field rice samples across agro-climatic zones. Bars represent the 25th and 75th percentiles. Differences between medians are shown by $p \leq 0.05$*, $p \leq 0.01$**, $p \leq 0.001$***

different agro-climatic zones. Essential elements (Fe, Se and Zn) and micropollutants As and Cd were considered in this analysis because of its importance in human diet. Highest Cd (0.0350 mg/kg), Se (0.0441 mg/kg), Zn (11.5 mg/kg) and Fe (7.94 mg/kg) lowest As_i (0.0305 mg/kg) were reported from wet zone. Highest DMA (0.00507 mg/kg) and lowest Cd (0.0270 mg/kg) and Fe (5.40 mg/kg) were reported from intermediate zone. The highest As_i (0.0405 mg/kg) and lowest Se (0.0398 mg/kg) and Zn (10.2 mg/kg) wre reported from dry zone.

Distribution of grain metal(loid)s in market rice across climatic zones follows the similar pattern of field rice, however, the distribution of metal(loid)s across climatic zones was not significant. As speciation and Cd concentration in pooled field and market samples are shown in Fig. 5. The median total As in field rice and market rice was 0.0560 mg/kg and 0.0456 mg/kg, respectively. The maximum As content detected in field rice was 0.258 mg/kg and only 0.3% of field rice samples exceeded the maximum allowable limit of inorganic As (0.25 mg/kg) (EU 2015). However, 18% of the field samples exceeded maximum recommended level of As in infant food (0.1 mg/kg) (EU 2015). None of the market rice samples exceeded the maximum tolerable inorganic As levels (0.2 mg/kg) (EU 2015)

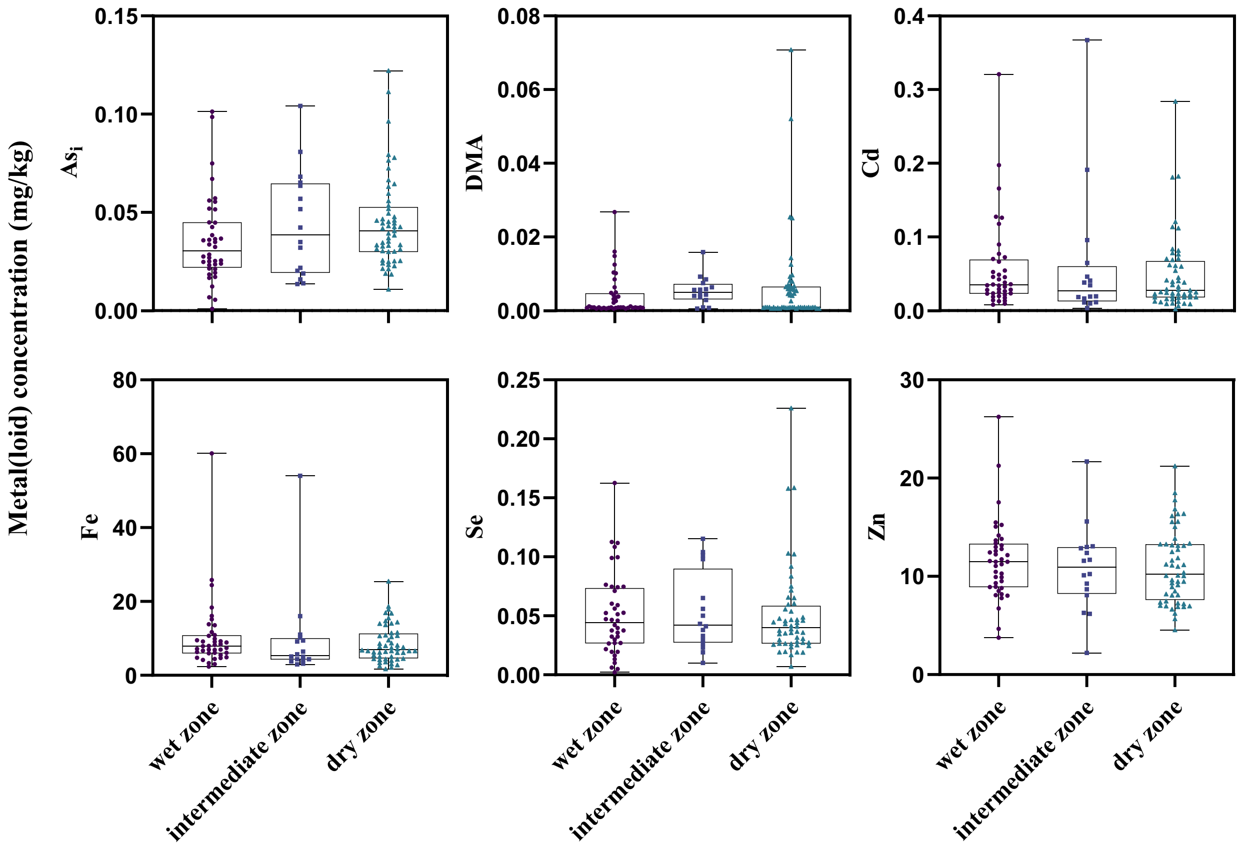

Fig. 4 Grain concentration (median, 25 and 75th quartile) of grain inorganic As, organic As, Cd, Fe, Se and Zn in market rice across different climatic zones. Bars represent the 25th and 75th percentiles

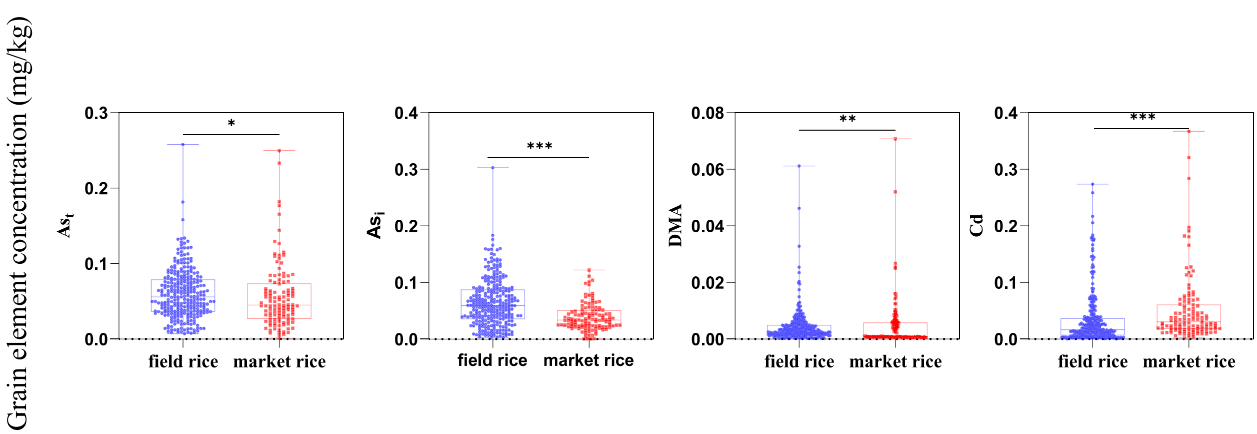

Fig. 5 Comparisons of median inorganic As (As$_i$), DMA and Cd concentrations in field rice (brown rice) and market rice (polished rice) samples collected from Sri Lanka. Bars represent the 25th and 75th percentiles. ($p \leq 0.05$*, $p \leq 0.01$**, $p \leq 0.001$***)

while 7% of market rice samples exceeded maximum permissible As level in infant food. Median Cd in field rice was 0.0166 mg/kg and was 0.0303 mg/kg in market rice samples. Field rice samples (1%) and Market rice samples (3%) of polished rice exceeded the maximum permissible Cd level in rice (0.2 mg/kg) (Commission Regulation 2006). Field rice samples (21%) and market rice samples (38%) exceeded the permissible Cd level in baby food (0.04 mg/kg) (Commission Regulation 2006). Total grain As (As_t) ($p = 0.030$), As_i ($p < 0.001$), DMA ($p = 0.003$) and Cd ($p < 0.001$) were significantly varied between field and market rice samples.

Essential metal(loid)s (Fe, Se and Zn) in field collected and market rice, given that the field is wholegrain and market is polished rice, are given in Fig. 6. Median Fe content in field rice was 12.2 mg/kg and 7.46 mg/kg in market rice. Median Se content in field rice was 0.0218 mg/kg and 0.0431 mg/kg in market rice. Median Zn content in field rice was 12.6 mg/kg and 11.2 mg/kg in market rice. Grain Fe, Se and Zn contents in field and market rice varied significantly with a significant value $p < 0.001$. Median metal(loid)s concentrations in market rice grains belonging to different rice varieties from local markets are shown in Table 3. These results shows that grain element contents could also vary within different rice varieties. In particular, the red grains tend to have higher As and Cd compared to white.

Discussion

Field rice and market rice collected from Sri Lanka contained different metal(loid)s in various concentrations. Except Cu and P, all the other analysed grain element contents varied across climatic zones in field rice analysis. Both field and market samples analysis showed that median grain As, Cd, Fe, Se and Zn followed the pattern Zn > Fe > As > Se > Cd. Most of the studies on metal(loid)s in Sri Lankan rice have been limited to either on couple of elements or sampling has been restricted to a limited area (Jayasumana et al. 2015; Kariyawasam et al. 2016; Magamage et al. 2017; Edirisinghe and Jinadasa 2020). Only one study has been reported on the variations in grain elemental contents across the climatic zones. Diyabalanage et al. (2016) reported that highest median concentrations of Ba, Cd, Mn, Mo and Zn found in the wet zone field rice, and the highest median Cu, Fe, Ni, Se, Sr, from the dry zone field rice. Here, Co, Cr and Pb were highest in the intermediate zone field rice of Sri Lanka. The result from the current study agrees with most of the findings of Diyabalanage et al. (2016), except for the distribution of As, Cu, Mn and Se. Highest Cu and Mn concentrations were reported from the samples collected from the intermediate zone and the highest median Se was reported from wet zone samples. Highest median As was reported in dry zone in current study.

Uptake of metal(loid)s by rice plant depends on several factors such as availability of the element in soil, pH, Eh, water management and cultivar. (Zeng et al. 2011; Zhang et al. 2020). The major soil types in Sri Lanka vary with the factors such as climate, parent materials, topography, vegetation and living organisms and time or age of the landscape (Panabokke 1996). Variation of soil chemistry across different regions could occur due to geological reasons and anthropogenic activities (Wong et al. 2002; Chandrajith et al. 2005a). In Sri Lanka, wet zone is dominated by well drained, strongly acidic red-yellow podzolic and mountain regosols (Alwis and Panabokke 1972; Panabokke 1996) while alkaline, imperfectly drained, and moderately fine textured, reddish-brown earths are the dominant soil group in dry zone. (Alwis and Panabokke 1972). Contrasting pH between major climatic zones would play a crucial role for the differences in grain element distribution across those regions. Variations of pH in soil strongly effect on trace metal solubility, whatever they are induced by reductive dissolution, CO_2 formation and carbonate precipitation, organic acid formation or other processes (Charlatchka and

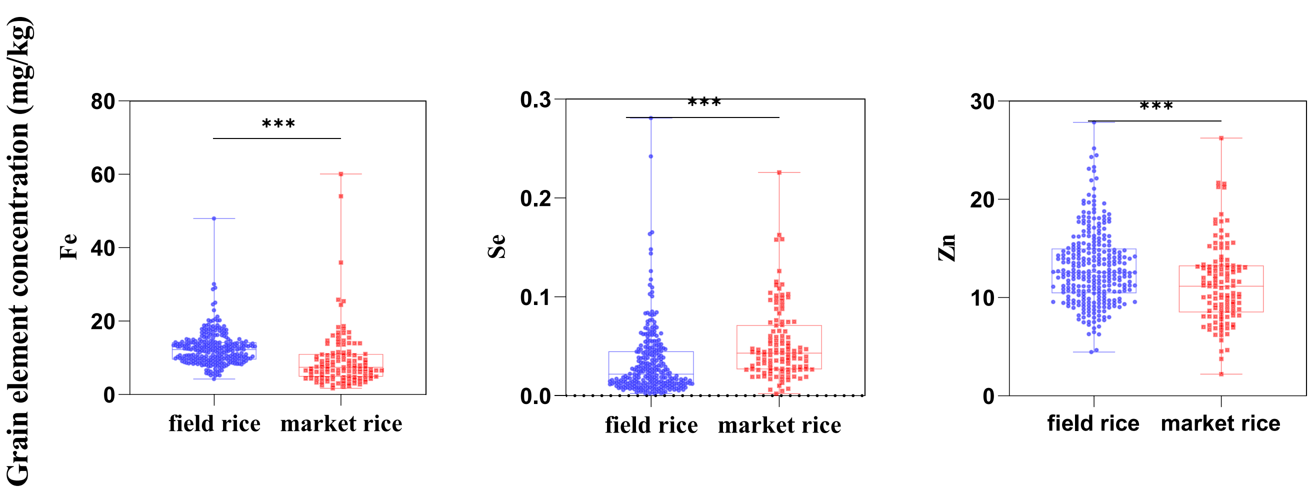

Fig. 6 Comparisons of Fe, Se and Zn concentrations in field rice (whole grain) and market rice (polished rice) samples collected from Sri Lanka. Bars represent the 25th and 75th percentiles. ($p \leq 0.05$*), $p \leq 0.01$**, $p \leq 0.001$***)

Table 3 Median, the range of metal(loid)s (mg/kg) in different rice varieties collected from different commercial markets in Sri Lanka

	As V	DMA	As	Cd	Co	Cu	Fe	Mn	Mo	P	Rb	Se	Sr	Zn
Red kekulu ($n = 13$)														
Median	0.0516	0.00494	0.0575	0.0773	0.0370	1.93	9.41	15.6	0.734	1734	5.13	0.0377	0.351	12.2
Minimum	0.0123	0.000740	0.00870	0.0111	0.0152	1.27	5.96	7.55	0.286	1122	1.73	0.0195	0.156	6.18
Maximum	0.0808	0.00926	0.177	0.367	0.0860	4.55	60.1	26.4	1.87	3764	27.1	0.101	0.599	21.7
Red kekulu samba ($n = 12$)														
Median	0.0472	0.00430	0.0637	0.0373	0.0438	2.17	9.40	18.4	0.735	2059	11.1	0.0466	0.419	14.3
Minimum	0.0167	0.0009	0.0135	0.0021	0.0222	1.46	2.50	9.00	0.198	664	3.61	0.0190	0.114	12.4
Maximum	0.111	0.0520	0.233	0.284	0.103	4.12	16.7	31.4	1.34	3636	18.0	0.158	1.63	26.2
Red nadu ($n = 14$)														
Median	0.0426	0.0009	0.0840	0.0687	0.0328	3.49	12.3	17.9	0.727	1950	7.76	0.0577	0.521	10.1
Minimum	0.0248	0.00074	0.0373	0.0235	0.0175	1.27	6.58	8.60	0.486	1245	1.03	0.0049	0.149	6.97
Maximum	0.101	0.0148	0.144	0.321	0.0801	5.69	25.8	41.0	1.309	3587	31.7	0.226	1.33	21.3
Rose kekulu ($n = 9$)														
Median	0.0445	0.0009	0.0441	0.0598	0.0267	2.15	7.96	10.4	0.674	1437	4.83	0.0367	0.288	9.91
Minimum	0.0185	0.000556	0.0136	0.0348	0.0187	1.62	3.99	7.54	0.492	1115	0.873	0.0163	0.0913	6.89
Maximum	0.0636	0.00850	0.101	0.166	0.0556	5.13	25.4	16.1	1.44	2348	13.8	0.104	0.506	21.2
Samba ($n = 20$)														
Median	0.0293	0.0009	0.0363	0.0229	0.0366	2.27	5.44	7.06	0.525	1057	9.93	0.0330	0.177	8.03
Minimum	0.0009	0.000556	0.0081	0.0092	0.0186	1.36	1.70	4.94	0.330	785	2.65	0.0022	0.0983	4.55
Maximum	0.0572	0.0104	0.111	0.0546	0.100	6.87	24.5	16.6	0.654	1299	13.6	0.108	0.495	13.0
White kekulu ($n = 18$)														
Median	0.034	0.0029	0.0422	0.0242	0.0386	2.23	6.32	11.1	0.584	1236	4.65	0.0406	0.237	11.7
Minimum	0.0056	0.000556	0.0062	0.0088	0.0098	1.07	3.57	7.48	0.381	945	0.535	0.0061	0.132	7.79
Maximum	0.122	0.0708	0.182	0.0459	0.119	4.45	17.8	16.1	2.07	2087	21.3	0.113	1.02	15.6
White kekulu samba ($n = 11$)														
Median	0.024	0.0009	0.0321	0.0115	0.0432	2.18	5.01	10.9	0.423	1141	4.14	0.0412	0.411	11.2
Minimum	0.0108	0.000556	0.0179	0.0035	0.0191	1.32	3.17	7.35	0.249	948	2.07	0.0168	0.145	8.07
Maximum	0.0664	0.00641	0.250	0.0783	0.0950	2.70	11.6	17.1	0.774	2372	11.4	0.0715	0.627	16.4
White nadu ($n = 12$)														
Median	0.0347	0.0009	0.0539	0.0235	0.0410	2.31	6.94	8.24	0.637	1316	10.3	0.0498	0.203	9.13
Minimum	0.0159	0.000556	0.0143	0.0095	0.0208	1.41	2.79	2.59	0.398	1018	2.24	0.0003	0.100	2.22
Maximum	0.1041	0.0161	0.129	0.120	0.110	3.74	54.0	17.7	0.997	2125	19.6	0.115	1.46	15.0
Traditional varieties ($n = 11$)														
Median	0.0154	0.000556	0.0178	0.0268	0.0612	2.37	10.3	17.5	0.499	2016	6.23	0.0878	0.459	12.7
Minimum	0.0006	0.000556	0.00135	0.0058	0.0137	0.960	2.62	10.6	0.241	835	1.88	0.0158	0.315	7.26
Maximum	0.0339	0.00359	0.0763	0.0584	0.152	5.22	36.0	28.4	1.13	3865	21.8	0.126	0.708	21.6

Cambier 2000). The wet zone paddy soil is subjected to prolonged flooding due to high rainfall compared to irrigated dry zone paddy field soil. Therefore, the wet zone soils are extremely reductive compared to dry zone paddy field soil (Chandrajith et al. 2005b). Studies have shown that reducing conditions increase the availability of certain elements in the soil and with prolonged submergence, these elements tend to be immobilized.

Grain Se contents depend both on soil Se level as and on soil properties such as soil organic carbon and clay mineral content (Fordyce et al. 2000). Several studies have shown that Se levels in rice grown in Sri Lanka can vary considerably even within the same climatic zone (Fordyce et al. 2000; Mahagama et al. 2020). Another study on locally grown, imported and traditional rice varieties collected from Kandy district have revealed that grain Se ranged between < 0.2 and 0.4706 mg/kg (Magamage et al. 2017). Some imported rice varieties contain high Se content compared to locally grown rice (Magamage et al. 2017). Zn deficiency is a common micronutrient deficiency prevailing among males, females, and children in Sri Lanka and the condition is related to their diet (Jayatissa et al. 2015). Zinc accumulation in rice was found to be inversely related to soil pH; the more alkaline soil pH, the less Zn uptake by rice (Yoshida and Tanaka 1969). Although adsorption and soil organic carbon control the amount of available Zn, due to high level of Zn in the soil also would result in high grain Zn level in wet zone rice. High levels of Sr in dry zone soil and high levels of Mo in wet zone samples also attribute to the high levels of those elements in the soil (Chandrajith et al. 2005a). Soil Rb is higher in dry zone paddy soils (Chandrajith et al. 2005a), however, the mobility of Sr decreases at higher pH, thus lower the grain Rb content (Kosla et al. 2002).

The concentration of the elements in rice grain does not only depend on the soil element concentration, but also on the availability of those elements in soil solution (Xie and Naidu 2006; Impa and Johnson-Beebout 2012). Grain As depend on plant-available P, poorly crystalline Fe, Si fertilizer and total C in soil (Bogdan and Schenk 2009). As is highly sensitive to redox changes in the soil. In reduced conditions, the bioavailability of As gets increased (Yamaguchi et al. 2011; Honma et al. 2016). However, a higher median concentration of As was reported from the dry zone. The pH-dependent dissolution of As is likely to occur due to high pH in dry zone paddy soil and elevated As in soil solution in dry zone (Podgorski et al. 2017). As accumulation in rice depends on the cultivar too (Hua et al. 2011; Islam et al. 2016). In both field and market rice, inorganic As was the dominant species. Carey et al. (2019) also found that Sri Lankan rice contained a very low content of DMA compared to samples collected from other main rice-growing countries across the world. The variation of DMA across argo-ecological zones could occur due to variation of factors such as pH, Eh and other soil elements which effect on microbial diversity in soil (Zhang et al. 2015). Availability of Cd is also governed by soil pH and Eh. Under reduced condition, Cd tends to precipitate as CdS or $CdCO_3$ (Zhang et al. 2012, 2020; Hussain et al. 2021). Application of $CaCO_3$ significantly reduces grain Cd concentration (Chen et al. 2018). This could attribute the low grain Cd concertation in the dry zone compared to the wet zone samples. Previous studies have shown that As and Cd exposure through rice exceeded recommended safe values in Sri Lankans (Edirisinghe and Jinadasa 2020; Liu et al. 2020). According to Liu et al. (2020), As in Sri Lankan market rice ranged between 0.019 and 0.217 mg/kg. Diyabalanage et al. (2016) have reported the As in Sri Lankan rice ranged between 0.0025 and 0.213 mg/kg (on DW basis). Both results were agreed with the results of current study (0.000916–0.353 mg/kg field rice, 0.000896–0.122 mg/kg market rice). Jayasumana et al. (2015), however, reported rice As concentrations ranged between 0.0266 and 0.54 mg/kg, in which the maximum values were higher than the values from current study. Liu et al. (2020) reported that market rice in Sri Lanka contained Cd ranged between 0.003 and 0.730 mg/kg. Edirisinghe and Jinadasa 2020 reported that rice As ranged between LOQ and 0.262 mg/kg (on WW basis). Median Cd content in market rice analysis agreed with the current study, however, the maximum values reported by Liu et al. (2020) were much higher than the results from current study.

Acknowledgements The Commonwealth Scholarship is thanked for AJDP's funding.

Author Contributions AJDP conducted the work and wrote the manuscript; MC assisted in chemical analysis; PMCSdeS helped design the study, collected field samples and was involved in manuscript preparation; CM was involved in the supervision of AJDP, study design and manuscript writing; AAM was involved in the supervision of AJDP, study design and manuscript writing.

Funding The authors have not disclosed any funding.

Data Availability Will be issued on reasonable request.

Declarations

Conflict of interest The authors have not disclosed any conflict of interest.

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