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Evaluation of Metal(loids) Concentrations in Soils of Selected Rice Paddy Fields in Malawi

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Abstract: The aim of this study was to obtain baseline data for heavy metal(loids) concentrations of rice paddy fields to evaluate the impacts of soil metal(loids) concentrations on quality of rice, and to identify sources of metal(loids) pollution of paddy fields in Malawi. In total, 66 soil samples were collected from 22 different smallholder rice farmers' paddy fields (sites) in Malawi. Concentrations of metal(loids) (arsenic (As), cadmium (Cd), cobalt (Co), chromium (Cr), manganese (Mn), lead (Pb), uranium (U), and gallium (Ga)) were measured using inductively coupled plasma mass spectrometry (ICP-MS) after acid block digestion with a mixture of concentrated nitric acid (70% HNO3) and hydrogen peroxide (30% H_2O_2). Measured soil metal(loids) concentrations were compared with Soil UK CLEA soil metal(loids) guidelines, maximum allowable limits (MAL) recommended by the World Health Organization (WHO), the Chinese Environmental Quality Standards (CEQS) for soil metal(loids) concentrations in agricultural soils, and the normally reported soil metal(loids) concentrations in agricultural fields worldwide. Results indicated that mean soil As (2.2 mg As kg^{-1}), Cd (0.044 mg Cd kg^{-1}), Pb (11 mg Pb kg^{-1}), Co (14 ± 6 mg Co kg^{-1}), Mn (601 mg Mn kg^{-1}), U (2.02 mg U kg^{-1}), and Ga (24 mg Ga kg^{-1}) concentrations were at least three times lower than the respective guidelines and MAL recommended by WHO, UK CLEA, and CEQS (20 mg As kg^{-1}, 0.3 mg Cd kg^{-1}, 32 mg Pb kg^{-1}, 50 mg Co kg^{-1}, and 2000 mg Mn kg^{-1}). The values obtained in this study were also within the normally reported metal(loid) concentrations for unpolluted agricultural soils worldwide. However, the mean Cr concentration (78.0 mg Cr kg^{-1}) obtained in this study was higher than that reported for agricultural soils in China (27 ± 5 mg Cr kg^{-1}; range: 22–39 mg Cr kg^{-1}) but was within the normally reported Cr concentrations (1–100 mg Cr kg^{-1}) for unpolluted soils. These findings suggest that metal(loids) concentrations of Malawian rice paddies pose no threat to production to elevated metal(loids) accumulation in rice, and that rice paddies should be safeguarded from contamination. However, further research is required to investigate the impacts of factors such as source of irrigation of water, water management regimes, soil cation exchange capacity, organic manure/composts amendments, and the application of inorganic fertilizers on uptake, transfer, and translocation of soil metal(loids) to various parts of rice plants, even when the soil metal(loids) concentrations are low.

Keywords: rice; soil; metal(loids); bioaccumulation

1. Introduction

Paddy field contamination with toxic metal(loids) such as arsenic (As), cadmium (Cd), cobalt (Co), chromium (Cr), manganese (Mn), lead (Pb), uranium (U), and gallium (Ga) poses a serious risk to rice farming and food safety worldwide [1]. Heavy metal(loids)

can not only negatively impact growth and physiological and biochemical processes of rice but can also accumulate in the soil and enter the rice through root absorption [2]. The heavy metal(loids) can then enter the human body through the food chain, thereby threatening human health. Furthermore, heavy metal(loids) contamination can also lead to the decline and deterioration of soil fertility and environmental quality, respectively [2]. Soil metal(loids) concentrations and soil conditions markedly influence the magnitude of metal(loids) accumulated in rice [3–10]. The accumulation of metal(loids) in rice grain is not only dependent on soil metal(loids) concentration but also on actual soil growth conditions [11,12]. For instance, Farrow et al. [13] reported a strong and positive linear correlation between soil As and grain As in rice grown under anoxic conditions. The observation confirmed that rice grain As accumulation is a function of soil As content, and that bioavailability of As in soil porewater significantly increases with soil As [14,15]. On the contrary, it was reported that rice grown under oxic soil conditions accumulated higher Cd, even when soil Cd was not significantly elevated [11,12].

Soil metal(loids) concentrations can be naturally high owing to elevated metal(loid) contents in parent rock or water bodies that supply water to the fields [16,17]. Long-term use of As-contaminated groundwater for irrigation has been linked to elevated As in rice and paddy soils of the Bengal region of India [18,19]. Elevated heavy metal(loids) concentrations in paddy soils has also been reported to result from anthropogenic activities such as the application of heavy metal(loids)-containing inorganic chemical fertilizers, chemical pesticides, and composted urban wastes and manure [5].

Studies have shown that heavy metal(loids) bioavailability in different soil–crop systems, soil types, and plant genotypes (cultivars) plays a pivotal role in controlling the uptake and accumulation of metal(loids) in rice [15,20–22]. The presence/absence of sorbents (such as iron (Fe), zinc (Zn), and manganese (Mn) hydr(oxides) and clay particles) in soil markedly influence the mobility and bioavailability of As, Cd, Pb, and U in soil and consequently the uptake and accumulation of the same in in rice.

Studies have also shown that toxicity and carcinogenicity of various heavy metal(loids) is also dependent on the chemical species of metal(loids). For instance, Cr (III) is more toxic that Cr (VI), whereas inorganic arsenicals (As (III) and As (V)) are more toxic compared to organic arsenicals [23,24]. Therefore, analyses of total soil metal(loids) concentrations may not provide accurate toxicity of soils. However, information of total metal(loids) concentrations of paddy fields is important as it provides a starting point for further studies, particularly for fields with total soil metal(loids) concentrations exceeding guideline values. With the enhancement of public health risk awareness, soil-rice heavy metal(loids) contamination and evaluation have become hot spots of research across the globe. However, there are few research data on heavy metal(loids) in paddy soils of Malawi despite the large amounts of rice produced [25–27]

Therefore, the purpose of this study was to obtain baseline data of heavy metal(loids) contents in soils of selected paddy rice fields and to evaluate the impacts of various heavy metal(loids) contents in paddy soils on the quality of rice cultivated in such fields and to identify sources of metal(loid) contents in paddy soils.

2. Materials and Methods

2.1. Sample Collection

Soil samples (*n* = 66) were collected in triplicate from twenty-two (22) smallholders' rice paddies in triplicate in Malawi (Figure 1) between June and September in 2018. Soil samples were collected from the top (0–20 cm depth) of a paddy field using a stainless steel sampling tube. After being air-dried and passed through a 3-mesh sieve, the soils were labelled and packed in zip lock bags with details of site location, soil type, soil pH, and date of sampling. Upon reaching the laboratory, the soils were oven-dried at 80 °C for 24 h to understand the influence of soil type and soil pH on eight soil metal(loids) concentrations, namely, arsenic (As), cadmium (Cd), cobalt (Co), chromium (Cr), manganese (Mn), lead (Pb), uranium (U), and gallium (Ga). Sampled paddy sites were grouped into soil types

and soil pH. Sites from the same agroecological zones were aggregated to one sample. For instance, sites number 1 and 2 were aggregated to one sample of Lufiliya, and sites 7–9 from Nkhotakota (KK) district were aggregated to one KK sample, etc., as shown in the caption of Figure 1.

For soil types, sites were grouped into three soil types, namely, vertisols (*n* = 35), luvisols (*n* = 14), and fluvisols (*n* = 12). Sites characterized by vertisols were Bwanje South (BWJ), Domasi (DOM), Kasinthula (KAS), and Lifuwu (LFW); sites characterized by fluvisols were Limphasa (LPH), Hara (HAR), and parts of Nkhotakota (KK); and sites characterized by alluvial soils were Salima (SA), Lufiliya (LFY), and Bwanje North (BWJ) [28].
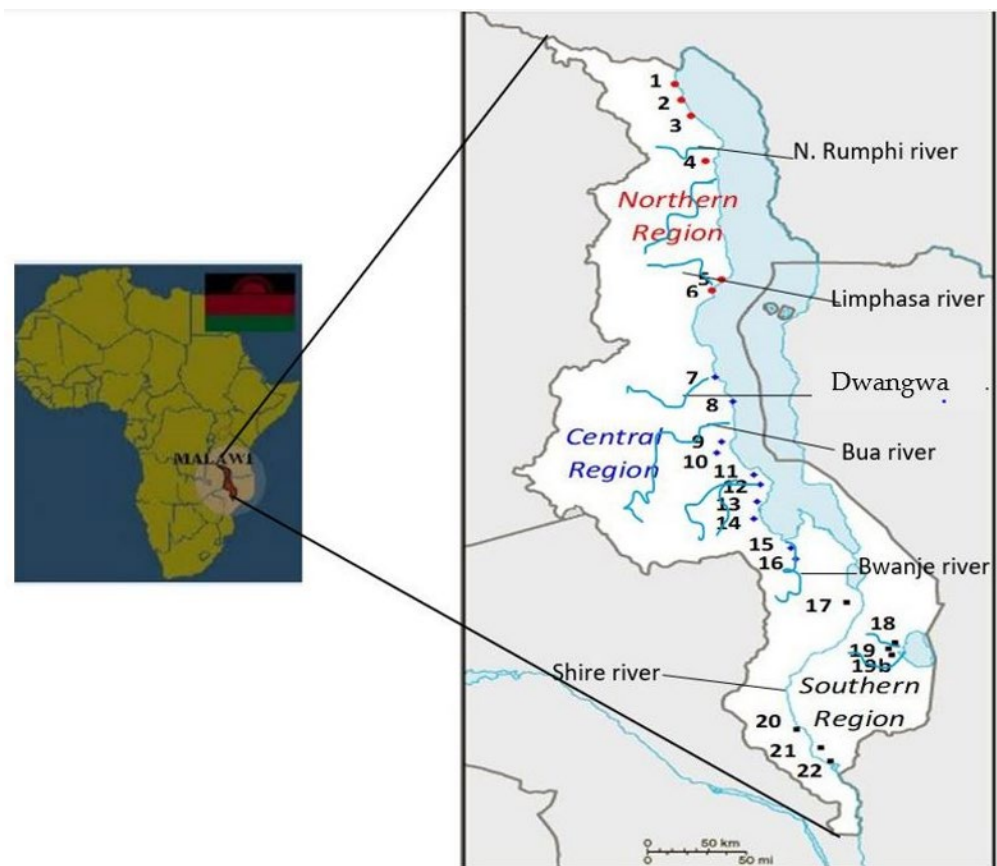

Figure 1. Map of Malawi showing sampled sites in three geographical regional of Malawi as adapted from Mlangeni et al. [29]. The sampled sites are Lufiliya (LFY; #1 and 2), Hara (HAR; #3), North Rumphi (NRU; #4), Limphasa (LPH; #5 and 6), Nkhotakota (KK; #7–9), Salima (SAL; #10, 12–14), Lifuwu (LFW; #11), Bwanje (BWJ; #15 and 16), Balaka (BLK; #17), Domasi (DOM; #18), Khanda (KHA; #19 and 19b), Kasinthula (KAS; #20), and Nkhate (NKH; #21 and 22). Red, Blue and black sites on the map are sites located in Northern, Central and Southern regions respectively.

For soil pH, soils were also grouped into soil pH ranges: of equal to or less than 6.0 (soil pH $\leq$ 6.0; *n* = 35); between 6.00 and 7.0 (6.0 < soil pH < 7.0; *n* = 12); and equal to or greater than 7.00 (soil pH $\geq$ 7.0; *n* = 11). Sites characterized by soil pH $\geq$ 7.0 were Bwanje (BWJ), Domasi (DOM), Kasinthula (KAS), and Lifuwu (LFW); sites characterized by soil pH $\leq$ 6.0 were Limphasa (LPH), Hara (HAR), and parts of Nkhotakota (KK); and sites characterized by soil pH between 6.00 and 7.0 were Salima (SA), Lufiliya (LFY), and Bwanje (BWJ) [28].

2.2. Sample Preparation

Accurately weighed oven-dried and finely powdered soil samples (0.10 g) in triplicates and certified reference material NCS DC73319 (0.10 g) were mixed with 2.5 mL of concentrated HNO_3 (70%) in clean, dry, glass digest tubes and left overnight to react. The following day, exactly 2.5 mL of hydrogen peroxide ($H_{[2]}O_{[2]}$) was added to each sample and were further digested using bloc digestion system programmed as follows: Heat slowly on the block to 100 °C for 1 h; heat at 120 °C for 1 h and 140 °C till the sample is fully digested ($\approx$1 h). Once the digestion was complete, the sample was cooled down in a refrigerator at 4 °C. The digests were made up to 10 mL in a 15 mL centrifuge tube. Exactly 1.0 mL of the sample extract was diluted with 9 mL (v/v) of ultra-pure water (Milli-Q water, 18.2 MO cm) in another 15 mL centrifuge tube to make 10 mL of sample solution.

Three blanks that contained 5% HNO3 in Milli-Q water (18.2 MQ cm) and certified reference materials (CRM) NCS DC73319 were prepared and measured alongside the soil samples. Rhodium (Rh) with a concentration of 10 µg/L was used as an internal standard (ISTD), and m/z =103 was selected for (Rh) to correct instrument mass drift.

2.3. Total Metal Determination

The concentrations of metal(loid)s including As, Cd, Co, Cr, Mn, Pb, U, and Ga in the resulting filtrates were analyzed using inductively coupled plasma mass spectroscopy (ICP-MS/MS, Model 8800 series, Agilent) in inorganic mode. The instrument was operated under normal multi-element tuning conditions and optimized for sensitivity (Table S1). External calibration was carried out using standards prepared from an accu-Trace multi-element standard solution diluted with 5% nitric acid (obtained from Mallinckrodt Chemicals, USA) (Table S2). For each analytical run (batch), mass charge ratios of As (m/z = 75), Cd (m/z = 110), Co (m/z = 59), Cr (m/z =52), Mn (m/z = 51), Pb (m/z = 208), U (m/z = 205), and Ga (m/z = 73) were selected for analyses. Concentrations of analytes were determined using a six-point external calibration curve of 0, 1.0, 5.0, 25, 50, and 100 µg kg^{-1} (Figure S1). Rhodium (Rh, m/z =103) with a concentration of 0.10 mg L^{-1} was used as an internal standard (ISTD) throughout the analytical run to ensure quality control, and all analyses were performed in triplicates. Samples were introduced using a concentric nebulizer and a double pass spray chamber through a tri-piece instrument.

2.4. Statistical and Exposure Analyses

Measured soil metal(loid) concentrations were compared with Soil UK CLEA soil guidelines (SGV), the Chinese environmental quality standards for agricultural soils, and the normally reported soil metal(loids) concentrations across the globe (Table 1). Data were analyzed using Minitab 19 Statistical Software and Excel 2016 for Windows 10. A two-way analysis of variance (ANOVA) was used to evaluate level of significance of impact of sites on metal(loid) concentrations. Fisher tests were used to decide level of significance at $p < 0.05$, <0.01, and <0.001 probability levels.

Table 1. Comparison between certified concentrations of As, Cr, Co, Mn, Pb, Cd, U, and Ga and respective mean measured concentrations in certified reference material NCS DC73319. Values are given in mg kg^{-1} ($n = 6$).

Parameter	As	Cr	Co	Mn	Pb	Cd	U	Ga
Mean	35 ± 4	39 ± 4	12.9 ± 4	1701 ± 201	101 ± 6	4.5 ± 0.8	2.7 ± 0.1	17.6 ± 2.0
CC	34 ± 4	62 ± 4	14.2 ± 1.0	1760 ± 63	98 ± 6	4.3 ± 0.4	3.3 ± 0.4	19.3 ± 1.1
MR	102%	62%	91%	97%	103%	105%	81%	91%
RR %	98–107	54–71	75–114	87–113	97–109	87–132	79–83	80–102
LOD	0.0075 ± 0.001	0.021	0.00062	0.013	0.013	0.001 ± 0.0002	0.003 ± 0.0006	
LOQ	0.025 ± 0.006	0.071	0.0021	0.043	0.042	0.017 ± 0.0011	0.009 ± 0.002	

CC: certified concentrations of the elements, MR: mean recoveries, RR: recoveries range, LOD: limit of detection, and LOQ: limit of quantification; mean ± SD: mean elements concentrations obtained in this study.

3. Results and Discussion

3.1. Quality Assurance and Control

The efficiency of digesting soil samples in a mixture of concentrated nitric acid (70%) and hydrogen peroxide (30%) assisted by a bloc digestion system was evaluated using certified reference material NCS DC73319 soil sample (China National Analysis Centre for Iron and Steel, Beijing, China). Certified reference values and measured values for As, Cd, Co, Cr, Mn, Pb, U, and Ga in the CRM are presented in Table 1. Recoveries of all analytes (As, Cd, Co, Cr, Mn, Pb, U, and Ga) were within the uncertainty limits of the certified reference values, except for Cr, which was lower than expected (Table 1). The limit of detection (LOD) and limit of quantification (LOQ) were calculated statistically, and both are reported in Table 1.

3.2. Soil Metal(Loid) Concentrations

For each metal(loids), the mean, median, minimum, and maximum concentration are reported in Table S3 in mg kg^{-1} of dry weight (d.w.t). The concentrations were in all cases above the limits of quantification (LOQs; Table 1) without exception.

3.2.1. Arsenic (As)

The highest mean As concentration was detected in soils from Lifuwu (site #11) (3.30 ± 0.55 mg As kg^{-1}) characterized by vertisols and soil pH ≥ 7.00, and the lowest was detected in soil from Limphasa (sites #5 and 6) (1.0 ± 0.20 mg As kg^{-1}) characterized by fluvisols and soil pH ≤ 6.0 (Table S3). Analyses of variance indicated that soil As concentration significantly differed with site ($p < 0.01$, F = 13.8), soil Mn ($p < 0.01$; F = 2.2), and soil Fe ($p < 0.01$; F = 2.2). For sites, mean As concentration in soils from Lifuwu, North Rumphi (site #4), and Domasi (site #18), mostly neutral to less alkaline vertisols, contained at least 50% higher As concentrations than those contained from Nkhotakota (sites #7–and 9) (1.8 ± 0.3 mg As kg^{-1}), Khanda (sites #19 and 19b) (1.7 ± 0.9 mg As kg^{-1}), Nkhate (site 21) (1.2 ± 0.2 mg As kg^{-1}), which are mostly acidic vertisols, and Limphasa (sites 5 and 6) (1.2 ± 0.2 mg As kg^{-1}), which are mostly acidic fluvisols (Table S3; Figure 2a). However, we observed no significant differences between the former set of soils and Salima (sites #10, 12, 13 and 14) (2.5 ± 0.5), Balaka (site #17) (2.4 ± 0.4 mg As kg^{-1}), Hara site #3) (2.4 ± 1.2 mg As kg^{-1}), Bwanje (site #15 only) (2.3 ± 0.4 mg As kg^{-1}), Nkhate (site #21) (2.1 ± 0.3 mg As kg^{-1}), Kasinthula (site #20) (2.0 ± 0.2 mg As kg^{-1}), Lufiliya (sites #1 and 2) (2.0 ± 0.2 mg As kg^{-1}), and Nkhate (site #22) (2.0 ± 0.2 mg As kg^{-1}) soil samples (Table S3, Figure 2a), which are mostly vertisols and luvisols and high in iron content [28,30,31]. Thus, higher soil Fe might have sequestered and/or immobilized greater amounts of As from runoff water, which increased cumulative As loading in the soil.
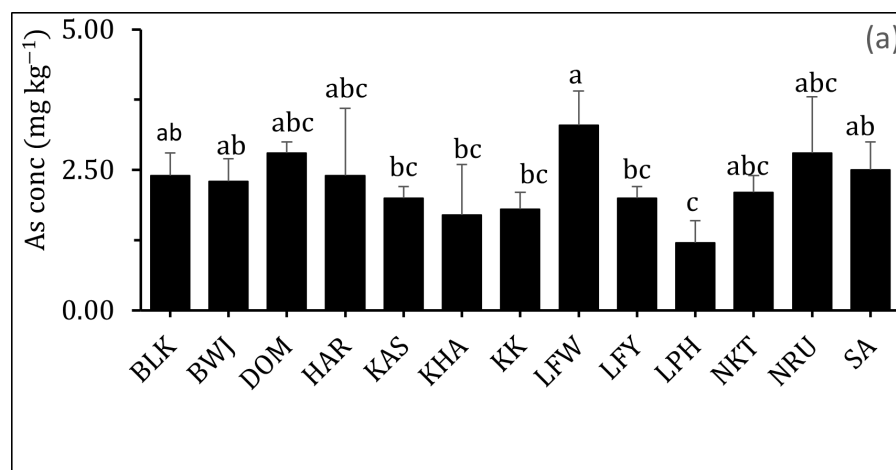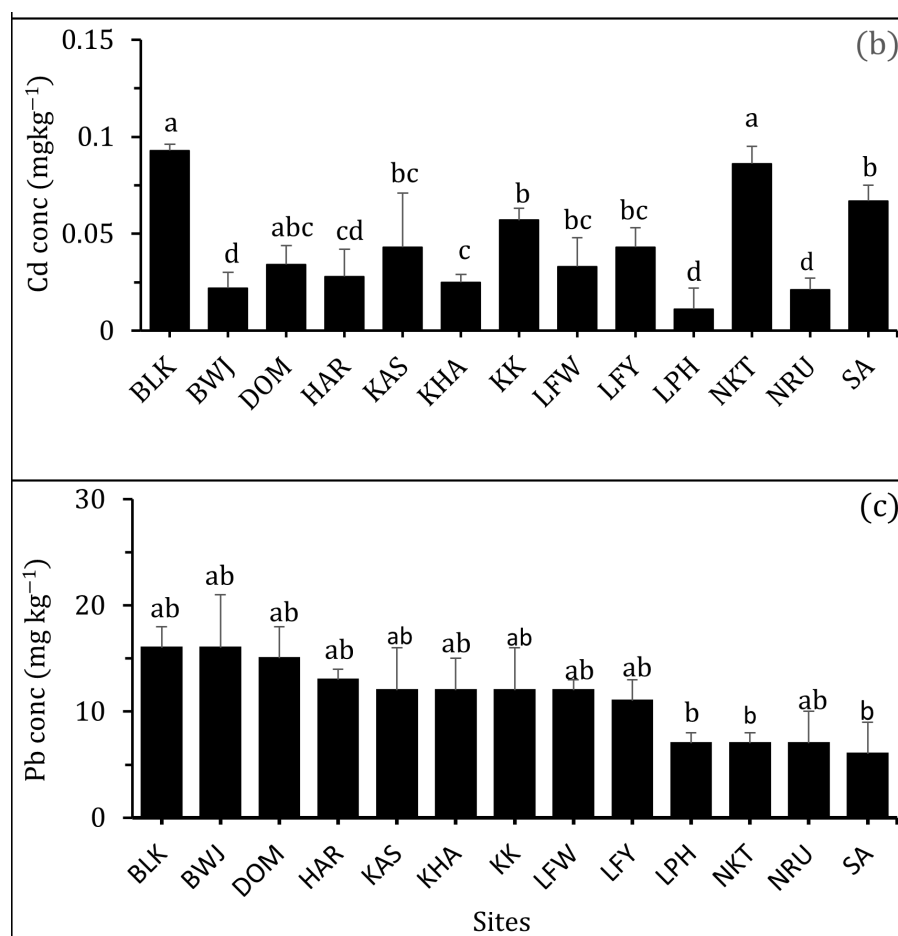

Figure 2. *Cont.*

Figure 2. Metal(loids) concentrations in soils of paddy fields of various sites showing (**a**) arsenic, (**b**) Cd, and (**c**) Pb concentrations evaluated by site. BLK: Balaka (17), BWJ: Bwanje (15 and 16), DOM: Domasi (18), HAR: Hara (3), KAS: Kasinthula (20), KHA: Khanda (19 and 19b), LFY; Lufiliya (1 and 2), LFW: Lifuwu (11), LPH: Limphasa (5 and 6), NKH: Nkhate (21 and 22), KK: Nkhotakota (7–9), NRU: North Rumphi (4), and SA: Salima (10, 12–14). Bars that share common letters (a, b, c, and d) are not significantly different from each other.

The higher As detected in soil samples from North Rumphi could be attributed to coal mining at Mchenga coal mines upstream of the North Rumphi river. Studies have reported that irrigating rice using water-associated coal mines significantly contributes to the elevation of soil As concentration of rice paddies [16], since coal may contain elevated arsenic through percolation of groundwater through volcanic deposits, which may leach arsenic and transfer it to underlying coal beds during or after coalification. Arsenic may be washed downstream to rice paddies after heavy rainfall. The higher soil arsenic observed in alkaline vertisols could be explained by the fact that sorption of arsenic to metal oxyhydroxides is generally pH-dependent, considering that at alkaline pH, mineral surfaces become increasingly negatively charged [16]. Thus, alkaline pH promotes arsenic desorption, which increases its transfer into paddy fields through water surface runoff. Furthermore, higher soil As in soil samples containing relatively higher soil iron could be explained either by increased arsenic retention or reduced leaching of arsenic to lower soil profiles due to enhanced sorption onto iron oxyhydroxides [16,32].

The countrywide mean soil As concentration (2.2 mg As kg^{-1}) obtained in this study for Malawi (Table S3; Figure 3) was about five times lower than mean soil As concentrations reported for UK rural soils (10.9 mg As kg^{-1}; range: 0.5–143 mg As kg^{-1}) [28] and eight times lower than mean soil As concentrations reported for China (mean = 16.8 ± 12.3 mg As kg^{-1}; range: 3.16–45.2 mg As kg^{-1}) [7,33–35]. Furthermore, the mean soil As concentration

obtained in this study was at least nine times lower than the UK CLEA minimum soil As concentration guidelines of 20 mg As kg^{-1} for unpolluted soil [17,36,37]. Malawian soils would not exceed permissible levels for agricultural soils under any regulations [7,34,38,39].
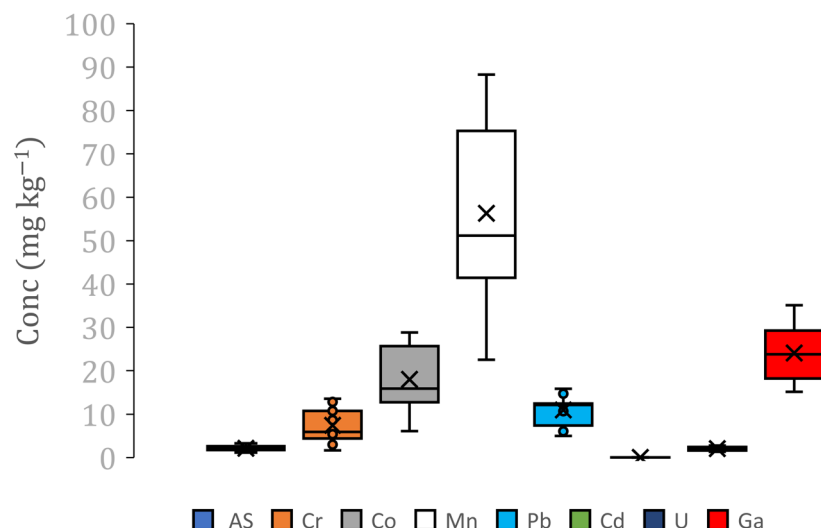

Figure 3. Mean soil metal(loids) concentrations showing countrywide mean As, Cd, Co, Cr (X 10^1), Mn (X 10^1), Pb, U, and Ga (mg kg^{-1}) concentrations. The boxes represent first and third quartile range of metal(loids) concentrations. The solid line across a box represents the median concentrations; the cross within the box represents the mean concentration, and whiskers represent minimum and maximum concentrations.

The findings showed that Malawian paddy soils are low in As content and can produce high quality low As containing rice. Hence, the paddy fields should be safe-guarded from contamination by restricting use of arsenic-containing pesticides and chemical fertilizers and the release of industrial wastes into the environment. Suitable agronomic practices should be adopted to conserve this low As concentration in soils by, among others, avoiding the use of contaminated irrigation water and contaminating fertilizers. In areas with soil As of about 3 mg kg^{-1}, the use of growth conditions for rice fostering low As uptake, e.g., intermitted irrigation, should be considered to reduce the uptake of As. Paddy fields such as Limphasa, Nazolo, Nkhate, Khanda, Nkhotakota, and Kasinthula were identified as having no risk of elevated accumulation of As in rice grain compared to Lifuwu, Domasi, North Rumphi, and Bwanje-North.

3.2.2. Cadmium (Cd)

Soil contamination by cadmium (Cd) is a major environmental concern because of its potential implications to human health [40]. As shown in Table S3, Cd concentrations in all 22 sites were highly variable. The highest (0.93 mg Cd kg^{-1}) and widest (range = 0.3–0.93 mg Cd kg^{-1}) Cd concentrations were found in Balaka soil samples, whereas the lowest soil Cd concentrations (0.011 mg Cd kg^{-1}) were found in Limphasa soil samples (Table S3b; Figure 2). Two-way analyses of variance indicated that soil Cd concentrations significantly differed with site (F = 17.1; $p < 0.01$) and mining activities (F = 12.3; $p < 0.001$). The mean Cd concentrations detected in soil from Balaka (0.093 ± 0.5 mg Cd kg^{-1}) and Nkhate (0.086 ± 0.006 mg Cd kg^{-1}) were at least 40% higher than those detected in soil from Nkhotakota (0.057 ± 0.005 mg Cd kg^{-1}), Nazolo (0.050 ± 0.004 mg Cd kg^{-1}), Kasinthula (0.043 ± 0012 mg Cd kg^{-1}), Lufiliya 0.043 ± 0.003 mg Cd kg^{-1}), Domasi (0.034 ± 0.003 mg Cd kg^{-1}), Lifuwu (0.033 ± 0.022 mg Cd kg^{-1}), and Hara (0.028± 0.002 mg Cd kg^{-1}), and at least four to nine times higher than those detected in soil samples collected from Khanda (0.025± 0.002 mg Cd kg^{-1}), Bwanje (0.022 ± 0.003 mg Cd kg^{-1}), North Rumphi (0.021 ± 0.009 mg Cd kg^{-1}), and Limphasa (0.011 ± 0.002 mg Cd kg^{-1}) (Table S3, Figure 2b). The countrywide mean Cd concentration

(0.044 mg Cd kg^{-1} obtained in this study for Malawi (Table S3; Figure 3)) is within the normal values reported for unpolluted soils and is below the maximum Cd limit allowed for agricultural soils of 0.3 mg Cd kg^{-1} regulated by World Health Organization (WHO) and European commission (EC) [7,29–31].

3.2.3. Lead (Pb)

The highest Pb concentrations were detected in soil samples from Lifuwu (47.1 mg Pb kg^{-1}), whereas the lowest concentration was detected in soil samples from Nazolo (4.2 mg Pb kg^{-1}). Analyses of variance indicated that soil Pb concentrations significantly differed with site (F =1.91.0; $p < 0.05$). The mean soil Pb concentration in soil samples from Lifuwu (47 mg Pb kg^{-1}) characterized by vertisols with slightly basic to alkaline soil pH (> 7.8) was at least four times higher than that in soil of all other sites. Furthermore, there were no significant mean soil Pb concentration differences observed between sites mostly characterized by slightly lower soil pH (pH < 7.0), irrespective of soil type (Limphasa (16 mg Pb kg^{-1}), Lufiliya (15 mg Pb kg^{-1}), Domasi (13 mg Pb kg^{-1}), Salima (12 mg Pb kg^{-1}), Hara (12 mg Pb kg^{-1}), and North Rumphi (12 mg Pb kg^{-1})). Nevertheless, mean soil Pb concentrations in soil samples, mostly from sites located in the southern region of Malawi, irrespective of soil types and soil pH, were at least five times lower than those from any other region.

The mean soil Pb concentration obtained in this study for Malawian rice paddies (11 mg Pb kg^{-1}) (Table S3; Figure 3) was three times lower than the reported mean global soil Pb concentration (32 mg Pb kg^{-1}), 40 times lower than that reported in paddy soils of China (460 mg Pb kg^{-1}) [37], 125 times lower than the maximum Pb limit (250 mg Pb kg^{-1}) allowed for agricultural soils in China (GB15618-1995), and 10 times lower than the UK CLEA soil guidelines (100 mg Pb kg^{-1}) [37,41]. Considering that high soil Pb content leads to elevated Pb uptake and bioaccumulation in rice [42], negligible Pb soil contamination observed in this study is likely to result in low Pb bioaccumulation in Malawian rice.

3.2.4. Chromium (Cr)

While chromium shortage in humans can cause cardiac problems, metabolic dysfunctions, and diabetes, excess Cr can result in respiratory tract problems, lung cancer, dermatitis, and permanent nose damage [38]. Highest mean Cr concentrations were detected in soil from Nkhate and Lufiliya (136 mg Cr kg^{-1}), whereas the lowest Cr concentration was detected in samples from Domasi (16.6 mg Cr kg^{-1}) (Figure 4a). Two-way analyses of variance indicated that soil Cr concentrations significantly varied with site (F = 4.8; $p < 0.001$) and soil type (F = 4.2; $p < 0.001$). The mean soil Cr concentrations in samples from Nkhate, Lufiliya, Salima, Balaka, and Nkhotakota (mean 120 mg Cr kg^{-1}; range = 108–135 mg Cr kg^{-1}), characterized by slightly acidic luvisols and vertisols, were at least 40% higher than those of Lifuwu (87 mg Cr kg^{-1}), Nazolo (71 mg Cr kg^{-1}), Bwanje North (59 mg Cr kg^{-1}), Hara (59 mg Cr kg^{-1}), Kasinthula (54 mg Cr kg^{-1}), and Khanda (44 mg Cr kg^{-1}), mostly characterized by slightly alkaline vertisols (mean = 65; range = 44–87 mg Cr kg^{-1}) (Table S3; Figure 2a), and at least four times significantly higher than those of Domasi, Limphasa, and North Rumphi (mean = 21 mg Cr kg^{-1}; range = 17–38 mg Cr kg^{-1}), characterized by soil pH < 6.5 (Table S3; Figure 4a). Tests on soils showed Cr concentrations ranging from 1 to 1000 mg/kg across the globe, with an average Cr concentration ranging from 14 to 70 mg Cr kg^{-1} [23]. The countrywide mean Cr concentration (78 mg Cr kg^{-1}; range = 16–135 mg Cr kg^{-1}) obtained in this study for Malawi (Table S3; Figure 3) was within the range reported elsewhere but exceeded the means from most countries [22]. For instance, the mean Cr concentration obtained in this study for Malawi (Figure 3; Table S3)

was higher than that reported for agricultural soils of China (mean = 27 ± 5 mg Cr kg^{-1}; range = 22–39 mg Cr kg^{-1}), Japan (20–70 mg Cr kg^{-1}), and Hawaii (45–67 mg Cr kg^{-1}) [23]. Compared to various guiding values or maximum allowable limit values, mean soil Cr for Malawi rice paddy soils, for paddy soil Cr concentration in unpolluted soil, was less than 100 mg Cr kg^{-1}. However, Cr concentration detected in five sites, namely, Nkhate (135 mg Cr kg^{-1}), Lufiliya (135 mg Cr kg^{-1}), Salima (128 mg Cr kg^{-1}), Balaka (127 mg Cr kg^{-1}), and Nkhotakota (108 mg Cr kg^{-1}), exceeded both the maximum soil guideline and maximum allowable limit values. Considering that chromium uptake, accumulation, and translocation depend on its speciation, there is a need for speciation analyses to be conducted to identify the most predominant Cr species in rice paddies. Cr(VI) is highly soluble, mobile, and toxic to humans, while Cr(III) has relatively low toxicity and mobility and is one of the micronutrients needed by humans.
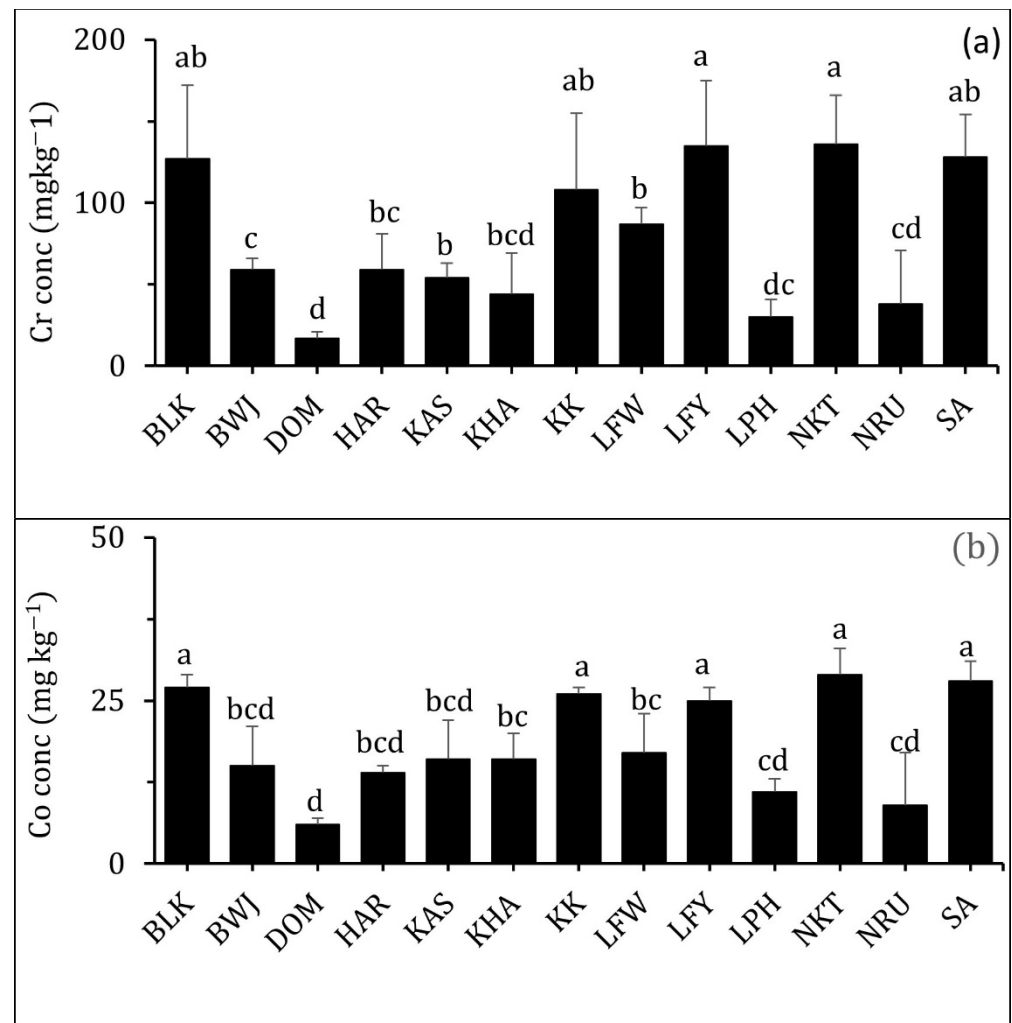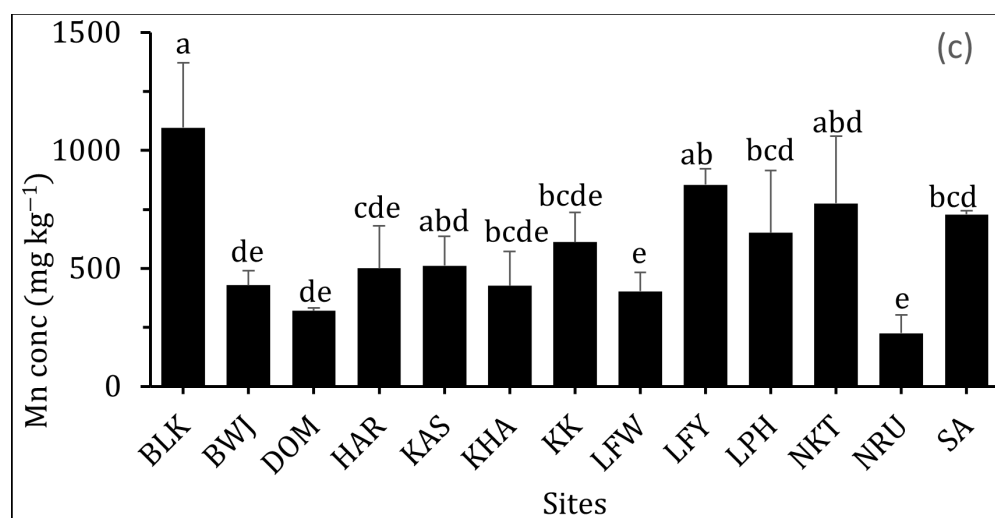

Figure 4. *Cont.*

Figure 4. Metal(loids) concentrations in soils of paddy fields of various sites showing (**a**) Cr, (**b**) Co, and (**c**) Mn concentrations evaluated by site. BLK: Balaka (17), BWJ: Bwanje (15 and 16), DOM: Domasi (18), HAR: Hara (3), KAS: Kasinthula (20), KHA: Khanda (19 and 19b), LFY; Lufiliya (1 and 2), LFW: Lifuwu (11), LPH: Limphasa (5 and 6), NKH: Nkhate (21 and 22), KK: Nkhotakota (7–9), NRU: North Rumphi (4), and SA: Salima (10, 12–14). Bars that share common letters (a, b, c, d and e) are not significantly different from each other.

3.2.5. Cobalt (Co)

The highest mean soil Co concentration was detected in Nkhate soil samples (29 mg Co kg^{-1}), whereas the lowest mean soil Co concentration was in Domasi soil samples (6 mg Co kg^{-1}; Figure 4b). We found no significant Co concentration variations among the following sites: Nkhate (29 mg Co kg^{-1}), Salima (27 mg Co kg^{-1}), Balaka (27 mg Co kg^{-1}), Nkhotakota (26 mg Co kg^{-1}), and Lufiliya (25 mg Co kg^{-1}) (F =0.08; $p > 0.05$) (Figure 4b), which are mostly characterized by luvisols. Nevertheless, mean Co concentrations detected in soils from these sites were at least two-fold higher than that detected in soil from Lifuwu (17 mg Co kg^{-1}; 2 times), Kasinthula (16 mg Co kg^{-1}; 2 times), Khanda (16 mg Co kg^{-1}; 2 times), Bwanje (15 mg Mn kg^{-1}; 2 times), Hara (14 mg Co kg^{-1}; 3 times), Limphasa (11 mg Co kg^{-1}; 3 times), North Rumphi (9 mg Co kg^{-1}; 3 times), and Domasi (6 mg Co kg^{-1}; 5 times) (Figure 4b). The countrywide mean Co concentration (14 ± 6 mg Co kg^{-1}) (Table S3; Figure 3) obtained in this study was four times lower than the maximum allowable limit of 50 mg Co kg^{-1} for soil Co in agricultural soils [17]. These results suggest that the soil Co concentrations detected in Malawian paddy fields soils are low and pose no risk for agricultural land.

3.2.6. Manganese (Mn)

The highest mean soil Mn concentrations were detected in soil samples collected from Balaka sites (1097 mg Mn kg^{-1}), whereas the lowest mean Mn concentration was detected in soil samples from North Rumphi (225 mg Mn kg^{-1}; Figure 4c). We observed no significant Mn concentration differences between sites associated with luvisols (Balaka (1097 mg Mn kg^{-1}), Nazolo (883 mg Mn kg^{-1}), Lufiliya (855 mg Mn kg^{-1}), and Nkhate (776 mg Mn kg^{-1}) ($p > 0.05$)). Mean Mn concentrations detected in these sites were at least two times higher than those associated with slightly acidic soil pH (Salima

(511 mg Mn kg^{-1}), Limphasa (511 mg Mn kg^{-1}), Kasinthula (511 mg Mn kg^{-1}), Hara (501 mg Mn kg^{-1})). On the other hand, mean Mn concentrations detected in samples from Bwanje (429 mg Mn kg^{-1}), Khanda (426 mg Mn kg^{-1}), Lifuwu (403 mg Mn kg^{-1}), Domasi (320 mg Mn kg^{-1}), and North Rumphi (225 mg Mn kg^{-1}; Figure 4c) mostly characterized by vertisols, were at least three times lower than those detected in sites characterized by the luvisol soil type. The mean Mn concentration (601 mg Mn kg^{-1}) obtained in this study for Malawi (Table S3; Figure 3) was two times lower than the UK CLEA guidelines for soil Mn concentration (2000 mg Mn kg^{-1}) [15,29] and was within normally reported Mn concentrations in soils (Table 1) [29]. Studies have shown that limited Mn content in rice paddy fields negatively impacts the magnitude of Mn bioavailable for rice uptake and consequent the magnitude of Mn bio-accumulated in rice [15]. Considering that Mn is an essential element required for various body function, its deficiency in rice significant impairs human health of rice consumers [15]. However, further research is required to ascertain the impact of soil Mn on Mn bioaccumulation in rice grains.

3.2.7. Uranium (U)

The highest mean soil U concentration was detected in soil from Lufiliya and Limphasa (2.8 mg U kg^{-1}) in the northern region, whereas the lowest was detected in soils from Nazolo (1.3 mg U kg^{-1}), a site located in the southern region. The mean soil U concentrations in samples of sites located in the northern region of Malawi (Lufiliya, Limphasa Hara, and North Rumphi (mean = 2.5 mg U kg^{-1}; range = 2.3–2.8 mg U kg^{-1})) were at least two times higher than those detected in samples collected from the southern region (Nkhate, Bwanje, Balaka, Khanda, and Nazolo (mean = 1.6 1 mg U kg^{-1}; range = 1.3–1.7 mg U kg^{-1})) (Figure 5a). However, the mean soil U concentration detected in soils from Lifuwu (located in the central region and characterized by vertisols) was not significantly different from mean soil U concentrations detected in all northern region sites (Lufiliya, Limphasa, Hara, and North Rumphi), regardless of soil type (Figure 5a). The U detected in soils from the northern region could be linked to uranium deposits discovered or mined in the northern region. On the contrary, the source of U detected in soils from Lifuwu could not be established. Nevertheless, the countrywide mean paddy soil U concentration (2.02 mg U kg^{-1}) found in this study for Malawi (Table S3; Figure 3) was within the reported range of global mean soil U concentration (0.8 to 11.0 mg U kg^{-1}) [17].
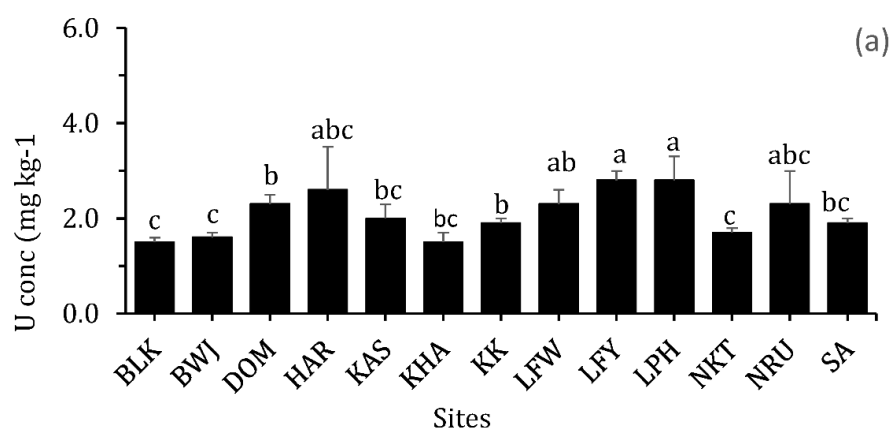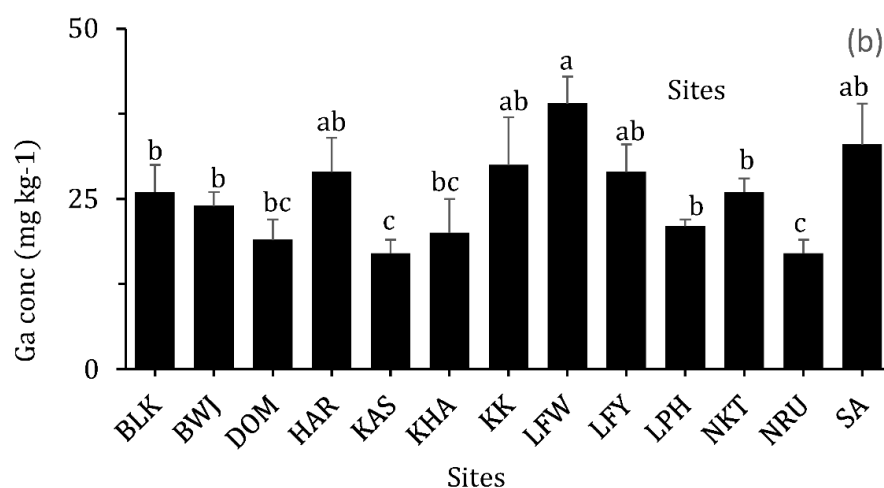

Figure 5. *Cont.*

Figure 5. Metal(loids) concentrations in soils of paddy fields of various sites showing (**a**) U and (**b**) Ga concentrations evaluated by site. BLK: Balaka (17), BWJ: Bwanje (15 and 16), DOM: Domasi (18), HAR: Hara (3), KAS: Kasinthula (20), KHA: Khanda (19 and 19b), LFY; Lufiliya (1 and 2), LFW: Lifuwu (11), LPH: Limphasa (5 and 6), NKH: Nkhate (21 and 22), KK: Nkhotakota (7–9), NRU: North Rumphi (4), and SA: Salima (10, 12–14). Bars that share common letters (a, b, c) are not significantly different from each other.

3.2.8. Gallium (Ga)

The highest mean Ga concentration was detected in soil samples collected from Lifuwu (39 mg Ga kg^{-1}) followed by those collected from Salima (35 mg Ga kg^{-1}) and Nkhotakota (30 mg Ga kg^{-1}), whereas the lowest Ga concentration was detected in soil samples collected from Nazolo (15 mg Ga kg^{-1}) (Table S3; Figure 5a). Mean Ga concentrations detected in soil samples collected from Lifuwu, Salima, and Nkhotakota were not significantly different from each other. Further analyses indicated that mean Ga concentrations detected in soil samples collected from these sites were at least two times higher than those from Nazolo (15 mg Ga kg^{-1}), Kasinthula and North Rumphi (17 mg Ga kg^{-1}), Domasi (19 mg Ga kg^{-1}), and Khanda (20 mg Ga kg^{-1}) (Table S3; Figure 5a). The countrywide mean Ga concentration (24 mg Ga kg^{-1}) obtained in this study for Malawi (Table S3; Figure 3) was lower than the mean Ga concentration reported for China (27 $\pm$ 5 mg Ga kg^{-1}; range: 22–39 mg Gakg^{-1}) and minimum soil guidelines and MAC for the soil Ga concentration in unpolluted soil (100 mg Ga kg^{-1}). These observations suggest that concerns for rising Ga do not occur for Malawi.

3.3. Correlations among As, Cd, Cr, Co, Cr, Mn, Pb, U, and Ga in Soils

A correlation matrix for As, Cd, Cr, Co, Cr, Mn, Pb, U, and Ga in the soils under study was calculated to evaluate whether they were interrelated with each other, and the results are presented in Table 2. The strongest correlations were observed between three couples of metal(loids), namely, Co–Cd (0.83), Cd–Cr (0.81), and Co–Cr (0.96), and weaker correlations were observed between Mn–Cr (0.78), Mn–Cd (0.75), and Mn–Co (0.79) (Table 2). The group composed of four elements (Mn, Cd, Cr, Co, and Ga) showed a noticeable multi-correlation, with values ranging 0.6 to 0.96 (Table 2). An interesting multi-correlation was also observed among two essential trace elements, Mn and Co, with coefficients slightly lower than 0.70 (Table 2). This observation suggests that soil Cr, Mn, Co, and Cd concentrations influence the availability and uptake of other metal(loid)s from porewater, considering that they may adsorb or sorb them, which limit their mobility in porewater. Fe and Mn oxides, oxyhydroxides, and hydroxides have long been recognized as scavengers playing a vital role in controlling the location, mobility, and bioavailability of metal contaminants in soils. Adsorption is considered an effective technique due to its properties of simple operation, low cost, and high efficiency over a wide concentration range of pollutants.

Table 2. Correlational relationship among metal(loids) detected in soil samples indicating correlational coefficients and levels of significance.

	As	Mn	Pb	Cd	Co	U	Ga	Cr
As	1.00	−0.33 *	0.20 *	0.08	−0.15	−0.0	0.35 **	0.03
Mn		1.00	−0.01	0.75 ***	0.79 ***	−0.15 *	0.31 *	0.78 ***
Pb			1.00	−0.01	−0.17	−0.28 *	−0.03	−0.16 *
Cd				1.00	0.83 ***	−0.51 **	0.31 *	0.81 ***
Co					1.00	−0.39 **	0.55 **	0.96 ***
U						1.00	0.08	−0.24 *
Ga							1.00	0.64 ***
Cr								1.00

The asterisks *, **, and *** stand for levels of significance at 0.05, 0.01, and 0.001, respectively.

For instance, higher high soil Cd, Co, and Cr concentrations in Nkhotakota and Kasinthula and Nkhate in Chikwawa observed in this study could be linked to elevated concentrations due to dissolution of the manganese parent material rich in Cr, Cd, and Co, considering reports that underlying rock in these areas have Cr, Cd, and Co (26). Therefore increased solubility of these elements may have led to toxicity [43]. Furthermore, elevated Mn concentration might have adsorbed As leached in top agricultural soils, which in turn limited its bioavailability in the agricultural soils [43].

4. Conclusions

Concentrations of As, Co, Mn, Pb, Cd, U, and Ga in Malawian paddy soils ranged from two to five times lower than respective worldwide mean concentrations and maximum contaminant limits, guidelines, or standards values regulated by various national and international standards regulatory bodies, including the World Health Organization (WHO), Alimentarius Commission, European Commission (EC), and Chinese Environmental Quality Standards (CEQS) for paddy soils. The finding indicated that in reference to soil metal(loids) concentrations found in this study, most paddy sites of Malawi are of high quality to produce safe rice. However, soil metal(loids) concentration is not the only factor that determines the magnitude of metal(loids) up-taken by rice plants. Thus, further research is required to investigate the impact of factors such as source of irrigation of water, water management regimes, soil cation exchange capacity, organic manure/composts amendments, and application of inorganic fertilizers on the uptake, transfer, and translocation of soil metal(loids) to various parts of rice plants, even when the soil metal(loids) concentrations are low. Nevertheless, we recommend that Malawian rice paddies be safeguarded from contamination. Considering that knowledge of soil metal(loids) concentrations has significant practical implications on management of inorganic fertilizers and the bioavailability of metal(loids) in soil, data generated in this research will help develop fertilizer requirements that limit the uptake and bioaccumulation of toxic metal(loids) in rice specific to the sampled agroecological zones.

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