Alleviating cobalt and lead toxicity in rice using zero valent iron (Fe\(^{0}\)) amendments

Angstone Thembachako Mlangeni, Andrea Rab, Joerg Feldmann

\(^{a}\) Department of Land and Water Resources, Natural Resources College, Lilongwe University of Agriculture and Natural Resources, Lilongwe, Malawi
\(^{b}\) TESLA-Analytical Chemistry, Institute of Chemistry, University of Graz, Austria
\(^{c}\) TESLA-Analytical Chemistry, Department of Chemistry, University of Aberdeen, Scotland, United Kingdom

HIGHLIGHTS

- Impact of rice cultivar × Fe\(^{0}\) amendments on Co and Pb accumulation in rice grains was studied.
- Fe\(^{0}\) dosages markedly inhibited available Co and Pb in porewater.
- Fe\(^{0}\) dosages marked inhibited translocation of Co and Pb from shoots to grain.
- Uptake of Co from soil was higher in Kilombero than in Faya while uptake of Pb was vice versa.
- Co and Pb accumulation in rice grains varied with cultivar and Fe\(^{0}\) dosages.

ARTICLE INFO

Keywords:
Cobalt (Co)
Faya
Kilombero
Lead (Pb)
Rice
Zero valent iron (Fe\(^{0}\))
Cultivar

ABSTRACT

Simultaneous impact of zero valent iron (Fe\(^{0}\)) and rice cultivar on uptake, translocation, and bioaccumulation of cobalt (Co) and lead (Pb) in rice (Oryza sativa L.) was investigated to alleviate Co and Pb toxicity in rice. Kilombero and Faya rice cultivars, amended with Fe\(^{0}\) dosages of 0, 6.20, and 12.40 g kg\(^{-1}\) soil, were cultivated under continuous flooding in pots in a greenhouse. Shoot and grain-Co and Pb concentrations were determined using inductively coupled plasma mass spectrometry (ICP-MS). For Co, amending Faya rice with at least 6.20 g Fe\(^{0}\) kg\(^{-1}\) reduced grain-Co accumulation by 33% or more compared to control plants (F = 17.5; p < 0.001) while inconsistent results were obtained for Kilombero. For Pb, Faya also accumulated more than 39% less grain-Pb than control plants while Kilombero accumulated more than 55% less grain-Pb than control plants under the same conditions. Despite reducing grain-Pb accumulation in both cultivar, Fe amendments of at least 6.20 g Fe\(^{0}\) kg\(^{-1}\) reduced grain-Pb accumulation with greater magnitude in Kilombero (55%) than in Faya (39%). Nonetheless, Fe amendments inhibited greater shoots-Co and Pb translocation (≥32%) to grains in Faya compared to Kilombero (≤20%). The work provides a novel promising agronomical practice of reducing Co and Pb bioaccumulation in rice.

1. Introduction

Contamination of food crops such as rice, maize and wheat with toxic metal(loid)s such as arsenic (As) [1, 2], cadmium (Cd) [3], cobalt (Co) [4] and lead (Pb) [5] is worsening globally due to inappropriate anthropogenic activities such as mining, indiscriminate use of toxicant-containing agrochemicals such as pesticides and fertilizers; and agronomical practices that stimulate uptake of toxic metal(loid)s [6]. It is becoming apparent that rice could be a major source of ingesting Co and Pb among the communities that solely depend on rice diets for subsistence living. Contamination of rice with elevated Co and Pb concentrations threatens food safety which calls for global collective efforts of adopting agricultural practices for mitigating the contamination [7].

Pb, as a toxic pollutant, is of public health concern and has no known benefits even at low non-phytotoxic concentrations [6]. Pb is ranked second after arsenic amongst the most hazardous metals [4]. In humans, elevated Pb concentrations can damage the nervous system and gastrointestinal and renal organs [8], and cause brain disorders and convulsions and/or death [9, 10]. Background concentrations of Pb ranges from 30000 - 100000 μg kg\(^{-1}\) in uncontaminated soils [11] and 100–500 μg
kg⁻¹ in less contaminated soils [11]. Rice plants readily uptake Pb through roots. Rice plants also efficiently transport Pb to edible parts such as grains which ultimately allows Pb enter the food chain. Rice cultivated in Pb-contaminated paddy soils bioaccumulate more Pb as compared to rice cultivated in uncontaminated soils [6]. The World Health Organisation (WHO) [12] and the European commission (EC) [13] set the maximum permissible limit for Pb in rice grains at 200 ug kg⁻¹ to protect trade and human health.

For Co, it is not considered as an essential element to humans in its inorganic form. Excessive consumption of Co has genotoxic, hepatotoxic, nephrotoxic, neurotoxic, and immunotoxic effects to human and animal health [14, 15]. Co consumption has been linked to certain diseases such as Alzheimer’s, Parkinson’s and autism [14, 15, 16]. There are as yet no maximum permissible levels set for Co concentrations in rice and other food commodities by either WHO or other organisation [17].

Several agronomical practices, such as use of Fe and silicon amendments, use of alternate wetting and drying irrigation, and selecting low metal(loids) accumulating cultivars and their interactions have been studied and reported to effectively regulate metal(loids), predominantly arsenic, accumulation in rice [18, 19, 20, 21]. Agronomical practices of interest in this investigation were the use of Fe and the selection of low metal(loids) accumulating cultivars and their interactions on Co and Pb. For Fe amendments, Fe has been reported to effectively remove pollutants including heavy metals from groundwater, wastewater and soil [22, 23]. In this study, Fe was chosen because due to its low cost, simplicity of application, being a non-toxic material and relatively environmentally friendly [23]. Nevertheless, presence of certain nanoscale zero-valent iron at elevated levels reduce soil microbial biomass and activity [22, 23]. Nevertheless, the presence of certain nanoscale zero-valent iron at elevated levels can reduce soil microbial biomass and activity [22, 23].

Previous studies showed that Fe and iron materials markedly regulate As and Cd bioaccumulation in rice [18, 19, 20, 21] by immobilizing As and Cd in soil or reducing their availability in soil porewater through sorption of As or Cd partilculates or ions onto ironoxides or iron hydroxides groups [18, 24, 25, 26]. Subsequently, As and Cd sorbed onto oxidised Fe may co-precipitate together with the iron materials which immobilise them [18, 24, 25, 26]. Considering that the chemistry of Co and Pb is similar to that of As and Cd, we expect Co and Pb to show similar trends of adsorption and co-precipitation processes which will eventually reduce availability and accessibility of Co and Pb to rice plants [18, 24, 25, 26]. Thus, the sorption of Co and Pb onto Fe can be utilised in paddy fields to regulate Co and Pb bioaccumulation in rice which has high potential of reducing health hazards associated with these metalloids.

There are many studies that have reported a positive impact of Fe amendments on the reduction of As and Cd accumulation in rice grains. For instance, amending rice with Fe has been reported to markedly reduce As and Cd accumulation in rice grains under certain soil conditions and in certain rice cultivars [11, 18, 21, 26, 27]. Mlangeni et al. [18, 21] showed that Fe amendments reduced grain-Cd and As concentrations in rice by more than 51% and 61%, respectively, in rice cultivated under low water (LW) and alternate wetting and drying irrigation compared to respective control treatments. Farrow et al. [26] also reported that amending soils with ferrous ion immobilized soil-As and reduced grain-As accumulation in rice grains.

However, most of these studies on impact of iron materials or Fe on metal(loids) transfer from soil to plants in rice fields refers to As and/or Cd accumulation with few materials or Fe. Few studies, if any, have investigated impact of iron materials or Fe on Co and Pb transfer to rice grains. Considering that Co and Pb are emerging contaminant that require attention, it is thus necessary to study impact of Fe on alleviating Co and Pb bioaccumulation in rice using similar experiments as have been carried out with As or Cd.

Therefore, uptake and bio-accumulation of Co and Pb in two most popular Malawian rice cultivars (Faya and Kilombero) [28] were investigated through greenhouse pot experiments. Both cultivars are aromatic and pure line selections from the Faya genotype pool. However, Faya rice flowers earlier than Kilombero rice cultivar [28]. The main aim of this study was to evaluate and understand the extent to which simultaneous use of Fe amendment and cultivar selection alleviate bioaccumulation of Co and Pb in rice. Specifically, the study evaluated simultaneous impact of various Fe amendment dosages and rice cultivar on uptake and bioaccumulation of Co and Pb in rice grains in order to alleviate Co and Pb toxicity in rice.

2. Methods and experiments

2.1. Greenhouse experiments

The greenhouse pot experiments used agricultural sand-loam soils collected at soil depth of 0–12 cm in Aberdeenshire, Scotland. Experimental soils, dried to a constant mass in a drying chamber [18, 21], were sieved using 4 mm sieve. The purpose for sieving was to remove plant materials, large soil aggregates and stones from the soils. One part of the sieved soils was mixed with one part of sand to make a homogeneous soil-sand mixture with 1:1 soil to sand ratio (v/v). The soil-sand mixture was used because it allows easy drainage of water into soil. Besides, it also enable easy extraction of roots from soil when determining root biomass [18, 21]. Overall metal(loids) concentrations plus physical and chemical properties of the soil-sand mixture were predetermined (Table SM1).

1.0 kg of soil-sand mixture was spiked with one of the three levels of Fe dosages (0, 6.20 and 12.40 g Fe kg⁻¹) before being placed in PVC pots (height: 25 cm and diameter: 22 cm) lined with plastic-liners [18, 21]. The plastic liners were used to reduce the loss of solubilised Fe, Co and Pb and other soil nutrients. The Fe used in this experiment had an average diameter of 3.9 ± 1.01 mm (Beijing North Yongbang Science and Technology, China). Rice plants were grown in the greenhouse with natural lighting, temperature range from 22 to 35 °C, and humidity ranging from 45 - 55%. Initial soil sample pH (6.1) was measured in deionized water (with soil to water ratio of 1:2.5) after shaking for one (1) hour [18, 29].

All treatment pots, planted with one seedling per pot of either Faya 14M69 or Kilombero rice, were continuously flooded with no less than 3 cm water level above soil surface to replicate continuous flooding (CF) irrigation practiced in smallholder rice farms in Malawi [30]. Four replicates were arranged for each treatment and all other conditions were as specified in our previous publication [21].

2.2. Collection of porewater and determination of Co and Pb concentrations in porewater

At predetermined time points (25th, 40th, 90th, 110th and 130th date after transplanting (DAT), porewater was sampled from each pot experiment using Rhizon samplers inserted into the soil at a 45° angle [18]. The porewater was collected through syringes attached to Rhizon samplers. The pH of porewater was determined on raw porewater prior to metal(loids) measurements using inductively coupled plasma mass spectrometry (ICP-MS/MS) operating conditions, including solution ICP-MS/MS and silicon reference material (CRM) were determined on 0.20 g (±0.01 g) of ball-

2
milled samples in triplicate, digested in 2.00 mL of 70% nitric acid overnight assisted by open vessel digestion using Mars 5 digestion system (CEM, US). Analytes (Co and Pb) concentrations in shoots, grains and CRM were determined using ICP-MS/MS (8800 model: Agilent Technologies, USA) in inorganic mode. Similarly, the instrument operating conditions were optimized as stated in section 2.3) by continuous introduction of a tuning solution having 1 μg/L Pb, Co, Y and Rh (Table 2).

2.4. Translocation factor

The soil-to-shoots cobalt translocation factors (soil-to-shoots Co-TF), soil-to-shoots lead translocation factors (soil-to-shoots Pb-TF), shoots-to-grains Co-TF and shoots-to-grains Pb-TF were calculated as ratios of Co and Pb concentrations in shoots or grains to that in corresponding soil or shoots [34] (Equation 1).

\[
\text{Translocation factor, } TF = \frac{[C]_a}{[C]_b}
\]

where \([C]_a\) is Co or Pb concentration in shoots or grains and \([C]_b\) is Co or Pb concentration in soil or shoots. Considering that TF values for metals vary with plant species, soil pH, soil chemistry and soil amendments [35], TF were compared across soil metal content, cultivar and Fe \(\text{Pb}\) concentration in soil or shoots. Considering that TF values for metals

3. Results

3.1. Impact of Fe amendments on porewater-pH and Co and Pb concentration

3.1.1. Soil-pH

Porewater was sampled for determination of porewater-pH at 25\(^{th}\), 40\(^{th}\), 90\(^{th}\) and 110\(^{th}\) day after transplanting (DAT) (Data not shown). No significant porewater pH differences were observed at all sampling points. However, mean porewater-pH under Kilombero (pH = 6.1) was lower than that under Faya (pH = 6.3) which indicated that Kilombero induced more acidic conditions in the porewater. Furthermore, mean porewater-pH in soils amended with 6.20 g kg\(^{-1}\) Fe (pH = 6.2) and 12.40 g kg\(^{-1}\) Fe (pH = 6.3) were higher than that under control (pH = 5.8) showing that Fe amendments enhanced alkalinity of porewater (Data not shown).

3.1.2. Porewater-Co

Results showed that Fe doses (p = 0.005; F = 8.09) and interactions of rice cultivar \(x\) Fe doses (p = 0.035; F = 4.41; Figure 1a) markedly affected porewater-Co mobilization whereas cultivar alone had no impact (p = 0.758; F = 0.10; Figure 1a). For impact of Fe doses, mean Co concentrations in porewater amended with 6.20 g Fe kg\(^{-1}\) (9400 μg kg\(^{-1}\)) and 12.40 g Fe kg\(^{-1}\) (7500 μg kg\(^{-1}\)) were 38% and 53%, respectively, lower compared to the control (15900 μg kg\(^{-1}\); Figure 1a) showing that Fe reduced available Co concentrations in porewater. For impact of interaction of cultivar \(x\) Fe amendment, Fe markedly reduced Co concentrations from 18740 μg kg\(^{-1}\) in control treatment to 7110 μg kg\(^{-1}\) (62%) and 9140 μg kg\(^{-1}\) (51%; Figure 1a) in porewater (under Kilombero cultivation) amended with 6.20 g Fe kg\(^{-1}\) and 12.40 g Fe kg\(^{-1}\), respectively. Conversely, while Fe doses of 6.20 g Fe kg\(^{-1}\) had no significant impact on Co concentrations, Fe dose of 12.40 g Fe kg\(^{-1}\) reduced Co concentrations from 13080 μg kg\(^{-1}\) in control treatment to 5080 μg kg\(^{-1}\) (62%) in porewater under Faya cultivation.

3.1.3. Porewater-Pb

Two-way ANOVA revealed that porewater-Pb was markedly affected by Fe amendment (p < 0.001; F = 81.28) only but not by Fe amendment (P = 0.499; F = 0.48) and interaction of cultivar \(x\) Fe amendment (p < 0.481; F = 0.77; Figure 1b). For impact of Fe doses, Pb concentrations in treatments amended 6.20 g kg\(^{-1}\) Fe (6900 μg kg\(^{-1}\)) and 12.40 g kg\(^{-1}\) Fe (6800 μg kg\(^{-1}\)) were 5% and 6%, respectively, higher than that under control (7100 μg kg\(^{-1}\); Figure 1b) showing that porewater Pb mobilisation was markedly impacted by Fe.

3.2. Interaction impact of cultivar \(x\) Fe doses on shoots-Co and Pb concentrations

3.2.1. Shoot-Co

Statistical description of measured parameters showing independent impact of cultivars type and Fe doses and interaction impact of cultivars type and Fe doses on Co and Pb accumulation in shoots and grains are summarized in Figure 2 and Table 2. Simple linear correlations and general linear regression analysis were also performed to evaluate impact of various Fe doses (Figure 2; Table 3).

Accumulation of Cobalt in shoots was markedly affected by cultivar (p < 0.1; F = 5.3), Fe amendment (p < 0.05; F = 1.3) and interaction of cultivar \(x\) Fe doses (p < 0.001; F = 13.2; Figure 2a, b, c, and d; Table 2). Regardless of Fe doses, the mean shoot-Co was measured to be 338 ± 86 μg kg\(^{-1}\) and 264 ± 59 μg kg\(^{-1}\) in Faya and Kilombero rice, respectively (Figure 2a). Thus, Faya shoots accumulated 22% more Co than Kilombero rice (Figure 2a). For Fe, rice amended with 6.20 and 12.40 g kg\(^{-1}\) of Fe doses accumulated mean shoot-Co concentrations of 335 ± 32 and 265 ± 29 μg kg\(^{-1}\), respectively, while shoot-Co concentrations in control plants averaged 319 ± 18 μg kg\(^{-1}\) (Figure 2a). While Fe amendment of 6.20 g Fe kg\(^{-1}\) soil induced no significant differences, Fe amendment of
12.40 g Fe\textsuperscript{0} kg\textsuperscript{-1} soil reduced shoot-Co accumulation by 17\% (Figure 2a). Linear regression equation ($r^2 < 0.61$; $p < 0.01$) and linear correlation ($r = -0.78$; $p < 0.01$) between Fe\textsuperscript{0} dosages and shoot-Co concentrations were significant (Figure 3a; Table 3) and suggested an inverse linear and negative correlation relationship.

For interaction impact of cultivar x Fe\textsuperscript{0} dosages in rice amended with 0, 6.20 and 12.40 g Fe\textsuperscript{0} kg\textsuperscript{-1} soil averaged 423 ± 51, 382 ± 36 and 284 ± 14 μg kg\textsuperscript{-1}, respectively, in Faya (Figure 2a) and 275 ± 34, 289 ± 56 and 265 ± 37 μg kg\textsuperscript{-1}, respectively, in Kilombero (Figure 2a). While Fe\textsuperscript{0} dosages induced inconsistent and non-significant shoots-Co variations in Kilombero rice, corresponding Fe\textsuperscript{0} dosages of 6.20 and 12.40 g Fe\textsuperscript{0} kg\textsuperscript{-1} reduced shoot-Co concentration by 10% and 33%, respectively, in Faya rice (Figure 2a). The observation shows that Fe\textsuperscript{0} amendments are more effective in Faya compared to Kilombero. Furthermore, Fe\textsuperscript{0} dosages strongly and negatively correlated with shoot-Co concentrations in Faya rice ($r = -0.97$; $r^2 = 0.93$, $p < 0.001$; Figure 3a; Table 3) whereas weaker and positive correlations were observed in Kilombero ($r = 0.66$; $r^2 = 0.42$, $p < 0.05$; Figure 3a; Table 3).
The observation showed that Fe accumulation in Faya was markedly greater than that in Kilombero (r2 = 0.55, p < 0.01). For Fe concentration, the translocation factor of elements from shoot to grain was 3.5 for Faya and 3 for Kilombero, showing linear equations and regression analyses revealed strong negative linear correlation between shoot-Pb and shoot-Co concentrations (r2 = -0.98, p < 0.001). Furthermore, linear regression analyses revealed significant positive linear correlation (r2 > 0.918; p < 0.001) between Fe dosages and grain-Co concentrations.

For interaction of cultivar x Fe, Fe markedly reduced grain-Co accumulation from 93 ± 26 μg kg−1 in control treatment to 62 ± 5 μg kg−1 (33%) and 48 ± 11 μg kg−1 (48%) rice grains amended with 6.20 and 12.40 g Fe kg−1, respectively, in Faya (Figure 2b); whereas corresponding Fe dosages stimulated inconsistent and/or non-significant variations in Kilombero (Figure 2b). While Fe dosages had weak and/or non-significant linear correlation relationships with grain-Co concentration in Kilombero, Faya had a strong linear (r2 = 0.96; p < 0.001) and negative correlation (r = -0.98; p < 0.05) relationships with grain-Co concentration in Faya (Figure 3b; Table 3).
For cultivar, soil-to-shoot Pb-TF in Faya rice (1.9) was 2.3 folds less than that in Kilombero rice (6.3) (Figure 4b) showing that Faya rice translocated Pb from soil to grains compared to Kilombero rice (Figure 4b). For Fe\textsuperscript{2+}, Fe\textsuperscript{2+} dosages of 6.20 and 12.40 g kg\textsuperscript{-1} reduced soil-to-shoot Pb-TF from 4.4 in control treatment to 2.3 (49%) and 2.7 (71%), respectively (Figure 4b), showing that Fe\textsuperscript{2+} dosages markedly regulated Co translocation.

3.5. Impact of cultivar, Fe\textsuperscript{2+} and their interaction on shoot-to-grain Co-TF and shoot-to-grain Pb-TF

3.5.1. Shoot-to-grain Co-TF

Shoot-to-grain Co-TF were markedly affected by Fe\textsuperscript{2+} dosages (p < 0.001; F = 112.6) and interactions of cultivar x Fe\textsuperscript{2+} (p < 0.01; F = 7.3) but not by cultivar (P > 0.05; Table 2; Figure 5a). For cultivar, shoot-to-grain Co TF in Faya and Kilombero rice averaged 0.23 and 0.19, respectively. Thus, Faya rice had translocated 16% less shoot-Co to grains than Kilombero rice had, though not markedly different (Figure 5a).

For Fe\textsuperscript{2+}, shoot-to-grain Co-TF in rice amended with 0, 6.20 and 12.40 g Fe\textsuperscript{2+} kg\textsuperscript{-1} soil were 0.25, 0.23 and 0.20, respectively, indicating that plants amended with Fe\textsuperscript{2+} amendment dosage of 12.40 g Fe\textsuperscript{2+} kg\textsuperscript{-1} soil had translocated 21% less shoot-Co to grains than the control plants had (Figure 5a) while shoot-Co translocated by plants amended with Fe\textsuperscript{2+} amendment dosage of 6.20 g Fe\textsuperscript{2+} kg\textsuperscript{-1} was not markedly different from that the control plants had. For interaction of cultivar x Fe\textsuperscript{2+} amendment, the shoot-to-grain Co-TF stimulated by Fe\textsuperscript{2+} dosages of 0, 6.20 and 12.40 g Fe\textsuperscript{2+} kg\textsuperscript{-1} soil averaged 0.22, 0.16 and 0.18, respectively, in Faya rice and 0.17, 0.23 and 0.17, respectively, in Kilombero rice. The observation showed that Faya rice amended with 6.20 g Fe\textsuperscript{2+} kg\textsuperscript{-1} soil had translocated 26% less shoot-Co to grains but translocated 34% more shoot-Co to grain in Kilombero rice (Figure 5a).

3.5.2. Shoots-to-grain-Pb translocation factor (TF)

Shoots-to-grain-Pb TF were markedly affected by Fe\textsuperscript{2+} dosages (p < 0.001; F = 62.1), Fe\textsuperscript{2+} amendment (p < 0.001; F = 8.3) and interactions of cultivar x Fe\textsuperscript{2+} amendment (p < 0.01; F = 4.1; Table 2; Figure 5b). Regardless of amending soils with Fe\textsuperscript{2+}, shoot-to-grain-Pb TF in Faya and Kilombero rice
averaged 1.9 and 4.2, respectively, with Faya rice translocating 2-folds less shoot-Pb to grains than Kilombero rice had (Figure 5b). For Fe\textsuperscript{6+}/C\textsubscript{14}, rice amended with 6.20 (2.0) and 12.40 g kg\textsuperscript{-1} of Fe\textsuperscript{6+}/C\textsubscript{14} dosages (1.3) translocated more than 26% less shoot-Pb to grains than control treatment had (2.7; Figure 5b) showing that Fe\textsuperscript{6+}/C\textsubscript{14} amendments markedly inhibited translocation of shoot-Pb to grains.

4. Discussion

The presence of contaminants in soil reduce soil microbial biomass as well as microbial activities [22]. It is reported that Fe\textsuperscript{6+} negatively affect bacterial abundance and microbial quality of contaminated soils but not of non-contaminated soil [22]. Considering that soils used in this study was not contaminated and was uniform in all treatments, impact of various Fe\textsuperscript{6+} dosages on rhizosphere microorganisms was not evaluated in this study. Nevertheless, impact of cultivar, Fe\textsuperscript{6+} dosages and their interaction were evaluated on porewater-pH and porewater-Co and Pb concentrations (Figure 1; Table SM3).

Porewater-pH is an important parameter because it can decide solubility and bioavailability of metal(loid)s such as Co and Pb. In this study, lower pH was observed in porewater planted with Faya (Table SM3). The observation suggested that Faya excreted exudates that induced more acidic conditions compared to that of Kilombero. Lower pH might be responsible for increased Co and Pb uptake in Faya under control treatments considering that bioavailability of metal(loid)s increases with soil pH decrease, resulting in increased uptake of Co and Pb [38]. Moreover, most micronutrients, including Co and Pb, are less available in alkaline soils (soil pH > 7.5) and are optimally available in slightly acidic soils and porewater (6.5 < soil-pH < 6.8) [38, 39].

In this study, Faya rice cultivar accumulated higher Co and lower Pb in shoots and grains compared to Kilombero rice. In addition to accumulating lower grain-Pb, Faya cultivar accumulated lower As concentrations (412 ± 116 μg/kg) in grains compared to Kilombero (700 ± 29 μg kg\textsuperscript{-1}) [21]. These observations confirm that selecting Faya cultivar compared to Kilombero has added benefits of regulating a wide spectrum of carcinogen bioaccumulation in rice grains. Furthermore, selecting Faya cultivar has also the observation confirms previous observations that rice cultivars have different ability of rice in up-taking of and bio-accumulating Co and Pb in shoots and grains varies considerably with rice plant species [40]. Consistent to our results, Rahman et al [17] reported that different rice cultivars show different Co accumulation rates in rice shoots and grain. For instance, Rahman et al [17] identified Japanese sushi rice as a low Co accumulating cultivars (mean: 9–14 μg kg\textsuperscript{-1}; range: 9–15 μg kg\textsuperscript{-1}) compared to Thai rice (mean: 21,700 μg kg\textsuperscript{-1};
through adsorption of Co or Pb ions onto Fe oxides - similar to reaction Co and Pb bioaccumulation in rice by immobilizing soil-Co and Pb which generates enormous amounts of iron oxides and iron hydroxides with previous shoots-Co and Pb translocated to grains. The observation is in agreement linked to elevated iron plaque on rice roots which might have reduced that higher soil-Fe abundance might be linked to elevated chelation of Co and Pb in shoots which indicates that Fe dosages influenced similar uptake and accumulation of grain-Pb and Co concentrations in Faya. For Kilombero, corresponding Fe dosages had no effect on grain-Co accumulation but had a decreasing effect on Pb uptake and accumulation. The finding shows that impact of Fe amendment in regulating grain-Co accumulation is dependent on both cultivar and Fe dosages with Faya rice having greater grain-Co and Pb reduction potential. The reduction could be linked to formation of greater magnitude of iron plaque on Faya rice roots which has greater potential of sequestering greater magnitude of soil-Co and Pb. Thus, the observation suggests genotypic differences between Faya and Kilombero in formation of iron plaques which is consistent with a previous report [47]. Wu et al. [48] reported significant positive correlation between Fe concentrations and As for hybrid cultivars and significant negative correlation for indica cultivars and attributed the differences to cultivar variation in formation of iron plaque.

Comparisons between grain-Pb concentrations with maximum contaminant limit (MCL) for Pb concentrations in rice (200 μg kg⁻¹) [12, 49], indicated that grain-Pb concentrations obtained in this study for control treatments of both Faya and Kilombero exceeded the MCL. Conversely, grain-Pb concentrations obtained in rice amended with Fe were lower than MCL. The observation suggests that amending rice with Fe of at least 6.20 g kg⁻¹ soil markedly reduce Pb bioaccumulation to safe levels for human consumption.

5. Conclusions

Our present study has revealed positive impacts of interaction of Fe x cultivar on quality of rice by reducing bio-accumulation of cobalt and lead in rice grains cultivated in soils under practical environmental conditions. The study has also increased our understanding of interaction impact of Cultivar x Fe dosages in rice systems. For instance, variable cultivar response and dosage dependent effects of zero valent iron amendments on both shoots and grain Cobalt and lead content and translocation seen in both cultivars suggested that Fe can effectively alleviate excessive accumulation of lead in rice and/or diminished Co supply in diets simultaneously. For Malawi, there is need to jealously guard contamination of rice paddies for Malawi to continue producing high quality rice with low grain-cobalt and lead content.

Declarations

Author contribution statement

Angstone Thembachako Mlangeni, PhD: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Andrea Raab: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Joerg Feldmann: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.
Funding statement
Dr Angstone Thembachako Mangeni was supported by Commonwealth Scholarship Commission [MWCS-2015-334].

Data availability statement
Data will be made available on request.

Declaration of interest’s statement
The authors declare no conflict of interest.

Additional information
Supplementary content related to this article has been published online at https://doi.org/10.1016/j.heliyon.2022.e11928.

Acknowledgements
ATM express profound gratitude to Dr Magali Perez for technical help with instrumentation.

References
[1] M. Wang, T. Tang, T. Chen, X. Wang, W. Zhou, Z. Tang, J. Zhang, F. Zhao, Water management impacts the soil microbial communities and total arsenic and methylated arsenicals in rice grains \*, Environ. Pollut. 247 (2019) 736–744.
[2] R. Ma, J. Shen, J. Wu, Z. Tang, Q. Shen, F. Zhao, Impact of agronomic practices on arsenic accumulation and speciation in rice grain, Environ. Pollut. 194 (2014) 217–223.
[3] R.L.V. Matalvelli, M.L. Buzo, L.J. De Arauz, M. De Fatima, H. Carvalho, E. Emý, K. Arakaki, R. Matsuuki, P. Tíglea, Total arsenic, cadmium, and lead determination in Brazilian rice samples using ICP-MS, J. Anal. Methods Chem. 2016 (2016) 1–9.
[4] Agency for Toxic Substances and Disease Registry (ATSDR), Public Health Surveillance Statement, Cobalt, Atlanta, USA, 2004.
[5] F. Zeng, S. Ali, H. Zhang, Y. Ouyang, B. Qiu, F. Wu, G. Zhang, The influence of pH and organic matter content in paddy soil on heavy metal availability and their uptake by rice plants, Environ. Pollut. 159 (2011) 84.
[6] R. Khanam, A. Kumar, A.K. Nayak, R. Tripathi, S. Vijayakumar, D. Bhaduri, U. Kumar, S. Mohanty, P. Panneerselvam, D. Chatterjee, B.S. Patapathy, H. Pathak, Metal (loid)s (As, Hg, Se, Pb and Cd) in paddy soil: bioavailability and potential risk to human health, Sci. Total Environ. (2019) 143330.
[7] D.R. Wang, Y.S. Cui, X.M. Liu, V.T. Dong, P. Christie, Soil contamination and plant uptake of heavy metals at polluted sites in China, J. Environ. Sci. Hea. Part A. 2016 (2016) 260–271.
[8] T.F. Menezes, P. Tommasini, A.S. Kumwenda, Genetic Analysis of NERICA Rice Size in 2 F Populations of Crosses between Malawi rice Landraces and NERICA Varieties, Second Africa Rice Congr., 2010, pp. 22–26.
[9] G.J. Norton, P.N. Williams, E.E. Adomako, A.H. Price, Y. Zhu, F. Zhao, S. Mcgrath, M. Islam, M. Jahiruddin, J. Feldmann, A.H. Price, A.A. Meharg, Identification of low inorganic and total grain arsenic rice cultivars from Bangladesh, Environ. Sci. Technol. 43 (2009) 6070–6075.
[10] T. Menezes, Genetic Studies of Grain and Morphological Traits in Early Generation Crosses of Malawi Rice (Oryza Sativa L.) Landraces and NERICA Varieties Tenyson Menezes A Thesis Submitted in Fulfillment of the Requirements for the Degree of Doctor of Philosophy, University of KwaZulu-Natal, 2010.
[11] J. Feldmann, A. Raab, E.M. Krupp, Importance of ICPMS for Speciation Analysis Is Changing: Future Trends for Targeted and Non-targeted Element Speciation Analysis, 2017.
[12] P. Bükner, A. Raab, P. Nuytens, A.M. Chioma Acta Validation and Inter-laboratory Study of Selective Hydride Generation for Fast Screening of Inorganic Arsenic in Fish (Turdus O. 2018.
[13] P.N. Williams, K.G. Scekhet, J. Feldmann, A. Raab, Y. Zhu, Specification and Localization of Arsenic in White and Brown Rice Grains, 42, 2008, pp. 1051–1057.
[14] S. Li, J. Shi, C. Wu, H. Zhao, Y. Qiu, W. Pan, W. Hanley, M. Cui, Cadmium and arsenic contamination in paddy soils of a mining area and their exposure e f f on human HEPG2 and keratinocyte cell-lines, Environ. Res. 156 (2017) 23–30.
[15] M.A. Khan, S. Khan, A. Khan, M. Alam, Soil contamination with cadmium , consequences and remediation using organic amendments, 601–602, Sci. Total Environ. (2017) 1591–1605.
[16] G. Rahimi, Z. Kolahchi, A. Charkhabi, Uptake and translocation of some heavy metals by rice crop (Oryza sativa) in paddy soils, Agricultural Research 6, 2016, pp. 163–175.
[17] I. Coelho, A. Rego, S. Gueif, M. Alla, N. Isabel, Application of chemometric methods for multi-elemental characterization of fruit juices and nectars analysed in the Portuguese Total Diet Studies pilot study, J. Chromatogr. 2017 (2017) 1–11.
[18] N.K. Fageria, Yield Physiology of Rice, 2017.
[19] A.T. Mangeni, S.T. Lancaster, A. Raab, E.M. Krupp, G.J. Norton, J. Feldmann, Impact of soil-type , soil-pH, and soil-metal (oids) on grain-As and Cd accumulation in Malawi rice grown in three regions of Malawi, Environ. Adv. 7 (2022) 100145.
[20] A. Kabata-pendias, H. Pendias, Trace Elements in Soils and Plants, third ed., CRC Press LLC, Boca Raton, 2001.
[21] U. Ahsraf, A.S. Kanu, Z. Mo, S. Hussain, S.A. Anjum, I. Khan, R.N. Abbas, X. Tang, Lead toxicity in rice: effects, mechanisms, and mitigation strategies—a mini review, Environ. Sci. Pollut. Res. 22 (2015) 18318–18322.
[22] C. Fangmign, Z. Ningchun, H. Ximing, L. Yi, Z. Wenfang, Cadmium and lead contamination in Japanese rice grains and its variation among the different locations in southeast China, Sci. Total Environ. 359 (2006) 156–168.
[23] B. Li, Z. Zhou, D. Wei, J. Long, L. Peng, B. Tie, Mitigating arsenic accumulation in rice (Oryza sativa L.) from typical arsenic contaminated paddy soil of southern China using nanostructured α-MnO 2 : pot experiment and field application, Sci. Total Environ. 650 (2019) 546–556.
[24] H.Y. Yu, X. Ding, F. Li, L. Wang, X. Zhang, J. Yi, C. Liu, X. Xu, Q. Wang, The availability of arsenic and cadmium in rice paddy field elds from a mining area: the role of soil extractable and plant silicon \*, Environ. Pollut. 215 (2016) 258–265.
[25] T. Kuma, H. Ohsaka, A. Kaneko, K. Nakamura, T. Makino, H. Katou, Effects of soil amendments on arsenic and cadmium uptake by rice plants (Oryza Sativa L. cv.,
Koshihikari) under different water management practices, Soil Sci. Plant Nutr. 62 (2016) 349–356.

[46] A.B. Siddique, M.M. Rahman, M.R. Islam, Influence of iron plaque on accumulation and translocation of cadmium by rice seedlings, Sustain. Artic. 13 (2021).

[47] C. Wu, Q. Zou, S. Xue, W. Pan, L. Huang, W. Hartley, J. Mo, M. Wong, The effect of silicon on iron plaque formation and arsenic accumulation in rice genotypes with different radial oxygen loss (ROL), Environ. Pollut. 212 (2016) 27–33.

[48] C. Wu, Q. Zou, S. Xue, J. Mo, W. Pan, L. Lou, M. Hung, Effects of silicon (Si) on arsenic (As) accumulation and speciation in rice (Oryza sativa L.) genotypes with different radial oxygen loss (ROL), Chemosphere 138 (2015) 447–453.

Codex Alimentarius Commission, Joint FAO/WHO Food Standards Programme Codex Committee on Contaminants in Foods: Working Document for Information and Use in Discussions Related to Contaminants and Toxins in the GSCTFF; Fifth Session, The Hague, The Hague, Netherlands, 2011, 21 - 25 March 2011.