



The effect of soil types, pH, and geographical locations on carcinogenic metal buildup in *Oryza sativa* cultivated in Ghana

Ebenezer Aquisman Asare · Dickson Abdul-Wahab · Anita Asamoah · Samuel Boakye Dampare · Elsie Effah Kaufmann · Rafeah Wahi · Zainab Ngaini · Charles Kofi Klutse · Nana Ama Browne Klutse · Crentsil Kofi Bempah · Joseph Richmond Fianko · Evelyn Ama Otoo

Received: 2 February 2024 / Accepted: 19 April 2024
© The Author(s), under exclusive licence to Springer Nature Switzerland AG 2024

Abstract This study investigated the impact of soil type, pH, and geographical locations on the accumulation of arsenic (As), lead (Pb), and cadmium (Cd) in rice grains cultivated in Ghana. One hundred rice farms for the sampling of rice grains and soil were selected from two regions in Ghana—Volta and Oti. The concentrations of As, Pb, and Cd were analyzed using ICP-OES. Speciation modeling and multivariate statistics were employed to ascertain the relations

among measured parameters. The results showed significant variations in soil-As, Pb, and Cd levels across different soil types and pH ranges, with the highest soil-As and Cd found in alkaline vertisols. For soil-As and Cd, the vertisols with a pH more than 7.0 exhibited the highest mean concentration of As ($2.51 \pm 0.932 \text{ mgkg}^{-1}$) and Cd ($1.00 \pm 0.244 \text{ mgkg}^{-1}$) whereas for soil-Pb, the luvisols of soil types with a pH less than 6.0 exhibited the highest mean concentration of Pb ($4.91 \pm 1.540 \text{ mgkg}^{-1}$). Grain As, Pb, and Cd also varied across soil types and pH levels. In regards to grain-As, the vertisols soil type, with a pH less than 6.0, shows the highest mean concentration of grain As, at $0.238 \pm 0.107 \text{ mgkg}^{-1}$. Furthermore, vertisols soil types with a pH level less than 6.0 showed the highest mean concentration of grain Cd, averaging at $0.231 \pm 0.068 \text{ mgkg}^{-1}$ while luvisols, with a pH less than 6.0, exhibited the highest mean concentration of grain Pb at $0.713 \pm 0.099 \text{ mgkg}^{-1}$. Speciation modeling indicated increased bioavailability of grains Cd^{2+} and Pb^{2+} ions in acidic conditions.

Highlights

- Soil As, Pb, and Cd varied by soil type, pH, location; highest in alkaline vertisols
- Grain As, Pb, and Cd also varied; grain-As highest in acidic vertisols, Pb in acidic luvisols
- Cd^{2+} and Pb^{2+} are more bioavailable in acidic soils; HAsO_4^{2-} , HAsO_3^{2-} in neutral to alkaline
- Soil Cd and pH interaction affected grain As uptake
- 51% of area had hazard risk >1 for grain consumption, but no carcinogenic risk found

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s10661-024-12654-7>.

E. A. Asare (✉) · A. Asamoah · C. K. Bempah
Nuclear Chemistry and Environmental Research Centre,
National Nuclear Research Institute (NNRI), Ghana
Atomic Energy Commission (GAEC), Box LG 80, Legon,
Accra, Ghana
e-mail: aquisman1989@gmail.com

D. Abdul-Wahab · S. B. Dampare · J. R. Fianko
Department of Nuclear Science and Applications, School
of Nuclear and Allied Sciences, University of Ghana,
Atomic, Kwabenya, Accra, Ghana

E. E. Kaufmann
Department of Biomedical Engineering, University
of Ghana, Legon, Accra, Ghana

R. Wahi · Z. Ngaini
Department of Chemistry, Faculty of Resource Science
and Technology (FRST), Universiti Malaysia Sarawak,
Kota Samarahan, Sarawak, Malaysia

A significant interaction was found between soil-Cd and pH, affecting grain-As uptake. The average concentrations of soil As, Pb, and Cd aligned with international standards. Generally, the carcinogenic metals detected in grain samples collected from the Volta region are higher than that of the Oti region but the differences are insignificant, and this may be attributed to geographical differences and anthropogenic activities. About 51% of the study area showed a hazard risk associated with grain metal levels, although, no carcinogenic risks were recognized. This study highlights the complex soil-plant interactions governing metal bioaccumulation and emphasizes the need for tailored strategies to minimize metal transfer into grains.

Keywords Carcinogenic metals · ICP-OES · Rice · Soil · Hazard risk

Introduction

Elevated levels of non-threshold carcinogens such as arsenic (As), lead (Pb), and cadmium (Cd) in cereal crops (e.g., rice, millet, sorghum, etc.) and their by-products have negative impacts on human health (Xu et al., 2022). According to Liu et al. (2012), long-term exposure to As, Pb, and Cd causes a variety of malignancies and other health complications.

To date, an extensive body of research has been conducted throughout many regions of the globe to evaluate the variables, processes, and routes underlying the absorption of Pb, Cd, and As from cereal grains (Aslam et al., 2021; Souza et al., 2020). Soil contents of sorbent, including hydroxides and oxides of manganese (Mn), zinc (Zn), aluminum (Al), and iron (Fe), have been observed to significantly affect the bioavailability, mobility, and absorption of

metalloids and metals in cereal systems (Violante et al., 2010). Sorbents reduce the uptake of As, Pb, and Cd by metalloids and metals present on their surfaces, rendering the metals immobile and unsuitable for absorption by plants (Amoah-Antwi et al., 2020; Radziemska, 2018). However, the bioavailability, solubility, and motility of As, Pb, and Cd in soil pore water are determined by the kind and quantity of sorbents present in the soil or pore water (Sipos et al., 2018). According to García-Sánchez et al. (2010) and Lin et al. (2008), the mobility of As in soil is negatively correlated with the concentration of sorbing elements in the soil's pore water. Specifically, the mobility of As in soil is inversely proportional to the levels of Al and Fe. Therefore, the amount of As immobilized decreases with the soil's Al and Fe contents. As in soil or soil/water solution has been demonstrated to be immobilized by adsorption onto Fe oxides, which occurs when the As ions displace the surface OH⁻ groups and cause the production of amorphous Fe(III) arsenate (Yang et al., 2023).

Speciation in soil has a significant impact on the bioavailability and toxicity of Pb towards plants and microorganisms (Yang et al., 2023). With soil constituents, it produces permanent complexes. Pb mobilization and soil-borne Fe dissolution are intimately related. Soil zinc also regulates the mobility and phytoavailability of Cd in the soil; research has shown that zinc significantly reduces Cd absorption (Kabata-Pendias, 2000). When considering the process of absorption, Cd and Zn are in competition for the same site. Consequently, the implementation of soil amendments functioning as adsorbents or sorbents can effectively mitigate the accumulation of grain borne As, Pb, and Cd in cereal crops like rice and millet (Yu et al., 2017)

According to Yang et al. (2023), the bioavailability and mobility of As, Pb, and Cd in soil pore water are influenced by sorbents through desorption/adsorption and co-precipitation with metalloid oxides. Numerous research investigations have been conducted on the potential of soil amendments to sorb As, Pb, or Cd onto their surfaces, rendering the elements immobile and unsuitable for absorption. To immobilize As, for instance, soil amendments comprising media containing Fe as sorbents have been the subject of much investigation (Mlangeni et al., 2022; Yang et al., 2023). According to a study by Moreno-Jiménez et al. (2016), zero-valent iron (Fe⁰) exhibits significant

C. K. Klutse
Nuclear Power Institute (NPI), Ghana Atomic Energy
Commission (GAEC), Box LG 80, Legon, Accra, Ghana

N. A. B. Klutse
Department of Physics, University of Ghana, Legon,
Accra, Ghana

E. A. Otoo
Biotechnology and Nuclear Agriculture Research Institute
(BNARI), Ghana Atomic Energy Commission (GAEC),
Box LG 80, Legon, Accra, Ghana

adsorption capacities for arsenic (As), particularly pentavalent arsenic (As^{5+}), in oxic soils. The authors specifically note that the As species, which is predominant in oxic soils, firmly binds to the minerals of Fe° . Trivalent arsenic, As (III) mobility is greater than that of arsenic (As^{5+}) in saturated soils, however, due to reductive dissociations of Fe-oxides and the subsequent reduction of Arsenic V to Arsenic III, a process prevalent in reducing ecosystems (Moreno-Jiménez et al., 2016; Yang et al., 2023; Yu et al., 2017). There has been speculation over the significant reduction in bioavailability of As in continuous flooding (CF) water systems resulting from the addition of Fe° (Mlangeni et al., 2022). On the contrary, the impact of incorporating Fe° into alternate wetting and drying (AWD) water management systems remains undisclosed. Selenium (Se) has also been proposed as a soil addition to reduce Cd/Pb accumulation (Moreno-Jiménez et al., 2016; Yu et al., 2017). Se-soil amendments significantly decreased Cd levels in rice seedlings, particularly by reducing Cd transfer from roots to shoots under hydroponic conditions (Derakhshan Nejad et al., 2021). Derakhshan Nejad et al. (2021) and Wang, Ma, and Yang (2018); Wang, Liu, et al. (2018) demonstrated that via decreasing Cd bioavailability, Se may also inhibit the absorption and accumulation of Cd in plants.

Rice plants grown in vertisol have the unique ability to accumulate less Cd due to the high CaCO_3 content of vertisol, which limits the amount of accessible Cd in the plant and, consequently, the plant's Cd absorption (Sebastian & Prasad, 2014; Yu et al., 2017). However, rice plants continue to uptake a significant amount of Cd even in soils with low Cd concentrations, owing to the facile transfer of Cd from soil to plants via the bio-concentration factor. Cd absorption by plants is negatively impacted by the concentrations of Fe and Zn in soil and soil solution, according to Ronzan et al. (2017). This is due to the fact that Cd has chemical characteristics with Fe^{2+} and Zn^{2+} , which vie for the same cellular transporters. Due to the fact that Zn^{2+} and Cd^{2+} are transported by the same transporters, Zn^{2+} can inhibit the transport of Cd^{2+} inside rice (Mlangeni et al., 2022). Cd mobilization into an ecological system may be the result of geogenic, anthropogenic, or both processes (Asare et al., 2019; Asare et al., 2022). The mining of zinc-bearing ores may result in the discharge of

measurable Cd into agricultural land and rivers as byproducts (Xie et al., 2016).

Scholars and researchers have extensively investigated the impact of soil types, soil pH, and soil sorbents on the accumulation of As, Pb, and Cd in rice grains (Du et al., 2020; Miller et al., 1977; Mlangeni et al., 2022; Ronzan et al., 2017; Sebastian & Prasad, 2014). For instance, soil pH is crucial for the bioavailability of metals in soil (Violante et al., 2010). Low pH soil tends to inhibit the sorption of most metalloids, including As, Pb, and Cd, increasing their bioavailability and mobility in pore water (Yu et al., 2017). Soil pH also regulates pH-dependent surface charges on sorbents, which influences the attraction of As, Pb, and Cd for sorption sites. Consequently, the dissolution of these elements is reduced under alkaline soil circumstances relative to acidic soil conditions (Violante et al., 2010). Consequently, when soil pH increases, so do the mobility and bioavailability of As, Pb, and Cd in the soil (Rafiq et al., 2014). Additionally, most studies have shown that the bioavailability of As, Pb, and Cd is soil-type dependent, with some soil types retaining As, Pb, and Cd better than others. Rice grown in andisols develops a more limited grain yield in comparison to rice grown in alternative soil types. The observed fluctuations can be attributed to the restricted bioavailability of As in andisols (Ishikawa et al., 2016).

Moreover, Mandal and Suzuki (2002) have documented that some alluvial and vertisol soils have the greatest levels of As, whereas sandy soils exhibit the lowest. In comparison to other soil types, vertisols have been shown to have a relatively low Cd accumulation. This has been attributed to the vertisol's high CaCO_3 concentration, which hinders the mobilization of Cd in pore water and its availability and absorption by rice plants (Sebastian & Prasad, 2014). Nevertheless, the impact of Ghana's geographical location, soil metalloids, soil types, and soil pH on the accumulation of As, Pb, and Cd in Ghanaian rice has not been addressed in any of the aforementioned research. Therefore, the objective of this study was to examine the impact of Ghana's geographical location, soil metalloids, soil types, and soil pH on the accumulation of As, Pb, and Cd in rice grains. Concerning the sustainable cultivation of safe, high-quality rice and the pollution-free preservation of Ghana's paddy-producing soils, this concern is critical.

Materials and methods

Sample collection and characterization

The procedure for sampling collection and characterization was adopted from the work of Mlangeni et al. (2022). From June to October 2021, a total of 100 rice grain samples and 100 soil samples were sampled from 30 distinct peasant rice farms situated in two distinct areas of Ghana: the Volta region (VoR; 44) and the Oti region (OtR; 56). Among the stations that were sampled, fluvisols, vertisols, and luvisols comprised the soil types at 42, 25, and 33 stations, respectively. Furthermore, a total of 30, 43, and 27 soil samples were identified based on their respective soil pH values: 6.0, 6.0 to 7.0, and > 7.0. Sampling involves the recording of several data points, such as the type of soil, geographical location, and soil pH.

Sample preparation

Every rice gain and soil sample underwent a 24-h drying process in an oven set at a temperature of 95 °C (h). By employing a Retsch MM400 ball mill, oven-dried samples were ball-milled (Retsch, Germany). In reference to the rice grain sample, a volume of around 0.30 g was utilized for both the certified reference material (CRM) NIST2039a and rice flour obtained from the National Institute of Technology (NIST), MD, USA. These materials were digested in 3.0 g of concentrated nitric acid (70% HNO₃ procured from Mallinckrodt Chemicals, USA) and left to react overnight in 60 mL centrifuge tubes. The subsequent day, the reaction was facilitated through the utilization of an open vessel microwave digestion system (MARS5, purchased from CEM, UK).

Concerning the soil samples, a volume of 0.20 g of each was combined with 5.0 g of concentrated nitric acid (70% HNO₃ procured from Mallinckrodt Chemicals, USA) and certified reference material (CRM) DC36102, which was obtained from the National Analysis Centre for Iron and Steel (NACIS), Beijing, China. The mixture was left to digest overnight in sterile glass digesting tubes. The next day, about 5.0 g of hydrogen peroxide (30% H₂O₂, purchased from Mallinckrodt Chemicals, USA) was added to the sample solution, which was subsequently cooked using the following Bloc Digestion System program: 45 min at 90 °C, 90 min at 110 °C, and 135 min at

130 °C, with a 15-min ramping interval between each level. Following filtration via a 0.45 µm microfilter, the digested materials were placed into a 25 mL centrifuge tube. A 15 g sample solution was obtained by diluting 1.5 g of the filtrates produced to a total of 15 g with 13.5 g of de-ionized water in separate 25 mL centrifuge tubes. Diluting factors were calculated using w/w for rice grain and soil sample digests.

Assessment of total As, Pb, and Cd in rice grain and soil samples

The analytes (As, Pb, and Cd) present in rice grains and soil were identified by means of inductively coupled plasma optical emission spectrometry (model 7000 DV ICP OES, Agilent Technologies, Santa Clara, CA, USA) operating in inorganic mode and standard multi-element turning conditions with external calibrations. The operational parameters for the ICP-OES equipment were as follows: 13 L/min for coolant gas, 0.9 L/min for nebulizer gas, 0.75 L/min for auxiliary gas, 1550 W for forward power, and 10 ms for dwell duration of the isotope. Ten duplicates of the total amounts of As, Pb and Cd in rice grain and soil samples were analyzed. Multi-element standards with appropriate ranges were generated using Accu-trace™ stock solution of ICP-OES grade, including 1000 mg As/kg, 1000 mg Pb/kg, and 1000 mg Cd/kg. Rhodium (103Rh) was employed as an internal standard (ISTD), while helium (He) was utilized in the collision cell at a flow rate of 4.5 mL/min.

Quality control and assurance (QC/QA)

Using certified reference materials (CRM) NCS DC36102 ($n = 6$) and NIST2039 ($n = 6$), an accuracy test was performed. The mean concentrations of As, Pb, and Cd in rice grain and soil samples collected with NCS DC36102 and NIST2039 were found to be within the $p > 0.05$ confidence interval limits of CRM values (Table 1). There were no significant discrepancies between certified and measured values, as determined by the paired t tests. This is because the paired t test significance values were all below $\alpha = 0.005$, which indicates a high degree of accuracy and precision. In order to assess the dissimilarity in concentrations of As, Pb, and Cd among the certified reference materials, a t test was conducted to determine the equality of means with

Table 1 Obtained results and *t* test for equality of means of analyses of NCS DC36102 and NIST2039 concentrations of As, Pb, and Cd (mg/kg)

Results of analyses of NCS DC36102 and NIST2039 concentrations of As, Pb, and Cd			
Parameter	As	Pb	Cd
NCS DC36102			
Certified values	35.5	40.2	5.70
Laboratory values	35.0	39.4	5.48
% recovery of Lab value	98.7%	98.1%	96.1%
N	6.00	6.00	6.00
SD	± 1.09	± 3.51	± 0.26
<i>t</i> test for equality of means			
<i>t</i> test	d.f.	<i>p</i> value	Mean difference
-2.95	11	0.013328	(As-Pb) = -4.40
+29.6	11	<0.00001	(As-Cd) = +29.54
+10.6	11	<0.00001	(Pb-Cd) = +33.94
NIST2039			
Certified values	0.394	0.528	0.018
Laboratory values	0.386	0.513	0.017
% recovery of Lab value	98.0%	97.2%	94.4%
N	6.00	6.00	6.00
SD	± 0.06	± 0.09	± 0.003
<i>t</i> test for equality of means			
<i>t</i> test	d.f.	<i>p</i> value	Mean difference
+1.29	11	> 0.05	(As-Pb) = -0.127
+6.72	11	< 0.05	(As-Cd) = +0.369
+4.16	11	< 0.05	(Pb-Cd) = +0.343

SD represents the standard deviation

df denotes the degree of freedom

a confidence level of 95%. As determined by the laboratory mean concentrations in NCS DC36102 CRM, the *p* values (As-Pb), (As-Cd), and (Pb-Cd) were <0.05 (Table 1). All three (As-Pb), (As-Cd), and (Pb-Cd) *p* values were less than the significance level of 0.05. Therefore, the laboratory values were deemed significant at a *p* value less than 0.05. On the contrary, the *p* values obtained from the laboratory mean concentrations of (As-Cd) and (Pb-Cd) in NIST2039 were both below the α -value threshold of 0.05, thus signifying substantial variations. Furthermore, the *p* value obtained from the laboratory mean concentrations of As and Pb in NIST2039 (As-Pb) surpassed the α -value of 0.05, indicating

that there is no statistically significant distinction between the average amounts of these elements.

Exposure and health risk assessment

The assessment of the safety of Ghanaian rice involved the comparison of grain-bound arsenic (As), lead (Pb), and cadmium (Cd) concentrations with threshold limits set by multiple regulatory bodies, including the Ghana Food and Drugs Authority (GFDA). In order to determine the extent of soil contamination, the obtained soil-bound arsenic, Pb, and Cd concentrations were also compared to the Chinese environmental quality standards for agricultural soils and the Soil UK CLEA soil guideline values (SGV) (Table 2). The daily intake (EDI) of As, Pb, or Cd (mgkg⁻¹day⁻¹person⁻¹) from oral consumption of Ghanaian rice was estimated using a model (Eq. 1) that was developed from the work of Zeng et al. (2011).

$$EDI = \frac{C_w - IR}{B_{wt}} \tag{1}$$

where C_w represents the ‘obtained mean concentration’ of As, Pb, or Cd (mgkg⁻¹) in rice, IR denotes a ‘mean ingestion rate of rice (kgday⁻¹person⁻¹), and B_{wt} signifies the calculated ‘body mass for Ghanaian adult consumers (kg)’.

The average body mass of Ghanaian adult consumers was estimated by weighing four hundred inhabitants’ body mass and the average body mass recorded (i.e., $B_{wt} = 59.53$ kg). During the estimation, IR of 0.05 and 0.10 kgday⁻¹person⁻¹ were used. Equation (2) was employed in calculating the cancer risk (CR) of ingesting As, Pb, or Cd via rice consumption.

$$CR = \frac{EDI \times ACD}{SF} \tag{2}$$

where CR is ‘the likely of excess lifetime of cancer risk and SF is ‘the gradient factor of cancerous metals (B_{wt} kgdaymg⁻¹) (Mlangeni et al., 2022).

The hazard quotient (HQ) can be described as the ratio of EDI and oral reference (RfD) was estimated using Eq. (3) adapted from Zeng et al. (2015). HQ were estimated employing the oral RfD for As = 3×10^{-4} mgkg⁻¹day⁻¹, Pb = 6.0×10^{-2} mgkg⁻¹day⁻¹, and Cd = 1×10^{-3} mgkg⁻¹day⁻¹ established by the US EPA (Mlangeni et al., 2022).

Table 2 Average concentrations for As, Pb, and Cd evaluated in this study; Chinese environmental quality standards for agricultural soils (GB15618-1995) for As, Pb, and Cd contents in uncontaminated soil; UK CLEA soil guideline values (SGV);

normally reported As, Pb, and Cd concentrations (NRMC) in uncontaminated soils; maximum acceptable levels (MAL) for As, Pb, and Cd, (mg/kg)

Parameter	As	Reference	Pb	Reference	Cd	Reference
Average soil-As, Pb, and Cd levels detected in this study	1.76 ± 0.65 mg/kg (pH < 6.0)	This study	3.75 ± 0.85 mg/kg (6 < pH < 7)	This study	0.733 ± 0.255 mg/kg (pH < 6.0)	This study
	2.51 ± 0.93 mg/kg (pH > 7.0)		4.91 ± 1.54 mg/kg (pH < 6.0)		1.00 ± 0.244 mg/kg (pH > 7.0)	
Chinese environmental quality standards for agricultural soils	30 (pH < 6.5)	Xie et al. (2016)	250	Yang et al. (2023)	0.3 (pH < 5.5)	Liu et al. (2012)
	25 (6.5 < pH < 7.0)		300		0.4 (5.5 < pH < 6.5)	
UK CLEA soil guideline value	32		300		10	
Normally reported As, Pb, and Cd concentrations (NRMC) in uncontaminated soils	1 – 25	Liu et al. (2012)			3 – 8	Liu et al. (2012)
Maximum acceptable levels (MAL)	20	Liu et al. (2012)			10	Liu et al. (2012)
Ghana Food and Drugs Authority standard value (GFDASV)	15		20		10	
Average soil-As and Cd concentrations measured in 3 regions of Malawi	2.2 (0.9 – 4.2)	Mlangeni et al. (2022).			0.56 (0.48 – 0.65)	Mlangeni et al. (2022).

$$HQ = \frac{EDI}{RfD} \quad (3)$$

Sum of HQ (Eq. (4)) which is called hazard index (HI) was employed to determine the possible adverse health impact of consuming Ghanaian local rice.

$$HI = HQ_{As} + HQ_{Pb} + HQ_{Cd} \quad (4)$$

where RfD denotes 'reference dose' ($\text{mgB}_{\text{wt}}^{-1}\text{kgday}$) (Ma et al., 2016).

Statistical analysis

The FactoMineR module (Lê et al., 2008) of the R statistical software (R Core Team, 2023) was utilized for all statistical calculations. In order to determine the level of significance of the interaction impact between grain-As, Pb, or Cd and soil-pH, soil type, or geographical location, one-way analysis of variance (ANOVA) plots of means were utilized. The Pearson correlation coefficient was utilized to examine the correlations among soil-Pb and Cd concentrations,

grain-As and Pb or Cd concentrations, grain-Pb and Cd concentrations, and soil-pH in diverse soil types and geographic regions where data were collected. For speciation analysis, we use PHEEQC (Parkhurst & Appelo, 2021), a computer program written in C++ designed for diverse aqueous geochemical calculations.

Results and discussion

Results

Concentrations of soil-As, Pb, and Cd

The amounts of carcinogenic metals identified in soils, with differences specified by soil type, topographical location, and soil pH, are illustrated in Figs. 1, 2, 3, and 4 and the supplementary materials (Supplementary Table 1, 2, and 3).

Soil-As The Fluvisols of soil types with a pH less than 6.0 exhibited the lowest mean concentration of

As ($1.76 \pm 0.651 \text{ mgkg}^{-1}$), whereas the Vertisols with a pH more than 7.0 exhibited the highest mean concentration of As ($2.51 \pm 0.932 \text{ mgkg}^{-1}$) (Supplementary Table 2). The influence of soil type and pH on soil-As concentrations is underscored by the box plots. It is evident that different soil types, particularly Vertisols, exhibit distinct As distributions, especially in more alkaline conditions ($\text{pH} > 7$). The distribution also tends to vary with pH across all soil types, with increased variability observed in more acidic conditions ($\text{pH} < 6$).

The data visually confirms differences in medians and spreads across two regions (Oti region and Volta region), suggesting that regional factors, potentially including natural soil composition, and environmental conditions, significantly influence arsenic levels in soil. The correlation between soil pH and soil-As concentration, while not strongly linear, does exhibit a weak positive correlation. This implies that soil pH might influence arsenic solubility and bioavailability. However, the correlation coefficient of 0.130, with a *p* value of 0.198, suggests that this correlation is not statistically significant, pointing to the potential

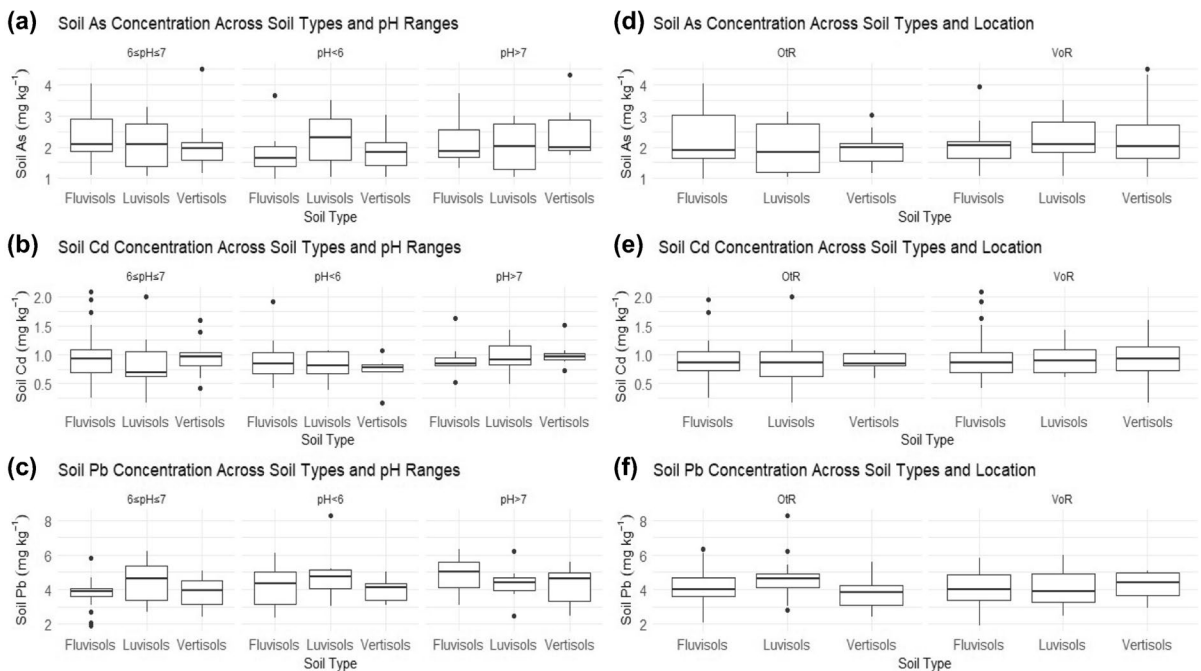


Fig. 1 a Variation of Arsenic (As) concentration by soil type and pH level. b Comparison of Arsenic (As) levels across soil types in different locations. c Distribution of Cadmium (Cd) concentration across various soils and pH ranges. d Cadmium

(Cd) levels in different soil types by location. e Lead (Pb) content variation in soils categorized by pH values. f Concentration of Lead (Pb) across soil types in contrasting regions

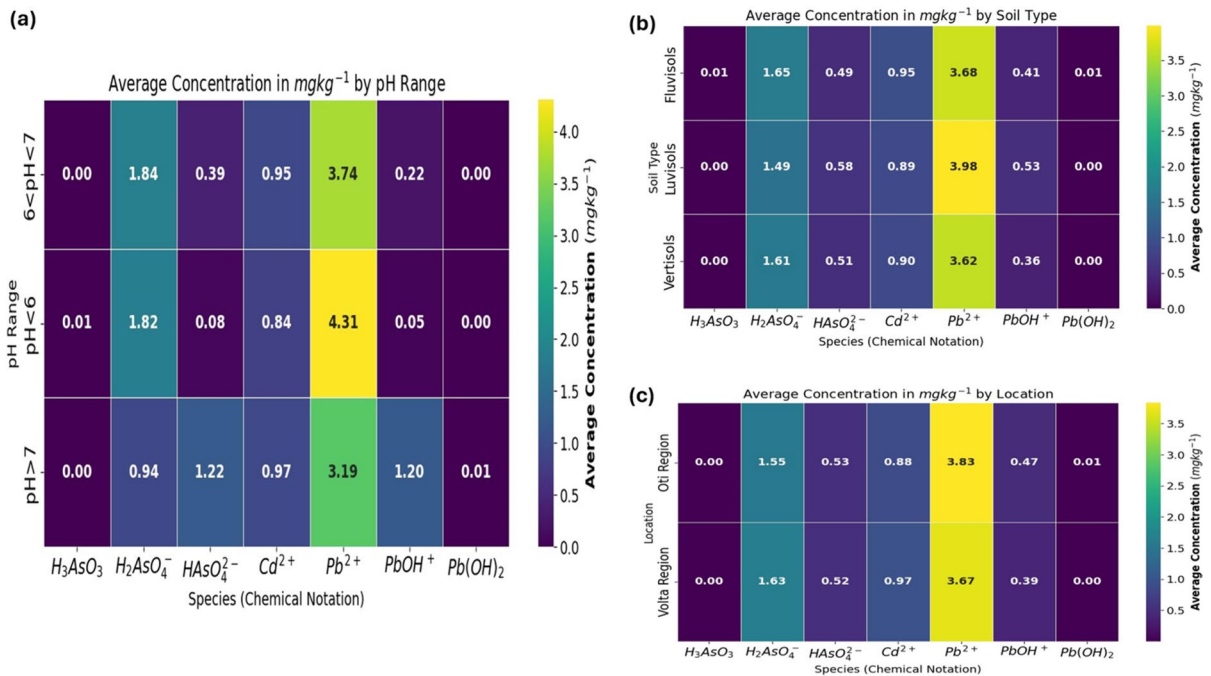


Fig. 2 a Heat map of average chemical species (As, Cd, Pb) concentrations in soil across pH ranges; b soil chemical species (As, Cd, Pb) concentration averages by soil type; c regional comparison of average chemical species (As, Cd, Pb) concentrations in soil

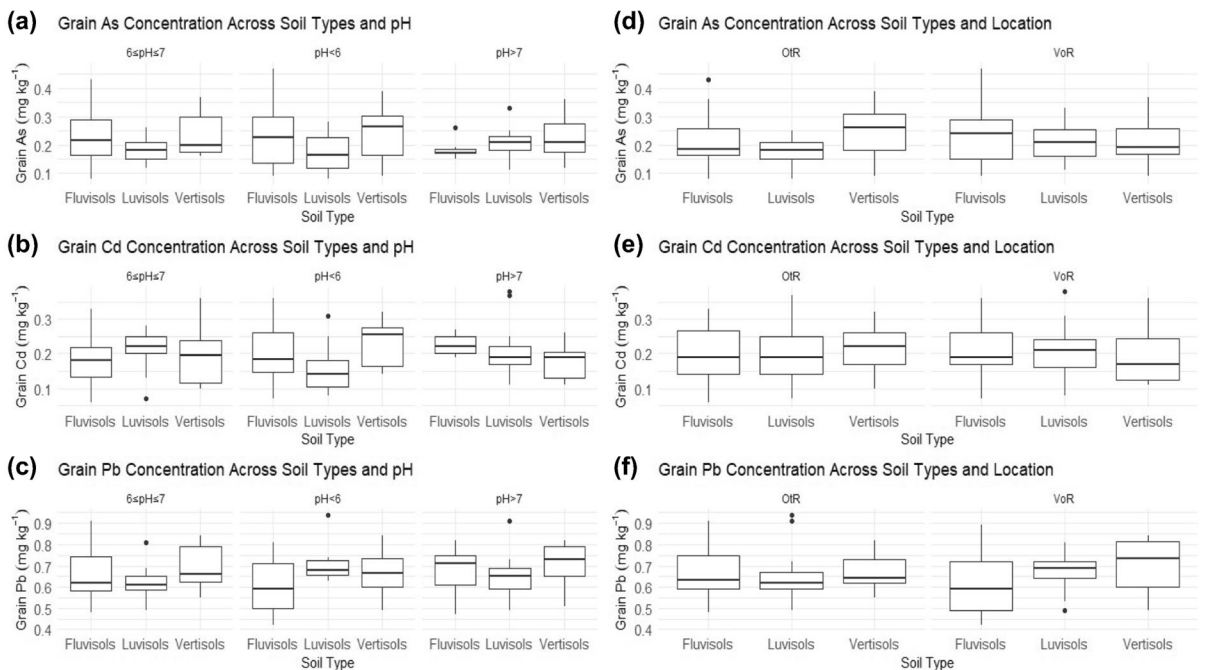


Fig. 3 a Arsenic (As) levels in grain across soil types, delineated by pH range; b spatial distribution of grain As concentration by soil type; c cadmium (Cd) content in grain relative to soil type and acidity; d grain Cd concentration comparison by soil types and regions; e lead (Pb) concentration in grains, sorted by soil pH categories; f regional variation of grain Pb levels across different soil types

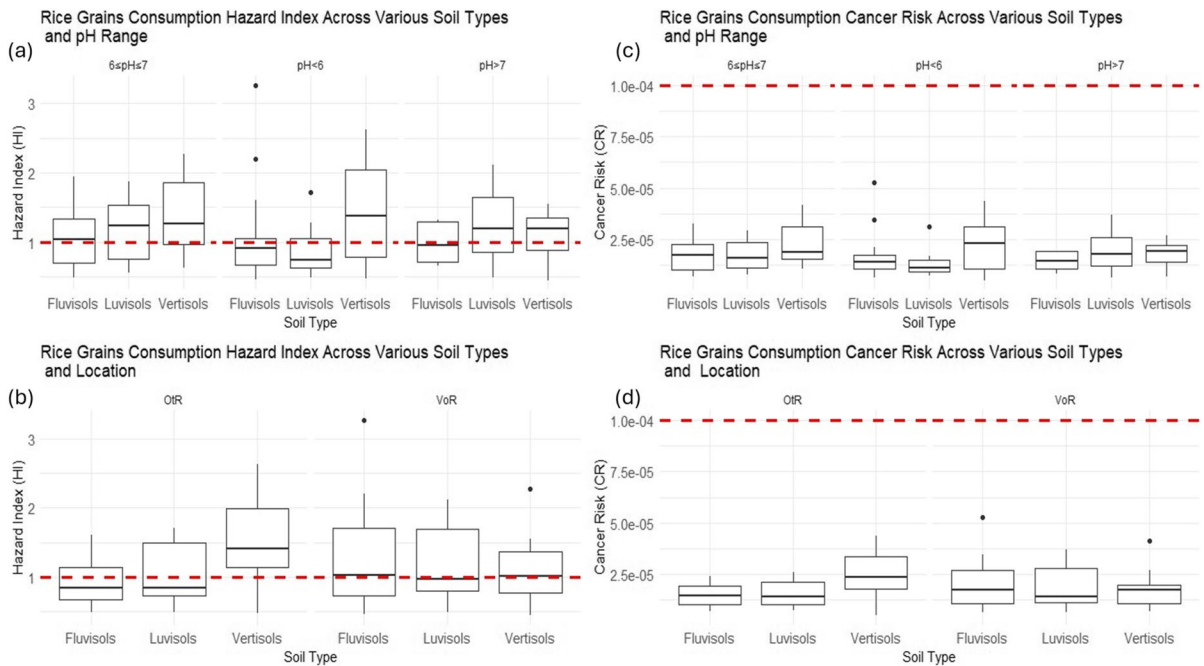


Fig. 4 **a** Rice consumption Hazard Index from soil type and pH level; **b** cancer risk associated with rice grain consumption across soil pH ranges; **c** regional comparison of Hazard Index

from rice grain consumption by soil type; **d** cancer risk from rice consumption compared by soil type and location

influence of other factors on arsenic levels in soil. Interestingly, the average soil-As concentration in this study falls below the thresholds set by Chinese environmental quality standards, UK CLEA guidelines, and the Ghana FDA standard value (Table 2). It aligns with concentrations typically reported in uncontaminated soils and is comparable to average levels measured in Malawi. Despite the average soil-As concentration being below international standards, the presence of arsenic poses health risks, particularly if it enters the food chain. It can lead to arsenic poisoning, disrupt soil nutrient cycles, and inhibit plant growth. Lastly, the ANOVA reveals no significant interaction effect between soil type and geographical location on soil-As concentrations. This suggests that the impact of soil type and location on arsenic levels is independent of each other within this dataset. This independence further emphasizes the complexity of the factors influencing soil-As concentrations.

Soil-Cd The Vertisols of soil types with a pH less than 6.0 exhibited the lowest mean concentration of Cd ($0.733 \pm 0.255 \text{ mgkg}^{-1}$), whereas the Vertisols with a pH more than 7.0 exhibited the greatest mean

concentration of Cd ($1.01 \pm 0.244 \text{ mgkg}^{-1}$) (Supplementary Table 2). Geographical variations are evident, with different regions showing distinct soil-Cd concentrations (Fig. 1e). This could be attributed to regional environmental conditions, agricultural practices. It is interesting to note that soil type also impacts soil-Cd concentrations, with different soil types displaying varying levels of cadmium. This suggests that the physical and chemical properties of the soil play a role in Cd accumulation.

The relationship between soil pH and soil-Cd concentration is not strongly linear, as a weak positive correlation is observed, hinting at a possible, but not dominant, influence of pH on cadmium availability in soil. The correlation coefficient between soil pH and soil-Cd concentration is 0.091 with a *p* value of 0.368, representing a very weak positive correlation. This is not statistically significant, indicating that other factors may play more crucial roles in determining cadmium levels in soil. Comparing with international standards, the average soil-Cd concentration in this study exceeds the Chinese environmental quality standards but remains well below the UK CLEA guideline and the Ghana FDA standard value

(Table 2). Interestingly, the concentration is also higher than the average levels measured in Malawi. The ANOVA test does not show a significant interaction effect between soil type and geographical location on soil-Cd concentrations for all the samples. This suggests that these two factors independently influence cadmium levels in the soil. The plots indicate that Cd concentrations are sensitive to both soil type and pH (Fig. 1b). For example, Luvisols show a consistent distribution across different pH levels, but there is noticeable variability in Cd levels at different pH values for Fluvisols and Vertisols.

Soil-Pb The Luvisols of soil types with a pH less than 6.0 exhibited the highest mean concentration of Pb ($4.92 \pm 1.54 \text{ mgkg}^{-1}$), whereas the Fluvisols with a pH range $6 < \text{pH} < 7$ exhibited the lowest mean concentration of Pb ($3.75 \pm 0.845 \text{ mgkg}^{-1}$) (Supplementary Table 2). However, the range for soil-Pb concentrations is quite wide at 6.40 mgkg^{-1} , indicating considerable variability. Geographical variation plays a significant role in soil-Pb concentrations. Factors such as regional industrial activities, historical land use, and environmental conditions can influence Pb deposition and retention in soils, leading to varied concentrations across different regions (Varol et al., 2020). The type of soil also appears to have an impact on soil-Pb concentrations. Different types of soil exhibit varied levels of Pb, suggesting that soil composition and properties play a crucial role in Pb mobility and bioavailability. However, the relationship between pH and soil-Pb concentration is not strongly pronounced, implying that while pH may have some effect, it is not a dominant factor in determining Pb concentration in soil. Statistical analysis reveals a weak correlation between pH and soil-Pb concentration, with a correlation coefficient of just 0.018 and a p value of 0.856. This suggests that factors other than pH are more significant in determining the lead levels in soil. Comparing the average concentration of soil-Pb in this study with international standards, it is significantly lower than the limits set by Chinese environmental quality standards and the UK CLEA guidelines (Table 2). However, it exceeds the Ghana FDA standard value, indicating a potential concern for local environmental and health impacts. Interestingly, the ANOVA test shows no significant interaction effect between soil type and geographical location on soil-Pb concentrations. This suggests that

these factors independently contribute to the variability in Pb levels in soils. The box plots (Fig. 1c) for Pb concentrations demonstrate that while soil type has a discernible impact on the distribution of Pb levels, the effect of pH is more nuanced (Fig. 1a). For instance, Fluvisols show a distinct increase in the median Pb concentration in more acidic conditions. Lead concentrations also exhibit geographical variability, with some soil types like Fluvisols and Vertisols showing significant differences in spread and median values between regions. The study of soil-Pb concentrations is a multifaceted issue, influenced by a range of factors including geographical location, soil type, and pH levels (Fig. 1). While some correlations exist, the complexity of the issue suggests that a comprehensive approach is needed to fully understand and address the presence of Pb in our soils. Generally, concentrations of selected cancerous-metal in soil increased in the order: fluvisols($6.0 \leq \text{soil-pH} \leq 7.0$) \leq fluvisols($\text{soil-pH} < 6.0$) $<$ luvisols($\text{soil-pH} < 6.0$) $<$ luvisols($6.0 \leq \text{soil-pH} \leq 7.0$) \leq vertisols($6.0 \leq \text{soil-pH} \leq 7.0$) $<$ vertisol($\text{soil-pH} < 6.0$) $<$ luvisol($\text{soil-pH} > 7.0$) $<$ fluvisol($\text{soil-pH} > 7.0$) \leq vertisol($\text{soil-pH} > 7.0$) (Supplementary Table 1).

Grain As, Cd, and Pb concentration

Grain-As The concentration of arsenic (As) in grains varies significantly across different soil types and pH levels. The Luvisols soil type, with a pH less than 6.0, has the lowest mean concentration of grain As, recorded at $0.171 \pm 0.075 \text{ mgkg}^{-1}$ (Supplementary Table 3). On the other hand, the Vertisols soil type, also with a pH less than 6.0, shows the highest mean concentration of grain As, at $0.238 \pm 0.107 \text{ mgkg}^{-1}$. Fig. 2, indicating this variability, shows the concentration of arsenic in grains across three soil types (Fluvisols, Luvisols, and Vertisols), and across different pH ranges (less than 6, between 6 and 7, greater than 7). Interestingly, when comparing two geographical locations (Oti and Volta region) (Fig. 3a), the figure shows similar distributions for each soil type in both regions. This implies a consistent behaviour of arsenic uptake in grains, regardless of the location. After analyzing the p values for the interaction between soil-As and soil-pH, a significant relationship ($p < 0.05$) was found for Luvisols. In contrast, in the Fluvisols and Vertisols the association with grain As, Cd, and Pb was not statistically

significant ($p > 0.05$). For all soil types, the p values for the interactions between soil Cd and pH and soil-Pb and pH are more than 0.05, suggesting that these relationships are not statistically significant.

Grain-Cd The concentration of Cd in grains varies across different soil types and pH levels. Specifically, Luvisols soil types with a pH less than 6.0 have the lowest mean concentration of grain Cd, averaging at $0.160 \pm 0.080 \text{ mgkg}^{-1}$ (Supplementary Table 3). On the other hand, Vertisols soil types with the same pH level exhibit the highest mean concentration of grain Cadmium (Cd), averaging at $0.231 \pm 0.068 \text{ mgkg}^{-1}$. The variability in grain Cd concentration is intriguing. Despite the discernible variation in concentrations among several soil types and pH levels, the box plots (Fig. 2b) fail to illustrate a robust correlation between soil pH and either an increase or decrease in concentration. This suggests that Cd concentrations in grains only vary slightly with soil pH. When considering the locations, Oti region and Volta region, none of the interactions between soil elements and soil pH are significant (Fig. 2d). This is also the case when considering the overall grain Cd concentration.

Grain-Pb There is variability in the concentration of Pb in grains across different soil types and pH levels. Fluvisols, with a pH less than 6.0, demonstrated the lowest mean concentration of grain Pb at $0.611 \pm 0.131 \text{ mgkg}^{-1}$ (Supplementary Table 3). On the other hand, the luvisols, also with a pH less than 6.0, exhibited the highest mean concentration of grain Pb at $0.713 \pm 0.099 \text{ mgkg}^{-1}$. The p values for the interaction between Soil As, Soil Cd, and Soil Pb with Soil pH were 0.270, 0.864, and 0.844 respectively. These values indicate a lack of significant interaction effects between these soil elements and pH on the concentration of Pb in grains. When considering the location factor, the p values for the Oti region and Volta region regions suggest some variability in the interaction effects between soil elements and soil pH on grain Pb concentration. This could be related to regional differences in environmental Pb levels or variations in how grains accumulate lead from the soil. For different soil types, the p values for the interaction between soil elements and soil pH in luvisols, fluvisols, and vertisols reveal a significant interaction only in the case of Soil As and Soil pH in vertisols (p value = 0.020).

This suggests that the type of soil might play a crucial role in the uptake of Pb in grains.

We explored the interaction effects between various soil properties and contaminants, specifically focusing on the concentrations of As, Cd, and Pb in grains. In a general interaction analysis encompassing all data, a significant interaction was discovered between soil Cd and pH, which notably affected the concentration of As in grains (p value < 0.05). However, other interactions involving soil As, Cd, Pb, and soil pH with grain As, Cd, and Pb did not yield statistically significant results. When the analysis was narrowed down to specific locations, the location “Volta region” stood out. Here, a significant interaction was observed between soil-Cd and pH, which had a substantial impact on the concentration of As in grains (p value < 0.05). No other significant interactions were detected within specific locations. Examining the interactions within the same soil type, Luvisols, significant interactions were found between soil As and soil pH affecting grain As concentration (p value < 0.05), and between soil Cd and pH affecting grain Cd concentration (p value < 0.05). In Vertisols, a significant interaction was noted between soil As and pH, which influenced grain Pb concentration (p value < 0.05). However, other interactions within specific soil types did not yield significant results. These findings suggest that while most interactions between soil contaminants and soil pH do not significantly influence the concentrations of grain contaminants, there are some notable exceptions. Specifically, the interaction between soil Cd and pH has a significant impact on grain As concentration, both across the entire dataset and within the Volta region soil samples. Furthermore, within Luvisols, the interactions of both soil As and soil Cd with pH significantly affect grain As and Cd concentrations, respectively. In Vertisols, the interaction between soil As and pH significantly influences grain Pb concentration. This highlights the complexity of soil-grain interactions and the need for further research in this area.

Speciation analysis

The PHREEQC hydrogeochemical modeling software was utilized to simulate and analyze the various forms of As, Cd, and Pb that could potentially be bioavailable

for grain absorption. Figure 2 represents heat map of average chemical species. Figure 2a reveals how the average concentrations of different chemical species within soil fluctuate across three pH ranges: less than 6, between 6 and 7, and greater than 7. It is intriguing to note that the concentration of certain species, such as Cd^{2+} and Pb^{2+} , was more available in more acidic conditions ($\text{pH} < 6$). This could imply that these ions are more mobile or bioavailable in acidic soils. On the other hand, species like HAsO_4^{2-} and HAsO^{2-} appear to be present in higher concentrations in neutral to slightly alkaline conditions (pH between 6 and 7), suggesting a pH-dependent solubility or adsorption behavior. The average concentrations of the same species by soil type (Fluvisols, Luvisols, and Vertisols) suggest that the concentrations of Cd^{2+} and Pb^{2+} are significantly higher in Vertisols (Fig. 2b). Interestingly, the average concentrations of the arsenic species are relatively consistent across the different soil types, indicating that soil type may not have as profound an impact on arsenic speciation as it does on cadmium and lead. A look at Fig. 2c, which compares the average concentrations of the species between two locations, the Oti and Volta regions, shows that the concentration of Pb^{2+} is higher in the Oti region compared to the Volta region, which could suggest local environmental factors or anthropogenic activities influencing lead levels (Varol et al., 2020). Meanwhile, the concentrations Cd^{2+} and the arsenic species remain relatively consistent between the two regions, implying that regional factors might not strongly influence these contaminants or that their sources are widespread in both areas (Varol et al., 2020).

Correlation analysis

Table 3 delineates the correlations between various soil parameters and grain contaminants, quantified

using Pearson's coefficients. The analysis showed moderate correlations amongst certain parameter pairs: notably, Soil-As and Soil-Cd ($r = 0.313$; $p < 0.05$), indicating a substantial link between As and Cd levels in the soil. Additionally, a moderate relationship was found between Soil-As and Grain-Cd ($r = 0.322$; $p < 0.05$), suggesting that soil arsenic levels have a considerable impact on Cd accumulation in grains. Another moderate correlation is between Soil Cd and Grain As ($r = 0.356$; $p < 0.05$), illustrating the influence of soil cadmium on arsenic concentration in grains. Soil-Cd and Grain-Cd also exhibited a moderate correlation ($r = 0.286$; p value < 0.01), indicating a meaningful relationship between soil-Cd levels and Cd concentration in grains. The significant correlations highlight specific interactions between soil contaminants and their accumulation in grains, emphasizing the importance of monitoring and managing soil contamination to ensure food safety. Conversely, certain pairs relationships displayed very weak and no significant correlation ($p > 0.05$), such as pH with Soil-As ($r = 0.138$), pH with Grain-Cd ($r = 0.083$), and Soil-Pb with Soil-Cd ($r = -0.002$).

Health risk assessment

Figure 4 shows the Hazard Index (HI) associated with consuming rice grown in the study area. The average consumption rate of rice is considered to be 0.10 kg per day per person, with an average body weight of 59.5 kg, considering the current concentrations of As, Cd, and Pb in grain. The hazard risk of consuming rice grown in Fluvisols and Luvisols soil types in the study was approximately 46.5% and 46.9% respectively. However, the risk significantly increases to around 64% when consuming grain associated with Vertisols. The study also considers the pH level of the soil in which the grains are grown. Grains grown

Table 3 Correlation matrix (Pearson) displaying relationships between soil pH, As, Pb, Cd levels, and their concentrations in grains

Variables	Soil pH	Soil As	Soil Pb	Soil Cd	Grain As	Grain Pb	Grain Cd
Soil pH	1	0.138	0.030	0.111	-0.035	0.070	0.083
Soil As	0.138	1	0.128	0.313	0.109	0.165	0.322
Soil Pb	0.030	0.128	1	-0.002	0.089	0.182	0.146
Soil Cd	0.111	0.313	-0.002	1	0.356	0.055	0.286
Grain As	-0.035	0.109	0.089	0.356	1	0.090	0.148
Grain Pb	0.070	0.165	0.182	0.055	0.090	1	0.069
Grain Cd	0.083	0.322	0.146	0.286	0.148	0.069	1

Values in bold are different from 0 with a significance level $\alpha = 0.05$

in soil with a pH less than 6 have a lower proportion (approximately 40%) of HI greater than 1. Interestingly, the proportions increase for grain samples in soil with a pH range of 6 to 7 and above 7, with about 55.8% and 55.6% respectively. The hazard risk for grains from both the Oti Region and Volta Region exceeds 50%, with approximately 50% and 52.2% of grain sampled having an HI greater than 1, respectively. Overall, within the study area, approximately 51% of the area is associated with a hazard risk (HI greater than 1) linked to the consumption of grains. However, it is important to highlight that there was no cancer risk associated with the consumption of grains within the study area (Cancer Risk greater than (1×10^{-4})) (Fig. 4c,d). This is a significant finding in terms of understanding the potential health risks associated with consuming rice from this area.

Discussion

Interpretation

Our findings indicate a significant variation in the concentrations of soil-As, Pb, and Cd, contingent on soil types and pH levels. Notably, our results demonstrate that Vertisols, particularly in alkaline conditions, exhibit higher concentrations of As and Cd. Vertisols, particularly in alkaline conditions, exhibit higher concentrations of As and Cd due to their high clay content and pH-dependent metal solubility, which enhance the adsorption and retention of these metal ions (Gankhurel et al., 2020). The speciation analysis, facilitated by PHREEQC modeling, revealed that certain metal species like Cd^{2+} and Pb^{2+} are more bioavailable in acidic soils (Nouri & Hashempour, 2023), while species like HAsO_4^{2-} and HAsO_2^- predominate in neutral to slightly alkaline conditions. Moreover, the higher concentrations of Pb^{2+} in the Oti region as compared to the Volta region suggest local environmental or anthropogenic factors significantly influencing Pb levels. The observed concentrations of As, Cd, and Pb in rice grains across various soil types and pH levels highlight the complex dynamics of metal uptake in plants. This is particularly evident in the significant interaction between soil-Cd and pH affecting grain-As concentration, found in this study. Such specificity in interaction patterns underscores the necessity for targeted strategies in agricultural practices to mitigate metal uptake

(Hussain et al., 2021). Interestingly, despite the variations in metal concentrations and speciation, the average concentrations of soil-As, Cd, and Pb are generally aligned with international standards, indicating a lower risk of immediate toxicity. However, this does not negate the potential long-term health risks associated with continuous exposure to these metals leading to the cumulative effects of low-level metal exposure on human health (Williams et al., 2009), especially through the consumption of contaminated rice. The Health Risk Assessment, showing a Hazard Index (HI) greater than 1 in about 51% of the study area, is a significant concern. It denotes a potential health risk associated with consuming rice from these areas, especially concerning the higher risk associated with Vertisols (Hosseini Koupaie & Eskicioglu, 2015).

Comparative studies

We compared our findings with other studies conducted in Africa, such as the study by Mlangeni et al. (2022). Their study investigated the impact of soil type, soil pH, and geographical location on the accumulation of As and Cd in rice grains. Mlangeni et al. (2022) found that the highest concentrations of soil As were present in alkaline vertisols ($\text{pH} > 7$) and the lowest in acidic fluvisols ($\text{pH} < 6$). The highest grain As was observed in rice grown in central region (CR) vertisols with soil As $\geq 2.5 \text{ mgkg}^{-1}$ and $\text{pH} > 7$. In contrast, the highest grain Cd was found in CR luvisols with soil As of $2.0\text{--}3.0 \text{ mgkg}^{-1}$ and $\text{pH} < 6$. They also noted a strong correlation between soil As and grain As ($r = 0.512$). Our study corroborated Mlangeni et al. (2022)'s findings regarding soil As levels, with the highest levels in alkaline vertisols and the lowest in acidic fluvisols. However, we observed the highest grain As and Cd accumulations in acidic vertisols ($\text{pH} < 6$), differing from Mlangeni et al. (2022)'s findings. We also found a strong correlation between soil As and grain As, particularly in fluvisols (0.74) and vertisols (0.65). We also compare our results with other studies other than Africa, For instance, Zeng et al. (2021) reported a soil-As concentration of 16.8 mg/kg in Hunan Province, China, which is much higher than the current study. Singh et al. (2011) also found a higher soil-As concentration of 7 mg/kg in Ramgarh Lake, Gorakhpur, UP, India. However, the soil-As concentrations in the current study are more comparable to those reported by

Choi et al. (2015) (0.54 mg/kg) in Gangneung, South Korea, and Juen et al. (2014) (0.6 mg/kg) in Kubang Pasu, Kedah, Malaysia. Regarding rice grain-As concentrations, the current study found the highest mean value in vertisols with soil-pH < 6.0 (0.238 ± 0.107 mg/kg) and the lowest in luvisols with soil-pH < 6.0 (0.171 ± 0.075 mg/kg). These values are generally higher than those reported in previous studies. For example, Singh et al. (2011) found a rice grain-As concentration of 0.08 mg/kg in Ramgarh Lake, Gorakhpur, UP, India, while Choi et al. (2015) reported 0.22 mg/kg in Gangneung, South Korea, and Juen et al. (2014) found 0.06 mg/kg in Kubang Pasu, Kedah, Malaysia.

The current study found the highest mean soil-Pb concentration in luvisols with soil-pH < 6.0 (4.913 ± 1.536 mg/kg) and the lowest in fluvisols with $6.0 \leq$ soil-pH ≤ 7.0 (3.746 ± 0.845 mg/kg) were lower compared to studies by Zeng et al. (2021) (51.4 mg/kg) in Hunan Province, China, and the mean soil-Pb levels (23 mg/kg) in Ramgarh Lake, Gorakhpur, UP, India found by Singh et al. (2011). The soil-Pb concentrations in the current study are more comparable to those reported by Payus et al. (2015) (8.03 mg/kg) in Kompipinan, Papar district, Sabah, Malaysia, and Choi et al. (2015) (5.93 mg/kg) in Gangneung, South Korea.

For rice grain-Pb concentrations, the current study found the highest mean value in luvisols with soil-pH < 6.0 (0.713 ± 0.0988 mg/kg) and the lowest in fluvisols with soil-pH < 6.0 (0.611 ± 0.131 mg/kg). These values were generally higher than those reported by Zeng et al. (2021) (0.02 mg/kg) in Hunan Province, China, while Choi et al. (2015) reported 0.1 mg/kg in Gangneung, South Korea, and Juen et al. (2014) found 0.21 mg/kg in Kubang Pasu, Kedah, Malaysia. With regard to Soil-Cd concentration, our study found the highest mean soil-Cd concentration in vertisols with soil-pH > 7.0 (1.01 ± 0.244 mg/kg) and the lowest in vertisols with soil-pH < 6.0 (0.7325 ± 0.255 mg/kg). These values are generally higher than those reported by Singh et al. (2011) (0.05 mg/kg) in Ramgarh Lake, Gorakhpur, UP, India, 0.1 mg/kg reported in Gangneung, South Korea (Choi et al., 2015), and Juen et al. (2014) (0.2 mg/kg) in Kubang Pasu, Kedah, Malaysia. However, the soil-Cd concentrations in the our study were lower than those reported by Zeng et al. (2021) (1.4 mg/kg) in Hunan Province, China, and Ismail et al. (2009) (0.78 mg/kg) in Kota Marudu,

Sabah, Malaysia. On rice grain-Cd concentrations, our study found the highest mean value in vertisols with soil-pH < 6.0 (0.231 ± 0.0683 mg/kg) and the lowest in luvisols with soil-pH < 6.0 (0.16 ± 0.0804 mg/kg) all higher than those reported by Singh et al. (2011) (0.01 mg/kg) in Ramgarh Lake, Gorakhpur, UP, India, 0.001 mg/kg in Gangneung, South Korea (Choi et al., 2015), and Juen et al. (2014) (0.01 mg/kg) in Kubang Pasu, Kedah, Malaysia. However, the rice grain-Cd concentrations in our study are lower than those reported by Zeng et al. (2021) (0.31 mg/kg) in Hunan Province, China, and Aziz et al. (2015) (0.54 mg/kg) in Ranau Valley, Sabah, Malaysia.

The study discovered that the consumption of grains is associated with a hazard risk (HI > 1) in about 51% of the study area, with grains grown in vertisols carrying the highest risk (64%). However, no cancer risk was found associated with the consumption of grains within the study area (Cancer Risk > 1×10^{-4}). These findings differ from previous studies, which generally reported lower non-carcinogenic risks and higher carcinogenic risks. For Pb, previous studies reported HRI values ranging from 0.269 to 1.11 for adults and 0.234 to 1.09 for children (Djahed et al., 2018; Huang et al., 2007; Ihedioha et al., 2016; Satpathy et al., 2014; Wang, Liu, et al., 2018; Wang, Ma, & Yang, 2018). For Cd, HRI values ranged from 0.042 to 11.8 for adults and 0.036 for children (Djahed et al., 2018; Fan et al., 2017; Ihedioha et al., 2016; Satpathy et al., 2014; Zeng et al., 2015). For arsenic (As), HQ values ranged from 0.34 to 8.18 for adults and 0.44 for children (Djahed et al., 2018; Fan et al., 2017; Fu et al., 2015; Huang et al., 2007; Zeng et al., 2015).

Regarding carcinogenic risk assessments, previous studies reported CR values for As ranging from 0.0003 to 0.04864 (Djahed et al., 2018; Fakhri et al., 2018; Fan et al., 2017; Fu et al., 2015; Praveena & Omar, 2017; Zeng et al., 2015), which are higher than the current study's finding of no cancer risk. The differences in heavy metal concentrations and associated health risks between the current study and previous studies can be attributed to a complex interplay of factors, including geographical location, soil properties, agricultural practices, industrial activities, rice cultivars, and analytical methods. Geographical differences play a significant role in the observed variations. For instance, the variation in Cd concentration in Hunan Province, China, was associated with the geological area and human mining activities (Zeng

et al., 2021). Soil properties, such as pH, organic matter content, and clay composition, also play a crucial role in heavy metal mobility and bioavailability (Zakaria et al., 2021). This is evident in the observed variation of soil heavy metal concentration for each soil type (Supplementary Table 3). Additionally, agricultural practices have also been reported to increase soil heavy metals for example, Zakaria et al. (2021) mentions that the application of phosphate fertilizers containing cadmium can increase soil-Cd levels over time, emphasizing the importance of agricultural practices in heavy metal accumulation. The use of different rice cultivars across studies could also contribute to the observed differences in rice grain concentrations. Zakaria et al. (2021) states that different rice varieties have shown significant differences in accumulating As, partly due to the surface characteristics of the rhizosphere and the formation of iron plaque on the root surface. This suggests that the genetic variability among rice cultivars influences their ability to absorb and accumulate heavy metals.

Conclusion

This research examined the concentrations and bioaccumulation patterns of arsenic, lead, and cadmium in rice grown in Ghana, considering factors such as soil types, pH, and geographical locations. The study found that the levels of these metals in the soil varied significantly across different soil types and pH ranges. Vertisols and acidic conditions were associated with higher arsenic and cadmium content and maintaining near-neutral pH in acidic vertisols could help reduce Cd and Pb uptake. Continuous monitoring of heavy metals in agricultural soils is essential to detect accumulation over time and implement timely mitigation measures. There were also noticeable regional differences in soil metal concentrations. The study used speciation modeling to reveal the impact of pH on the bioavailable fractions of metals in soils. It was found that Cd²⁺ and Pb²⁺ were dominant in acidic soils, and soil type also affected speciation. The research observed complex interactions between soil metals and properties that influenced grain accumulation patterns. Notably, there was a significant interaction between soil cadmium and pH that affected grain arsenic uptake. The hazard risk assessment conducted as part of the study indicated that over half of the study

area had grain metal levels that could pose health risks from dietary exposure. However, no cancer risks were identified. The study suggests that further research on multi-element interactions, speciation, geographical sourcing, and health risk pathways could support effective mitigation policies to prevent metal transfer into the food chain. These findings will contribute to safe and sustainable agricultural practices and rice cultivation in Ghana and similar contexts worldwide.

Acknowledgements The authors acknowledge the contribution of colleagues from the Nuclear Chemistry and Environmental Research Centre, National Nuclear Research Institute (NNRI), Ghana Atomic Energy Commission (GAEC), Box LG 80, Legon-Accra, Ghana and Biotechnology & Nuclear Agriculture Research Institute, Ghana Atomic Energy Commission (GAEC), Box LG 80, Legon-Accra.

Author contribution Ebenezer Aquisman Asare conceived of the study and carried out the design of the experiment. Ebenezer Aquisman Asare, Dickson Abdul-Wahab, and Anita Asamoah carried out the sample preparation and analysis. Ebenezer Aquisman Asare, Dickson Abdul-Wahab, Anita Asamoah, Samuel Boakye Dampare, Rafeah Wahi, Elsie Effah Kaufmann, Zainab Ngaini, Charles Kofi Klutse, Joseph Richmond Fianko, Crentsil Kofi Bempah, and Nana Ama Browne Klutse assessed the data, and Ebenezer Aquisman Asare, Dickson Abdul-Wahab, Anita Asamoah, and Evelyn Ama Otoo helped to draft and edited the manuscript. The author(s) read and approved the final manuscript.

Data availability The dataset used during this study is available from the corresponding author on reasonable request

Declarations

Conflict of interest The authors declared no potential conflict of interest concerning the research, authorship, and/or publication of this article.

References

- Amoah-Antwi, C., Kwiatkowska-Malina, J., Szara, E., Thornton, S., Fenton, O., & Malina, G. (2020). Efficacy of woodchip biochar and brown coal waste as stable sorbents for abatement of bioavailable cadmium, lead and zinc in soil. *Water, Air, & Soil Pollution*, 231(10), 515. <https://doi.org/10.1007/s11270-020-04885-4>
- Asare, E. A., Assim, Z., Wahi, R., Bakeh, T., & Dapaah, S. S. (2022). Trend analysis of anthropogenic activities affecting trace metals deposition in core sediments from the coastal and four rivers estuary of Sarawak, Malaysia. *Environmental Science and Pollution Research*, 29(11), 16294–16310. <https://doi.org/10.1007/s11356-021-17008-1>

- Asare, E. A., Assim, Z. B., Wahi, R. B., Droepenu, E. K., & Iya, N. I. D. (2019). Geochemistry examination of surface sediments from Sadong River, Sarawak, Malaysia: Validation of ICP-OES assessment of selected heavy metals. *Eurasian Journal of Analytical Chemistry*, *14*(3), 9–20.
- Aslam, M., Aslam, A., Sheraz, M., Ali, B., Ulhassan, Z., Najeeb, U., Zhou, W., & Gill, R. A. (2021). Lead toxicity in cereals: Mechanistic insight into toxicity, mode of action, and management. *Frontiers in Plant Science*, *11*. <https://doi.org/10.3389/fpls.2020.587785>
- Aziz, R. A., Rahim, S. A., Sahid, I., & Idris, W. M. R. (2015). Speciation and availability of heavy metals on serpentinized paddy soil and paddy tissue. *Procedia - Social and Behavioral Sciences*, *195*, 1658–1665. <https://doi.org/10.1016/j.sbspro.2015.06.235>
- Choi, E. M., Yang, J. Y., Yoon, H. J., & Park, K. S. (2015). Safety assessment of heavy metals in rice, cultivated habitats (soil and water, etc) and cooked rice that may arise from environment. *International Journal of Research in Chemical, Metallurgical and Civil Engineering*, *2*(2). <https://doi.org/10.15242/ijrcmce.iae0915410>
- Derakhshan Nejad, Z., Rezaia, S., Jung, M. C., Al-Ghamdi, A. A., Mustafa, A. E. Z. M. A., & Elshikh, M. S. (2021). Effects of fine fractions of soil organic, semi-organic, and inorganic amendments on the mitigation of heavy metal(loid)s leaching and bioavailability in a post-mining area. *Chemosphere*, *271*, 129538. <https://doi.org/10.1016/j.chemosphere.2021.129538>
- Djahed, B., Taghavi, M., Farzadkia, M., Norzaee, S., & Miri, M. (2018). Stochastic exposure and health risk assessment of rice contamination to the heavy metals in the market of Iranshahr, Iran. *Food and Chemical Toxicology*, *115*, 405–412. <https://doi.org/10.1016/j.fct.2018.03.040>
- Du, J., Wang, Z., Liu, J., Zhong, S., & Wei, C. (2020). Distribution characteristics of soil heavy metals, their source identification and their changes influenced by anthropogenic cultivation activities in purple hilly regions of Sichuan Basin, China. *Journal of Soil Science and Plant Nutrition*, *20*(3), 1080–1091. <https://doi.org/10.1007/s42729-020-00194-1>
- Fakhri, Y., Björklund, G., Bandpei, A. M., Chirumbolo, S., Keramati, H., Hosseini Pouya, R., Asadi, A., Amanidaz, N., Sarafraz, M., Sheikhmohammad, A., Alipour, M., Baninameh, Z., Mohseni, S. M., Sarkhosh, M., & Ghaseini, S. M. (2018). Concentrations of arsenic and lead in rice (*Oryza sativa* L.) in Iran: A systematic review and carcinogenic risk assessment. *Food and Chemical Toxicology*, *113*, 267–277. <https://doi.org/10.1016/j.fct.2018.01.018>
- Fan, Y., Zhu, T., Li, M., He, J., & Huang, R. (2017). Heavy metal contamination in soil and brown rice and human health risk assessment near three mining areas in Central China. *Journal of Healthcare Engineering*, *2017*. <https://doi.org/10.1155/2017/4124302>
- Fu, Q. L., Li, L., Achal, V., Jiao, A. Y., & Liu, Y. (2015). Concentrations of heavy metals and arsenic in market rice grain and their potential health risks to the population of Fuzhou, China. *Human and Ecological Risk Assessment*, *21*(1), 117–128. <https://doi.org/10.1080/10807039.2014.884398>
- Gankhurel, B., Fukushi, K., Akehi, A., Takahashi, Y., Zhao, X., & Kawasaki, K. (2020). Comparison of chemical speciation of lead, arsenic, and cadmium in contaminated soils from a historical mining site: Implications for different mobilities of heavy metals. *ACS Earth and Space Chemistry*, *4*(7), 1064–1077. <https://doi.org/10.1021/acsearthspacechem.0c00087>
- García-Sánchez, A., Alonso-Rojo, P., & Santos-Francés, F. (2010). Distribution and mobility of arsenic in soils of a mining area (Western Spain). *Science of the Total Environment*, *408*(19), 4194–4201. <https://doi.org/10.1016/j.scitotenv.2010.05.032>
- Hosseini Koupaie, E., & Eskicioglu, C. (2015). Health risk assessment of heavy metals through the consumption of food crops fertilized by biosolids: A probabilistic-based analysis. *Journal of Hazardous Materials*, *300*, 855–865. <https://doi.org/10.1016/j.jhazmat.2015.08.018>
- Huang, S. S., Liao, Q. L., Hua, M., Wu, X. M., Bi, K. S., Yan, C. Y., Chen, B., & Zhang, X. Y. (2007). Survey of heavy metal pollution and assessment of agricultural soil in Yangzhong district, Jiangsu Province, China. *Chemosphere*, *67*(11), 2148–2155. <https://doi.org/10.1016/j.chemosphere.2006.12.043>
- Hussain, B., Umer, M. J., Li, J., Ma, Y., Abbas, Y., Ashraf, M. N., Tahir, N., Ullah, A., Gogoi, N., & Farooq, M. (2021). Strategies for reducing cadmium accumulation in rice grains. *Journal of Cleaner Production*, *286*, 125557. <https://doi.org/10.1016/j.jclepro.2020.125557>
- Ihedioha, J. N., Ujam, O. T., Nwuche, C. O., Ekere, N. R., & Chime, C. C. (2016). Assessment of heavy metal contamination of rice grains (*Oryza sativa*) and soil from Ada field, Enugu, Nigeria: Estimating the human health risk. *Human and Ecological Risk Assessment*, *22*(8), 1665–1677. <https://doi.org/10.1080/10807039.2016.1217390>
- Ishikawa, S., Makino, T., Ito, M., Harada, K., Nakada, H., Nishida, I., Nishimura, M., Tokunaga, T., Shirao, K., Yoshizawa, C., Matsuyama, M., Abe, T., & Arai, T. (2016). Low-cadmium rice (*Oryza sativa* L.) cultivar can simultaneously reduce arsenic and cadmium concentrations in rice grains. *Soil Science and Plant Nutrition*, *62*(4), 327–339. <https://doi.org/10.1080/00380768.2016.1144452>
- Ismail, B., Yap, D., Adezrian, J., Khairiah, J., & Ahmad-Mahir, R. (2009). The uptake of heavy metals by paddy plants (*Oryza sativa*) in Kota Marudu, Sabah, Malaysia. *American-Eurasian Journal of Agricultural & Environmental Sciences*, *6*(1), 16–19.
- Juen, L. L., Aris, A. Z., Ying, L. W., & Haris, H. (2014). Bioconcentration and translocation efficiency of metals in paddy (*Oryza sativa*): A case study from Alor Setar, Kedah, Malaysia. *Sains Malaysiana*, *43*(4), 521–528.
- Kabata-Pendias, A. (2000). *Trace elements in soils and plants*. CRC press.
- Lê, S., Josse, J., & Husson, F. (2008). FactoMineR: An R package for multivariate analysis. *Journal of Statistical Software*, *25*(1), 1–18. <https://doi.org/10.18637/jss.v025.i01>
- Lin, H. T., Wang, M. C., & Seshiah, K. (2008). Mobility of adsorbed arsenic in two calcareous soils as influenced by water extract of compost. *Chemosphere*, *71*(4), 742–749. <https://doi.org/10.1016/j.chemosphere.2007.10.022>

- Liu, L., Hu, L., Tang, J., Li, Y., Zhang, Q., & Chen, X. (2012). Food safety assessment of planting patterns of four vegetable-type crops grown in soil contaminated by electronic waste activities. *Journal of Environmental Management*, 93(1), 22–30. <https://doi.org/10.1016/j.jenvman.2011.08.021>
- Ma, L., Wang, L., Jia, Y., & Yang, Z. (2016). Arsenic speciation in locally grown rice grains from Hunan Province, China: Spatial distribution and potential health risk. *Science of the Total Environment*, 557–558, 438–444. <https://doi.org/10.1016/j.scitotenv.2016.03.051>
- Mandal, B. K., & Suzuki, K. T. (2002). Arsenic round the world: A review. *Talanta*, 58(1), 201–235. [https://doi.org/10.1016/S0039-9140\(02\)00268-0](https://doi.org/10.1016/S0039-9140(02)00268-0)
- Miller, J. E., Hassett, J. J., & Koeppel, D. E. (1977). Interactions of lead and cadmium on metal uptake and growth of corn plants. *Journal of Environmental Quality*, 6(1), 18–20. <https://doi.org/10.2134/jeq1977.00472425000600010005x>
- Mlangeni, A. T., Lancaster, S. T., Raab, A., Krupp, E. M., Norton, G. J., & Feldmann, J. (2022). Impact of soil-type, soil-pH, and soil-metal (loids) on grain-As and Cd accumulation in Malawian rice grown in three regions of Malawi. *Environmental Advances*, 7, 100145. <https://doi.org/10.1016/j.envadv.2021.100145>
- Moreno-Jiménez, E., Fernández, J. M., Puschenreiter, M., Williams, P. N., & Plaza, C. (2016). Availability and transfer to grain of As, Cd, Cu, Ni, Pb and Zn in a barley agri-system: Impact of biochar, organic and mineral fertilizers. *Agriculture, Ecosystems and Environment*, 219, 171–178. <https://doi.org/10.1016/j.agee.2015.12.001>
- Nouri, H., & Hashempour, Y. (2023). Phytoremediation of Cd and Pb in polluted soil: A systematic review. *International Journal of Environmental Analytical Chemistry*, 103(17), 6017–6026. <https://doi.org/10.1080/03067319.2021.1946688>
- Parkhurst, D.L., and Appelo, C. A. J. (2021). PHREEQC Version 3 (3). <https://doi.org/10.3133/tm6A43>
- Payus, C., Talip, A. F. A., & Hsiang, T. W. (2015). Heavy metals accumulation in paddy cultivation area of Kompipinan, Papar district, Sabah. *Journal of Sustainability Science and Management*, 10(1), 76–86.
- Praveena, S. M., & Omar, N. A. (2017). Heavy metal exposure from cooked rice grain ingestion and its potential health risks to humans from total and bioavailable forms analysis. *Food Chemistry*, 235, 203–211. <https://doi.org/10.1016/j.foodchem.2017.05.049>
- R Core Team. (2023). R: A language and environment for statistical computing (R version 4.3.2). R Foundation for Statistical Computing. <https://www.r-project.org/>. Accessed 25 Nov 2023.
- Radziemska, M. (2018). Study of applying naturally occurring mineral sorbents of Poland (dolomite halloysite, chalcodinite) for aided phytostabilization of soil polluted with heavy metals. *Catena*, 163, 123–129. <https://doi.org/10.1016/j.catena.2017.12.015>
- Rafiq, M. T., Aziz, R., Yang, X., Xiao, W., Rafiq, M. K., Ali, B., & Li, T. (2014). Cadmium phytoavailability to rice (*Oryza sativa* L.) grown in representative Chinese soils. A model to improve soil environmental quality guidelines for food safety. *Ecotoxicology and Environmental Safety*, 103(1), 101–107. <https://doi.org/10.1016/j.ecoenv.2013.10.016>
- Ronzan, M., Zanella, L., Fattorini, L., Della Rovere, F., Urgast, D., Cantamessa, S., Nigro, A., Barbieri, M., Sanità di Toppi, L., Berta, G., Feldmann, J., Altamura, M., & Falasca, G. (2017). The morphogenic responses and phytochelatin complexes induced by arsenic in *Pteris vittata* change in the presence of cadmium. *Environmental and Experimental Botany*, 133, 176–187. <https://doi.org/10.1016/j.envexpbot.2016.10.011>
- Satpathy, D., Reddy, M. V., & Dhal, S. P. (2014). Risk assessment of heavy metals contamination in paddy soil, plants, and grains (*Oryza sativa* L.) at the east coast of India. *BioMed Research International*, 2014. <https://doi.org/10.1155/2014/545473>
- Sebastian, A., & Prasad, M. N. V. (2014). Vertisol prevent cadmium accumulation in rice: Analysis by ecophysiological toxicity markers. *Chemosphere*, 108, 85–92. <https://doi.org/10.1016/j.chemosphere.2014.02.077>
- Singh, J., Upadhyay, S. K., Pathak, R. K., & Gupta, V. (2011). Accumulation of heavy metals in soil and paddy crop (*Oryza sativa*), irrigated with water of Ramgarh Lake, Gorakhpur, UP, India. *Toxicological and Environmental Chemistry*, 93(3), 462–473. <https://doi.org/10.1080/0277248.2010.546559>
- Sipos, P., Balázs, R., & Németh, T. (2018). Sorption properties of Cd, Cu, Pb and Zn in soils with smectitic clay mineralogy. *Carpathian Journal of Earth and Environmental Sciences*, 13(1), 175–186. <https://doi.org/10.26471/cjees/2018/013/016>
- Souza, J. P., Cerveira, C., Miceli, T. M., Moraes, D. P., Mesko, M. F., & Pereira, J. S. F. (2020). Evaluation of sample preparation methods for cereal digestion for subsequent As, Cd, Hg and Pb determination by AAS-based techniques. *Food Chemistry*, 321, 126715. <https://doi.org/10.1016/j.foodchem.2020.126715>
- Varol, M., Sünbül, M. R., Aytap, H., & Yılmaz, C. H. (2020). Environmental, ecological and health risks of trace elements, and their sources in soils of Harran Plain, Turkey. *Chemosphere*, 245, 125592. <https://doi.org/10.1016/j.chemosphere.2019.125592>
- Violante, A., Cozzolino, V., Perelomov, L., Caporale, A. G., & Pigna, M. (2010). Mobility and bioavailability of heavy metals and metalloids in soil environments. *Journal of Soil Science and Plant Nutrition*, 10(3), 268–292. <https://doi.org/10.4067/S0718-95162010000100005>
- Wang, L., Ma, L., & Yang, Z. (2018). Spatial variation and risk assessment of heavy metals in paddy rice from Hunan Province, Southern China. *International Journal of Environmental Science and Technology*, 15(7), 1561–1572. <https://doi.org/10.1007/s13762-017-1504-y>
- Wang, X., Liu, T., Li, F., Li, B., & Liu, C. (2018). Effects of simultaneous application of ferrous iron and nitrate on arsenic accumulation in rice grown in contaminated paddy soil. *ACS Earth and Space Chemistry*, 2(2), 103–111. <https://doi.org/10.1021/acsearthspacechem.7b00115>
- Williams, P. N., Lei, M., Sun, G., Huang, Q., Lu, Y., Deacon, C., Meharg, A. A., & Zhu, Y.-G. (2009). Occurrence and partitioning of cadmium, arsenic and lead in mine impacted paddy rice: Hunan, China. *Environmental*

- Science & Technology*, 43(3), 637–642. <https://doi.org/10.1021/es802412r>
- Xie, W.-J., Che, L., Zhou, G.-Y., Yang, L.-N., & Hu, M.-Y. (2016). The bioconcentration ability of heavy metal research for 50 kinds of rice under the same test conditions. *Environmental Monitoring and Assessment*, 188(12), 675. <https://doi.org/10.1007/s10661-016-5660-1>
- Xu, D., Shen, Z., Dou, C., Dou, Z., Li, Y., Gao, Y., & Sun, Q. (2022). Effects of soil properties on heavy metal bio-availability and accumulation in crop grains under different farmland use patterns. *Scientific Reports*, 12(1), 9211. <https://doi.org/10.1038/s41598-022-13140-1>
- Yang, X., Wen, E., Ge, C., El-Naggar, A., Yu, H., Wang, S., Kwon, E. E., Song, H., Shaheen, S. M., Wang, H., & Rincklebe, J. (2023). Iron-modified phosphorus- and silicon-based biochars exhibited various influences on arsenic, cadmium, and lead accumulation in rice and enzyme activities in a paddy soil. *Journal of Hazardous Materials*, 443, 130203. <https://doi.org/10.1016/j.jhazmat.2022.130203>
- Yu, H.-Y., Wang, X., Li, F., Li, B., Liu, C., Wang, Q., & Lei, J. (2017). Arsenic mobility and bioavailability in paddy soil under iron compound amendments at different growth stages of rice. *Environmental Pollution*, 224, 136–147. <https://doi.org/10.1016/j.envpol.2017.01.072>
- Zakaria, Z., Zulkafflee, N. S., Mohd Redzuan, N. A., Selamat, J., Ismail, M. R., Praveena, S. M., Tóth, G., & Abdull Razis, A. F. (2021). Understanding potential heavy metal contamination, absorption, translocation and accumulation in rice and human health risks. *Plants*, 10(6). <https://doi.org/10.3390/plants10061070>
- Zeng, D., Chen, G., Zhou, P., Xu, H., Qiong, A., Duo, B., Lu, X., Wang, Z., & Han, Z. (2021). Factors influencing groundwater contamination near municipal solid waste landfill sites in the Qinghai-Tibetan plateau. *Ecotoxicology and Environmental Safety*, 211, 111913. <https://doi.org/10.1016/j.ecoenv.2021.111913>
- Zeng, F., Ali, S., Zhang, H., Ouyang, Y., Qiu, B., Wu, F., & Zhang, G. (2011). The influence of pH and organic matter content in paddy soil on heavy metal availability and their uptake by rice plants. *Environmental Pollution*, 159(1), 84–91. <https://doi.org/10.1016/j.envpol.2010.09.019>
- Zeng, F., Wei, W., Li, M., Huang, R., Yang, F., & Duan, Y. (2015). Heavy metal contamination in rice-producing soils of Hunan province, China and potential health risks. *International Journal of Environmental Research and Public Health*, 12(12), 15584–15593. <https://doi.org/10.3390/ijerph121215005>

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Springer Nature or its licensor (e.g. a society or other partner) holds exclusive rights to this article under a publishing agreement with the author(s) or other rightsholder(s); author self-archiving of the accepted manuscript version of this article is solely governed by the terms of such publishing agreement and applicable law.