Varietal differences influence arsenic and lead contamination of rice grown in mining impacted agricultural fields of Zamfara State, Nigeria

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HIGHLIGHTS

- First study on influence of rice variety on Pb and As co-uptake in Zamfara, Nigeria.
- Cultivation of rice is on the rise in mining-impacted farmlands of Zamfara State.
- Mean Pb content in all ten rice varieties was far above the Codex recommendation.
- Negative correlation between As and Pb in rice grains was observed.

GRAPHICAL ABSTRACT
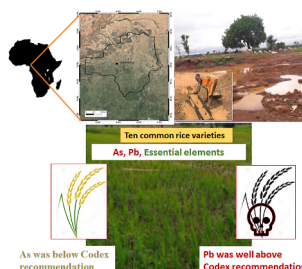
ABSTRACT

In Zamfara state, Nigeria, rice is cultivated in fields contaminated with Pb (lead) from artisanal and illicit mining activities. Rice grown in such contaminated agricultural areas risks not only Pb contamination but also contamination from other toxic elements, like arsenic (As); co-contamination of Pb and As in rice cultivated in mining impacted areas has been previously reported and rice is a hyperaccumulator of As. A field study was conducted with ten different commonly-cultivated Nigerian rice varieties in the mining-impacted farmlands of Dareta village, Zamfara State. The aim was to determine the optimal rice variety for cultivation on these contaminated farmlands; an optimal variety would have the lowest contaminant concentrations and highest essential elements concentrations in the rice grains. A total of 300 paired soil and rice plants were collected. The mean As and Pb concentrations in paddy soils were 0.91 ± 0.82 mg kg^{-1} and 288.5 ± 464.2 mg kg^{-1}, respectively. Mean As (30.4 ± 15.1 µg kg^{-1}) content in rice grains was an order of magnitude lower than the Codex recommendation of 200 µg kg^{-1} (for milled rice) while the Pb content in all the rice varieties (overall mean of 743 ± 327 µg kg^{-1}) was approximately four times higher than the Codex recommendation of 200 µg kg^{-1}.

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Contrary to previous studies, a negative correlation was observed between As and Pb in rice grains across all the varieties. Rice variety Bisalayi was the variety with the lowest Pb transfer factor (TF = 0.08), but the average Pb concentration in rice grain was still above the Codex recommendation. Bisalayi also had the highest TF for iron. Variety ART_15, which had the lowest As uptake (TF = 0.10), had the highest TF for essential elements (magnesium, potassium, manganese, zinc, and copper). In areas of Pb contamination, Bisalayi rice may therefore be a suitable variety to choose for cultivation.

1. Introduction

In many developing nations, artisanal mining is a necessary activity since it provides a valuable source of income, especially in areas where economic opportunities are limited. Unfortunately, operations both during and after mining are typically accompanied by substantial environmental degradation (Orisakwe et al., 2017). Artisanal and illegal mining is the major source of heavy metal contamination in Zamfara State, Nigeria where the incidence of lead (Pb) poisoning was described as an "unprecedented environmental emergency" by the World Health Organisations (WHO) in 2010 (Moszynski, 2010). During mining activities mainly for gold, the extraction of the ores involves digging the soil to form a cave or tunnel, exposing the rock deposits. Subsequently, erosion due to rainfall causes mixing of the ore contaminants, in this case Pb, with the top soil (Warra and Prasad, 2018). During the extraction process, the crushing of the ores into powder results in release of further Pb into the environment in the form of dust. The Pb contaminated dust is transported and deposited onto the surrounding land area based on the prevailing climatic conditions (predominantly wind speed, wind direction and rainfall) (Tirima et al., 2018). Extraction is followed by washing of the extracted minerals and this washing solution contains high Pb concentrations (Uriah et al., 2013), leading to further contamination of the surrounding environment. Lead poisoning is said to have killed 400–500 children during 2010–2013 and sickened many more (Tirima et al., 2018). The odds ratio of childhood Pb poisoning or Pb contamination was 3.5 times higher in ore-processing villages than non-ore-processing villages (95% confidence interval: 1.1, 11.3) (Lo et al., 2012). A study conducted by Bello et al. (2016) revealed that Pb levels in the blood of the general population (both children and adults) living in Adudu community of Obi local government area, another state in the central region of Nigeria, exceeded the Centres for Disease Control and Prevention recommended level of 5 µg dL^{-1}. The maximum blood Pb level detected was 14.8 µg dL^{-1} and for children 11% of the samples exceeded the blood Pb level of 5 µg dL^{-1} (Bello et al., 2016). Artisanal gold mining and processing in the villages were discovered to be the source (Tirima et al., 2018; Udiba et al., 2019). In fact, soil Pb levels up to 60,000 mg kg^{-1} were reported from mining impacted areas of Zamfara State (UNEP/OCHA Report 2010).

In Dareta and other Pb contaminated villages of Zamfara, the major occupations are farming and mining (Clement and Patrick, 2017; Orisakwe et al., 2017) and rice is the dominant crop cultivated in the area (Dogo, 2014). Rice is a staple food in the region and dietary intake of rice in Zamfara State (Mani et al., 2018), other states of Nigeria (Akande, 2001), and generally in sub-Saharan Africa has increased by more than 50% in the past two decades (Mohanty, 2013). In Nigeria, rice is one of the most consumed staples (32 kg per capita in 2017) (PwC, 2017). The rice production in Nigeria rose from 3.7 million metric tonnes in 2017 to 4.0 million metric tonnes in 2018 (Kamai et al., 2020).

The three rice production environments in Nigeria are rainfed lowland (69.0%), irrigated lowland (2.7%), and rainfed upland (28.3%) (GRiSP, 2013). With soil Pb levels often exceeding very high values, high concentrations of Pb in cultivated rice could be seen in Zamfara (Tirima et al., 2018). For example, local whole grain rice samples collected from Anka market had Pb concentration of 440 µg kg^{-1} (Tirima et al., 2018) which exceeded the guideline value of 200 µg kg^{-1} (JECFA, 2017). Along with Pb, a variety of toxic elements can accumulate in rice, for example, arsenic (As) (Sohn, 2014).

Rice plants can accumulate As and serve as a dominant source of As exposure (Mondal and Polya, 2008; Mondal et al., 2010; Mandal et al., 2021). Arsenic has been found in Nigerian rice, for instance, rice samples collected from the markets of Akure, Ore, Ondo and Ikare in Ondo State, South-Western, Nigeria had mean As concentration of 47.0 ± 0.6 µg kg^{-1} (Adeyemi et al., 2016). Several studies already reported the relationship between As and Pb in rice grains and often a positive relationship has been noted. For example, coexistence of Pb and As in rice grain grown in mining impacted soils of China has been previously reported (Williams et al., 2009). A positive correlation (p < 0.05) between As and Pb in rainfed rice from Bangladesh have been reported (Jahiruddin et al., 2017). In a previous study, average As concentration of 167 ± 71 µg kg^{-1} in Peruvian rice was found to be significantly correlated (p < 0.05) with Pb, having an average concentration of 86 ± 54 µg kg^{-1} (Mondal et al., 2020). A positive significant correlation between As and Pb in rice was reported by Wang-da et al. (2006) in nine rice varieties from China. The presence of As along with Pb in rice has also been reported from middle eastern countries (Fakhri et al., 2018).

The literature on As and Pb levels in Nigerian rice varieties, as well as the relationship between them and information on essential nutrient content is scarce. There is little or no information available regarding the As levels in rice and soils in Pb contaminated areas of Nigeria. Hence, As and Pb contamination in locally cultivated rice in farmlands impacted by mining activities demands investigation to enable the policy makers and stakeholders take necessary steps to address any potential health risk and nutritional security from rice consumption. This comparative study on different rice varieties will provide valuable information for local farmers to make an informed decision about the safety of the rice they grow and consume. Moreover, it is of significant local, national and global interest to ensure that dietary exposure to contaminants, such as Pb in Zamfara State, is identified, quantified and mitigated.

We studied ten common rice varieties cultivated in Pb-contaminated farmlands of Dareta village, Zamfara State, Nigeria. Some of the rice varieties were of Nigerian origin (IRAT_170, ITA_315, WITA_4, NERICA_L19, NERICA_L34, Bisalayi), some were of African origin (ART3_7L, ART_15, NCRO_49), and one of Taiwanese origin (SIPI_692033). According to local farmers, variety Bisalayi has been in existence for decades and is known for its taste and disease resistance (Ejebe, 2013). The IRAT_170, ITA_315, SIPI_692033 varieties were released in Nigeria in 1992; WITA_4 in 1997; NERICA_L19, NERICA_L34 and NCRO_49 in 2011; and the ART3_7L and ART_15 in 2014 and 2015 respectively (Maji et al., 2007). We investigated the i) contamination levels of As and Pb content in the soil and the differences in Pb and As accumulation in the grains; ii) relationship between the two contaminants; and iii) relationship of different soil properties with As and Pb contents in the rice grains. We then explored the optimum rice variety for cultivation in contaminated sites in terms of reduced As and Pb content along with presence of substantial concentrations of essential elements using transfer factor (TF) values. Soil-to-plant TF is one of the main parameters used to assess human exposure to metals through the food chain; the higher the TF values are, the more mobile/available the metals are (Cui et al., 2004; Khan et al., 2008; Dean, 2007).

2. Materials and methods

2.1. Study site and sample collection

The rice grain and corresponding soil samples were collected from the rice farm situated in a Pb contaminated sites of Dareta village (12° 1′ 50″ N, 5° 57′ 17″ E) of Zamfara state in Nigeria (Fig. 1). Zamfara has a Subtropical steppe climate. The yearly average temperature is 30.22 °C, 0.76% higher than the Nigerian average. Zamfara typically receives about 61 mm of precipitation and has 81.9 rainy days (22.44% of the time) annually (Aliyu, 2014). The rice grains collected on maturity were from the rice crop grown in entirely rainfed condition during the growing season between June and November, known as the wet season in the northern Nigeria. According to FAO crop calendars Nigeria has only one rice growing season (Dimou et al., 2018). Altogether, 30 samples from each of ten commonly grown rice varieties were collected for this study resulting in a total of 300 paired rice and soil samples (10 varieties × 30 replicates = 300 paired samples). The varieties sampled were namely IRAT_170 (V_1), SIPI_692033 (V_2), ITA_315 (V3), WITA_4 (V_4), NERICA_L19 (V_5), NERICA_L34 (V_6), NCRO_49 (V_7), ART3_7L (V_8), ART_15 (V_9), Bisalayi (V_{10}) (Table 1). Among the rice varieties V_1 IRAT_170, V_3 (ITA_315), V_8 (ART3_7L) and V_9 (ART_15) were short duration upland varieties; V_2 (SIPI_692033), V_4 (WITA_4), V_5 (NERICA_L19) and V_6 (NERICA_L34) were irrigated short duration rice varieties; and V_7 (NCRO_49) and V_{10} (Bisalayi) were lowland short duration rice varieties. All the varieties were of short height except V_8 having a plant height of 140–147 cm.

2.2. Preparation and analysis of soil and plant samples

Soil and rice samples were air-dried in the laboratory to constant mass and then stored at room temperature in double zip-locked bags until analysis. The pH of the soil was determined in 1:1 (soil: water) suspension using a combined glass and calomel electrode by digital pH meter. Soil organic carbon (OC) was determined by Walkley and Black (1934) method, Cation Exchange Capacity (CEC) was determined by ammonium acetate method and soil texture by Bouyoucos hydrometer method. All the methods were outlined in International Institute of Tropical Agriculture (IITA, 2016). Rice and soil samples were analysed at The University of Newcastle, Australia following the established protocols from Rahman et al. (2009a), Rahman et al. (2009b) and Alloway (2013). The microwave-assisted digestion system (model: MARS 5, CEM) was used for the digestion of soil with aqua regia using the USEPA 3051A method (USEPA, 2007). Digestion of rice samples were conducted as per procedure of Rahman et al. (2009). Determination of trace elements in soil and rice were carried out with an inductively coupled plasma mass spectrometry (ICP- MS) (PerkinElmer NexIon 350). Major elements such as potassium (K), magnesium (Mg), calcium (Ca), and iron (Fe), were analysed using an inductively coupled plasma optical emission spectrometer (ICP-OES, PerkinElmer Avio 200, USA).

2.3. Quality assurance and quality control

For quality control, Standard reference materials (SRM) from the National Institute of Standards and Technology (NIST), USA (Rice flour (SRM 1568b) and Montana soil (SRM 2711a)) were used. The CRM, blanks, duplicates, and continuing calibration verification (CCV) were
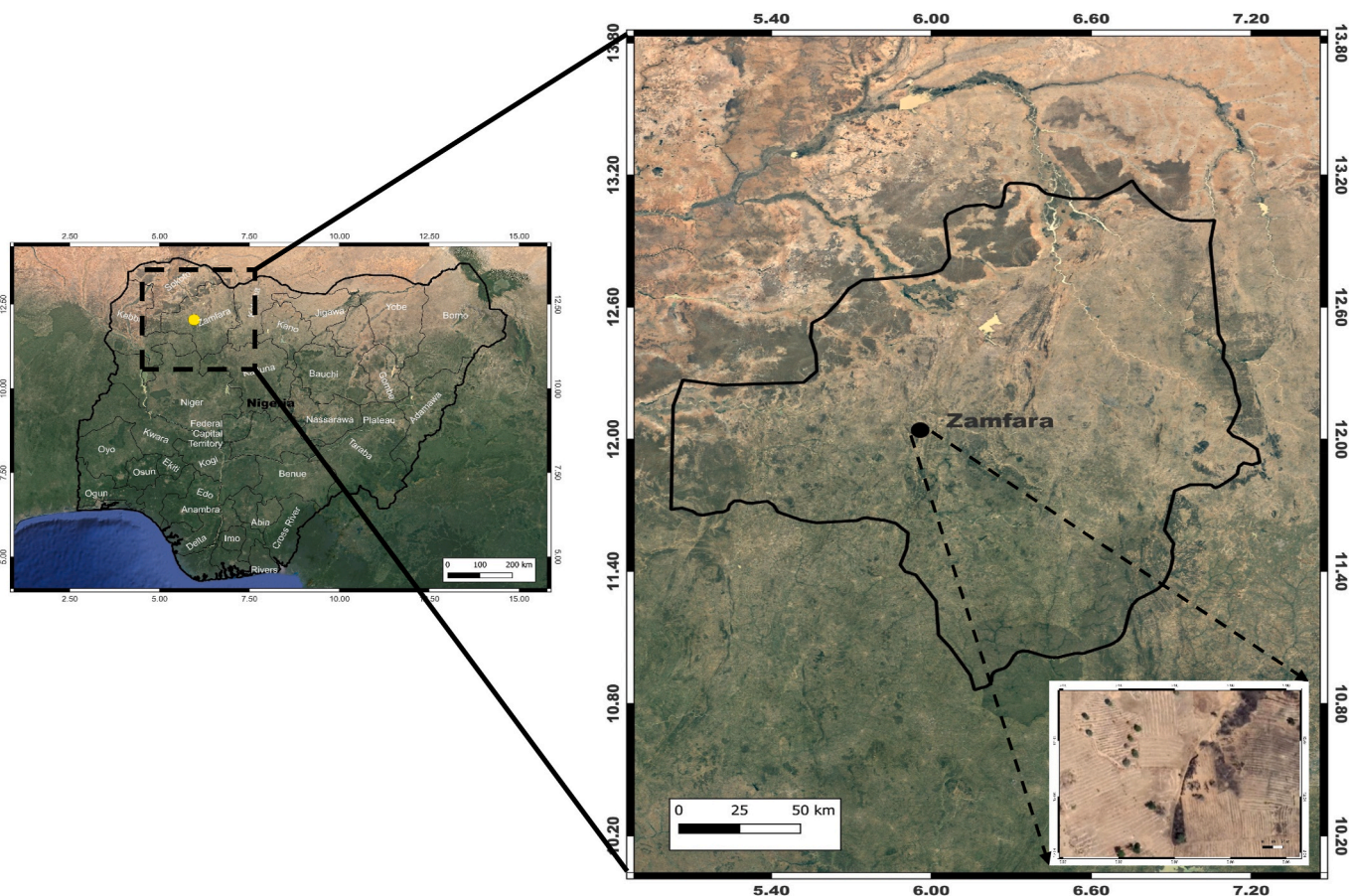

Fig. 1. Location of the sampling site.

Table 1
Morphological characteristics of the rice varieties (NCRI, 2017).

Variety	Origin	Habitat	Plant height (cm)	No. of Tillers	Maturity (Days)	Potential Yield (t ha^{-1})
IRAT_170 (V$_1$)	Nigeria	Upland	80–90	10–15	115–120	1.0–4.0
SIPI_692033 (V$_2$)	Taiwan	Irrigated	110–120	15–20	110–120	4.0–8.0
ITA_315 (V3)	Nigeria	Upland	77–89	12–18	115–120	2.0–3.5
WITA_4 (V$_4$)	Nigeria	Lowland Irrigated	95–105	12–18	125–130	3.0–7.0
NERICA_L19 (V$_5$)	Africa	Lowland Irrigated	100–115	15–20	95–100	8.0
NERICA_L34 (V$_6$)	Africa	Lowland Irrigated	90–100	18–25	95–100	7.0
NCRO_49 (V$_7$)	Africa	Lowland	110–115	16–20	120–125	6.0
ART3_7L (V$_8$)	Africa	Upland	140–147	8–10	95–100	6.0
ART_15 (V$_9$)	Africa	Upland	130–135	6–10	110–115	6.0
Bisalayi (V$_{10}$)	Nigeria	Upland/Lowland	110–120	15–20	110–120	4.0–8.0

included in each batch throughout the elemental analysis. Mean total recoveries (n = 8) from both rice and soil SRMs were within the range of 70–103% confirming accuracy of rice and soil digestion and analysis (Table 2). Only for Mg there was a low recovery (70%) in rice SRM and for Ca and Ba there was a low recovery 75% in Montana soil SRM.

2.4. Data analysis

For all variables, descriptive statistics and point estimates: mean ± standard deviation, range (minimum and maximum) and interquartile range (IQR) represented by 25th and 75th percentiles were determined. Spearman correlation (rho) was used to determine relationships. Principal Component Analysis (PCA) was performed using the soil and rice grain data, to explore the grouping of elements. The Duncan's Multiple Range Test (DMRT) was performed to compare the varieties in terms of As and Pb content in rice and soil, and the Transfer Factor (TF). The TF for As and Pb and different essential elements between soil and grain was calculated as per the following equation:

$$TF = \frac{Concentration\ of\ As\ or\ Pb\ or\ essential\ element\ in\ rice\ grain(mg/kg)}{Concentration\ of\ As\ or\ Pb\ or\ essential\ element\ in\ soil(mg/kg)}$$

The analysis was performed using R-Studio (*Version March 1, 1093 2.3.1*). PCA was performed using the *'princomp' (version 4.0.3) and 'factoextra'*, and DMRT was done using the package *'agricolae'* (version 1.3–3). All plots were done using the *'ggpubr'* (version 0.40) package. The Kaiser–Meyer–Olkin (KMO) test was performed using the *'EFAtools'* (version 0.4.0) to measure the sample adequacy for PCA.

3. Results

3.1. Soil physio-chemical properties of the study site

The physio-chemical properties of the soil indicated that the pH of the soil ranged from 4.5 to 8.5 with a mean of 6.5 ± 0.8. The mean OC content was 4 ± 0.9 g kg^{-1} and ranged from low 1.5 to high 7.7 g kg^{-1}. The clay content of the soil from the study area ranged from 2.0 to 37.4% with a mean of 14.6 ± 7.3% and the silt and sand content ranged from 2.0 to 69.1% and 11.5–94.0% with mean of 39.7 ± 14.6% and 45.6 ± 16.8% respectively. The mean CEC of the soil was 26.1 ± 7.9 cmol kg^{-1} and ranged from 12.9 to 43.3 cmol kg^{-1}. The EC of the soil ranged from 0.30 to 2.5 dS m^{-1} with a mean value of 1.9 ± 0.4 dS m^{-1}.

3.2. As and Pb in rice and relationship with soil parameters

The average As and Pb concentrations in the rice grains were 30.4 ± 15.1 µg kg^{-1} (with the range of 5.0–126.0 µg kg^{-1}) and 743.8 ± 327.1 µg kg^{-1} (with the range of 25.0–2510.0 µg kg^{-1}) respectively (Table 3). The As and Pb concentrations in the post-harvest soil ranged from 0.06 to 4.6 mg kg^{-1} and 0.47–1468.3 mg kg^{-1} with mean values of 0.91 ± 0.82 mg kg^{-1} and 288.5 ± 464.2 mg kg^{-1} respectively. The As content in rice was positively correlated with the soil As, Pb, Se and Ba (p < 0.05) and negatively correlated with soil CEC, Manganese (Mn), Zinc (Zn), Copper (Cu), Chromium (Cr), Antimony (Sb) and Selenium (Se) (p < 0.05) content (Table 3). The Pb content in rice was positively correlated with the soil Pb and Fe (p < 0.05) and negatively correlated with OC and CEC (p < 0.05) (Table 3). Using the KMO test it was observed that for soil parameters the measure of sampling adequacy (MSA) was 0.813 and

Table 2
Percentage recovery of As and other elements in NIST SRMs (n = 8 for both rice and soil).

Elements	NIST SRM 1568b (Rice flour)			NIST SRM 2711a (Montana soil)		
	Certified values	Measured Values	Recovery (%)	Certified Values	Measured Values	Recovery (%)
As (µg kg^{-1})	285 ± 1	292.6 ± 8.7	102	107,000 ± 5000	103,410 ± 6200	96
V (µg kg^{-1})	–			80,700 ± 5700	69,838 ± 655	86
Cr (µg kg^{-1})	–			52,300 ± 2900	45,800 ± 3460	87
Co (µg kg^{-1})	17.7 ± 0.05	17.68 ± 0.6	99	9890 ± 180	8600 ± 224	87
Ni (µg kg^{-1})	–			21,700 ± 700	19,810 ± 2310	91
Se (µg kg^{-1})	365 ± 2	356.9 ± 18.4	97	2000	1860 ± 130	93
Cd (µg kg^{-1})	22.4 ± 1.3	22.2 ± 1.6	99	54,100 ± 500	54,488 ± 432	100
Sb (µg kg^{-1})	–			23,800 ± 1400	19,673 ± 222	82
[a]Pb (µg kg^{-1})	8 ± 3	137.0 ± 18.9		0.140 ± 0.001[b]	0.144 ± 0	102
Mn (mg kg^{-1})	19.2 ± 1.8	18.17 ± 0.21	94	675,000 ± 18,000	585,300 ± 22,000	87
Cu (mg kg^{-1})	2.3 ± 0.2	2.2 ± 0.03	93	140,000 ± 2000	112,866 ± 735	81
Zn (mg kg^{-1})	19.4 ± 0.3	20.0 ± 0.1	103	414,000 ± 11,000	364,680 ± 14,450	88
Ca (mg kg^{-1})	118.4 ± 3.1	113.7 ± 3.6	95	2.42 ± 0.06[b]	1.73 ± 0.01	75
Fe (mg kg^{-1})	7.4 ± 0.4	5.8 ± 0.3	78	2.82 ± 0.04[b]	2.43 ± 0.02	85
K (mg kg^{-1})	1282 ± 11	1038 ± 8.3	80	2.53 ± 0.10[b]	2.36 ± 0.00	94
Mg (mg kg^{-1})	559 ± 10	395 ± 2	70	1.07 ± 0.06[b]	0.92 ± 0.00	81
Ba (mg kg^{-1})	–			730,000 ± 15,000	544,600 ± 21,000	75
Sr (mg kg^{-1})	–			242,000 ± 10,000	232,800 ± 8500	96

[a] Reference values.
[b] Concentration in percentage.

Table 3
Total As and Pb in rice grains and summary of all measured soil parameters including the relationship with As and Pb in rice grains (n = 300).

Parameter	Minimum	Maximum	Mean ± SD	IQR (Q3-Q1)	Spearman rho[a]	Spearman rho[b]
As Rice ($\mu g\ kg^{-1}$)	5.0	126.0	30.4 ± 15.1	40.0–19.0	–	−0.56**
Pb Rice ($\mu g\ kg^{-1}$)	25.0	2510.0	743.8 ± 327.1	932.3–510	−0.56**	–
As ($mg\ kg^{-1}$)	0.06	4.6	0.91 ± 0.82	1.44–0.08	0.16*	0.10
Pb ($mg\ kg^{-1}$)	0.47	1468.3	288.5 ± 464.2	268.6–7.1	0.12*	0.30*
Clay (%)	2.0	37.4	14.6 ± 7.3	19.4–8.5	−0.08	−0.03
Silt (%)	2.0	69.1	39.7 ± 14.6	49.5–30.8	−0.03	−0.03
Sand (%)	11.5	94.0	45.6 ± 16.8	51.8–37.1	−0.008	0.04
pH	4.5	8.5	6.5 ± 0.8	7.2–6.0	−0.01	0.08
N ($mg\ kg^{-1}$)	1.3	7.3	3.1 ± 1.6	4.0–1.8	−0.01	0.10
P ($mg\ kg^{-1}$)	0.62	14.0	7.7 ± 2.8	9.56–5.67	−0.01	−0.11
EC ($dS\ m^{-1}$)	0.30	2.5	1.9 ± 0.4	1.4–1.0	−0.05	0.04
OC ($g\ kg^{-1}$)	1.5	7.7	4 ± 0.9	4.5–3.4	0.03	−0.14*
CEC ($cmol\ kg^{-1}$)	12.9	43.3	26.1 ± 7.9	29.0–20.8	−0.12*	−0.15*
Al ($mg\ kg^{-1}$)	5826.1	14793.4	9067.0 ± 1635.9	10061–7832	0.01	−0.02
Ca ($mg\ kg^{-1}$)	971.6	2505.6	1458.5 ± 307.3	1724.7–1193.7	0.08	−0.16**
K ($mg\ kg^{-1}$)	318.5	3046.5	1400.3 ± 707.1	1487.8–944.7	0.09	−0.07
Mg ($mg\ kg^{-1}$)	684.7	3015.3	1759.4 ± 586.8	2006.3–1345.4	0.07	−0.09
Na ($mg\ kg^{-1}$)	0.05	296.8	27.1 ± 43.2	51.9–0.1	−0.06	−0.11
Fe ($mg\ kg^{-1}$)	10626.2	26641.4	16678.6 ± 3273.5	19265–13839	0.06	0.17**
Mn ($mg\ kg^{-1}$)	6.3	1800.5	184.1 ± 177.9	299.7–14.4	−0.14*	−0.02
Zn ($mg\ kg^{-1}$)	0.4	83.9	11.4 ± 9.9	18.7–0.7	−0.16*	0.02
Cu ($mg\ kg^{-1}$)	0.3	79.9	10.7 ± 11.4	13.6–0.5	−0.21*	0.10
Cs ($\mu g\ kg^{-1}$)	0.8	1.9	0.9 ± 0.1	0.9–0.9	−0.01	0.01
Sr ($\mu g\ kg^{-1}$)	3.8	15.3	9.5 ± 1.3	9.3–9.1	0.05	−0.07
V ($\mu g\ kg^{-1}$)	1.1	53.5	20.5 ± 15.6	32.3–1.9	−0.11	0.05
Cr ($\mu g\ kg^{-1}$)	0.82	45.4	15.7 ± 12.2	24.8–1.3	−0.17*	0.09
Co ($\mu g\ kg^{-1}$)	0.19	34.2	4.3 ± 3.9	6.6–0.3	−0.06	0.04
Se ($\mu g\ kg^{-1}$)	0.06	0.91	0.22 ± 0.13	0.31–0.08	−0.19*	−0.10
Sb ($\mu g\ kg^{-1}$)	0.00	2.44	0.11 ± 0.23	0.08–0.01	−0.22*	0.08
Ba ($\mu g\ kg^{-1}$)	4.2	266.5	37.5 ± 28.9	57.5–7.6	0.15*	−0.01

*Significant at (p < 0.05) **Significant at (p < 0.01).
[a] Correlation with rice grain As.
[b] Correlation with rice grain Pb.

for rice grain parameters it was 0.847 indicating the sampling was adequate. The scree plot (Figure S1) for soil PCA revealed that the first two components explained 47.5% (PC1: 32.6% and PC2: 14.9%) of the information contained in the variables while the ten components together explained the 90% of the variability observed. From the soil PCA biplot (Fig. 2A) it can be observed that the contribution of CEC, K, Mg, Ca, Ba, Zn, Cu, Mn, Fe, Se, Pb, Sb, Cr, As and V to the principal components was more compared to that of Sand, Silt, Clay, pH, N, P, Cs, Sr and EC. A close association of As with elements like Cr, V, Ba, Co, Zn, Cu, Mn, and Se was observed whereas Pb was observed to be associated with Ca and closely associated with K, Mg, and CEC. The grain PCA scree plot (Figure S2) demonstrated that the first two components explained 38.8% of the information contained in the variables (PC1: 23.1% and PC2: 15.7%), while the ten components explained 87.7% of the total variability. From the grain PCA biplot (Fig. 2B) it can be seen that As had close association with Fe, Co, Cr and V whereas Pb had the association with K, Mg, Mn, Zn, Ca, Cu, Na, Ba.

The correlation (Spearman rho) of the essential elements with As in rice grains (Figure S3) revealed that As in rice was negatively correlated with Ca, Mg, Fe, Mn, Zn and Cu (significantly with Zn (−0.45) at p < 0.001 and Fe (−0.15) at p < 0.05) and positively correlated with Se and K. Lead in rice grains was negatively correlated with Se, Mn, Fe and K
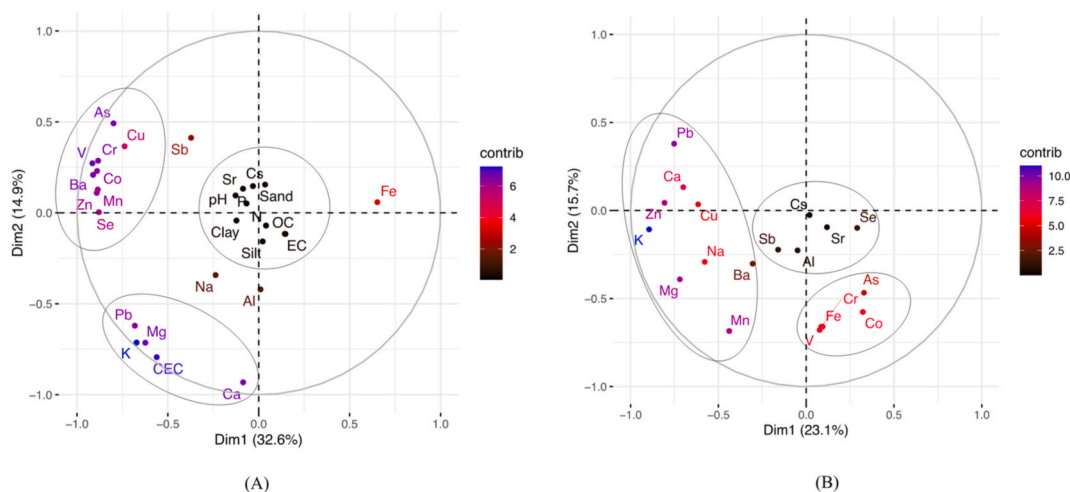

Fig. 2. Principal Component Analysis plot of the (A) soil parameters of the field under study and (B) rice grain elemental concentrations. The contribution of each parameter to the components is scaled in terms of colour intensity (Blue, Red and Black). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

(significantly only with Se (−0.22) at p < 0.001) and positively correlated with Zn, Ca, Mg and Cu (significantly with Zn (0.55) and Ca (0.20) at p < 0.001).

3.3. Comparison between the rice varieties

Arsenic content of the rice varieties followed the order $V_5 > V_4 > V_6 > V_2 > V_7 > V_{10} > V_3 > V_1 > V_8 > V_9$ (Table 4). While there was no significant difference in the soil As content where different varieties were cultivated, certain varieties like V_8 (mean = 18.8 μg kg^{-1}) and V_9 (17.4 μg kg^{-1}) had significantly lower grain As content (p > 0.01) and V_5 (mean = 48.0 μg kg^{-1}) had significantly higher As content. The soil Pb content was also not significantly different between the soils where different varieties were cultivated (p > 0.01), still variety V1 had significantly high (1123.6 μg kg^{-1}) and V_{10} had significantly low (381.4 μg kg^{-1}) Pb content. The Pb content in the varieties followed the order $V_1 > V_7 > V_3 > V_8 > V_9 > V_5 > V_2 > V_4 > V_6 > V_{10}$ (Table 4). The As TF of the varieties followed the order $V_5 > V_6 > V_4 > V_7 = V_3 > V_{10} > V_2 > V_1 > V_8 = V_9$ while the Pb TF of the varieties followed the order $V_9 > V_1 > V_3 > V_8 > V_4 > V_5 > V_6 = V_7 = V_2 > V_{10}$. Overall, a significant negative correlation (Spearman rho = −0.56 at p < 0.01) was observed between As and Pb content in the rice grains and the relationship varied between the different varieties (Fig. 3). A significant (p < 0.05) negative correlation (Spearman rho) was observed for varieties V_3 (−0.73), V_4 (−0.42), V_6 (−0.79), V_7 (−0.43) and V_8 (−0.63) while for the varieties V_5, V_9 and V_{10} the Spearman rho coefficients was negative but was not statistically significant (p > 0.05). The variety V_1 have a weak positive Spearman rho (0.026) but was statistically non-significant (p > 0.05).

Fig. 4 shows the comparison of essential elements present in the grains of the ten rice varieties. Different rice varieties had different essential elemental uptake, for example, V_1 had the highest Fe (23.4 ± 4.6 mg kg^{-1}); V_7 had the highest Ca (143.4 ± 22.1 mg kg^{-1}), and V_8 had the highest Mg (974.4 ± 67.1 mg kg^{-1}) content in grains. The essential nutrient elemental concentrations were not significantly different between the soils where different varieties were cultivated (p > 0.01) as can be observed from Table S1. Table 5 illustrates the best variety based on the TF of both contaminants As and Pb (highest score for the lowest TF) and eight essential elements (highest score for the highest TF) and ranked 1 to 10 based on the highest to lowest score which followed the order $V_9 > V_3 > V_7 > V_8 > V_{10} > V_1 > V_5 > V_4 = V_6 > V_2$. In fact, the variety V_9 had the highest concentration of essential elements like K (2206.4 ± 126.4 mg kg^{-1}), Mn (25.2 ± 2.5 mg kg^{-1}), Zn (26.9 ± 2.4 mg kg^{-1}), Cu (5.9 ± 0.5 mg kg^{-1}) and Se (0.11 ± 0.01 mg kg^{-1}) and lowest

Table 4
Comparison between the mean As and Pb content of rice grains and transfer factors (TF) in the ten varieties (n = 30 for each variety).

Variety	Soil As (mg kg^{-1})	Rice grain As (μg kg^{-1})	TF (As)	Soil Pb (mg kg^{-1})	Rice grain Pb (μg kg^{-1})	TF (Pb)
IRAT_170 (V$_1$)	0.85^a	21.1^{cd}	0.12^b	299.9^a	1123.6^a	0.18 ^{a}
SIPI_692033 (V$_2$)	1.1^a	35.3^b	0.17^{ab}	347.2^a	627.1^d	0.09^b
ITA_315 (V3)	0.82^a	28.4^{bc}	0.20^{ab}	247.4^a	874.2^{bc}	0.16^a
WITA_4 (V$_4$)	0.83^a	36.2^b	0.22^{ab}	290.1^a	610.0^d	0.12^{ab}
NERICA_L19 (V$_5$)	0.98^a	48.0^a	0.27^a	314.2^a	714.7^{cd}	0.10^b
NERICA_L34 (V$_6$)	0.88^a	35.7^b	0.26^a	262.4^a	563.7^d	0.09^b
NCRO_49 (V$_7$)	1.0^a	32.9^b	0.20^{ab}	286.4^a	923.7^b	0.09^b
ART3_7L (V$_8$)	0.8^a	18.8^d	0.10^b	306.4^a	881.0^{bc}	0.13^{ab}
ART_15 (V$_9$)	0.8^a	17.4^d	0.10^b	274.5^a	738.4^{bcd}	0.21^a
Bisalayi (V$_{10}$)	1.0^a	30.7^b	0.18^{ab}	267.7^a	381.4^e	0.08^b

Means with same letter are not significantly different (p > 0.01) as per the *Duncan's Multiple Range Test* (DMRT).

concentration of As, though it had substantial amount of Pb (mean = 738.4 μg kg^{-1}).

4. Discussion

To our knowledge, this is the first study investigating co-uptake of As and Pb in commonly grown Nigerian rice varieties to determine the influence of rice variety on As and Pb contamination. This study benefits from being field-based, under natural conditions of Nigerian rice growing practices and all samples were collected from rice cultivated in Pb contaminated farmlands of Dareta village in Zamfara State, Nigeria. The mean rice Pb content of 743.8 ± 327.1 μg kg^{-1} was about four times the Codex recommendation of 200 μg kg^{-1} Pb in rice while total As content in rice grains of 30.4 ± 15.1 μg kg^{-1} was an order of magnitude below the Codex recommendation of 350 μg kg^{-1} of inorganic As in brown rice (JECFA, 2017). The As in soil was far below the concentrations of 14.0 mg kg^{-1}, an appropriate guideline value for Asian paddy soil above which rice grains cultivated in fields will exceed the Codex recommended maximum allowable concentrations (Mandal et al., 2021). Despite, rice being a hyperaccumulator of As and the cultivation being in agricultural land contaminated by mining activities, the overall As concentration was far below the concentrations reported from the As contaminated areas (soils contaminated from irrigation water) of Bangladesh (290–650 μg kg^{-1}), India (360–1560 μg kg^{-1}), Taiwan (290–660 μg kg^{-1}), Italy (220 μg kg^{-1}), Peru (68.39–345.31 μg kg^{-1}) etc. (Rahman et al., 2014; Chowdhury et al., 2018; Hsu et al., 2012; Williams et al., 2005; Mondal et al., 2020). In comparison with other mining impacted soils, As content in rice grain in Zamfara was higher than in Hunan province China (0.723 μg kg^{-1}, Williams et al., (2009); 0.624 μg kg^{-1}, Zhu et al., (2008)) and lower than Changsa city, Southern China (172.9 ± 64.8 μg kg^{-1}, Ma et al., (2017)). In fact, the mean As content (30.4 ± 15.1 μg kg^{-1}) was lower than previously reported 132 ± 100 μg kg^{-1} by Mwale et al., (2018) and 58.8 ± 0.7 μg kg^{-1} by Adeyemi et al., (2016) in Nigerian rice samples collected from the market. In another study, As concentration in Ghanaian rice was found to be 110 μg kg^{-1} (Adomako et al., 2011). On the contrary, the high Pb content in Zamfara rice found in this study was also reported previously by Simba et al. (2018). The authors noted high Pb content in whole grain local rice sampled from Bagega market (730 μg kg^{-1}) and Anka market (440 μg kg^{-1}), while the whole grain rice with hulls collected from Bagega farms had lower Pb content (200 μg kg^{-1}). In a large-scale survey of rice samples (n = 1578) collected from markets (13 countries) and fields (6 countries), only 0.6% of the samples were found to exceed the Codex recommendation of 200 μg kg^{-1} Pb in rice (JECFA, 2017), but the authors reported high Pb content (676 ± 804 μg kg^{-1}) in samples collected from the fields in China impacted by mining activities (Norton et al., 2014). In the same study, authors reported much lower Pb in Ghanaian rice samples collected from market (24 ± 26 μg kg^{-1}; n = 43) and from the fields (7 ± 7 μg kg^{-1}; n = 138) (Norton et al., 2014).

In our study we observed a negative correlation between As and Pb in rice grains across all the varieties which differed with reports from previous studies where a positive relationship was noted (Mondal et al., 2020; Wang-da et al., 2006). Those studies were from the As contaminated areas in Peru and China with a high total soil As (8.6 ± 7.8 mg kg^{-1}) in Peru and DTPA (Diethylenetriaminepentaacetic acid) extractable soil As in China was 0.17 mg kg^{-1} compared to lower total As in soil (0.91 ± 0.82 mg kg^{-1}) in this study. The total soil Pb content in Peru was low (40.9 ± 38.3 mg kg^{-1}) whereas in China it was 2.9 mg kg^{-1} (DTPA extractable Pb) compared to high total Pb in soil (288 ± 464 mg kg^{-1}) in this study. The As content in Zamfara was much below the European Union (EU) recommended As for agricultural soil of 20 mg kg^{-1} (Hussain et al., 2021) whereas the Pb content was far above the threshold value of 60 mg kg^{-1}. The Pb content was also above the lower guideline value of 200 mg kg^{-1} (Ministry of Environment, Finland, 2007; Toth et al., 2016). As our study was conducted in a Pb contaminated site, this might have resulted in this observed negative relationship. Besides, the
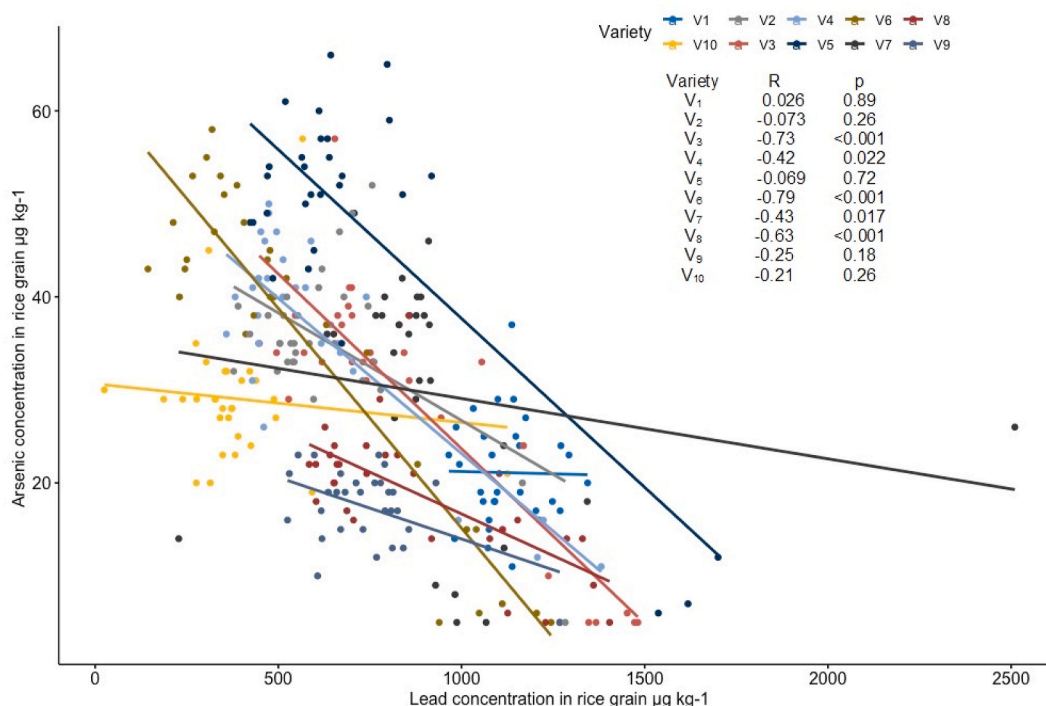
Fig. 3. Spearman correlation between As and Pb content in rice varities (n = 30).
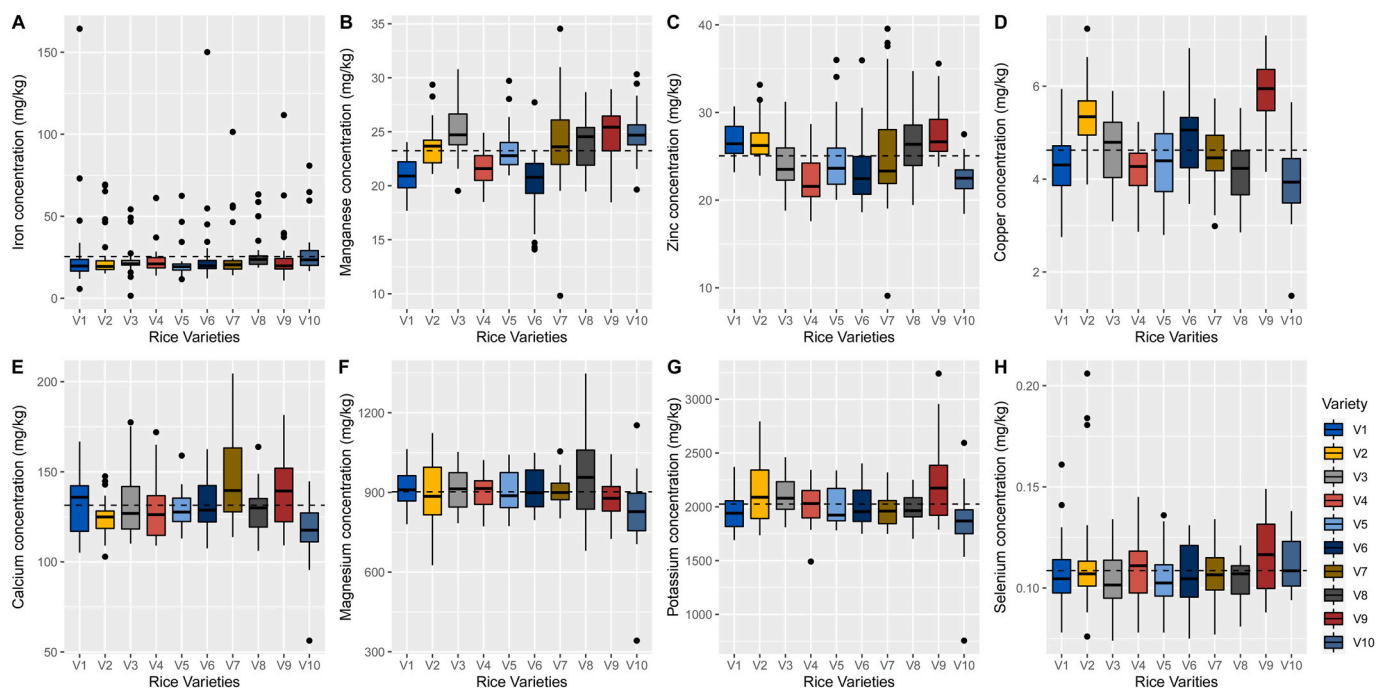

Fig. 4. Comparison between the rice varities in terms of essential element content (A) iron, (B) manganese, (C) zinc, (D) copper, (E) calcium, (F) magnesium, (G) potassium, (H) selenium (n = 30), dotted lines representing the overall mean value.

Pb accumulation in all the rice varieties was very high with maximum concentration (2510 µg kg^{-1}) reaching more than 10-fold the Codex recommendation of 200 µg kg^{-1} Pb in rice, while maximum As concentration (126 µg kg^{-1}) was well below the Codex recommendation of 350 µg kg^{-1} of inorganic As in brown rice (JECFA, 2017).

Both As and Pb content in rice had a significant positive correlation with respective As and Pb contents in the soil. Observed positive correlation of rice Pb with Fe content in soil could be because availability of

Pb in soil is governed by the Fe-oxides present in the soil (Sipos et al., 2014). Similarly, the negative correlation of rice Pb with OC and CEC could be due to the fact that the bioavailability of Pb in soil is governed by the OC (acts as the binding sites) and CEC. In fact, a negative correlation of OC and CEC with the soil Pb has been previously reported (Yan et al., 2019; Guo et al., 2020). A negative correlation of rice Pb content with soil Ca could be due to the fact that soil Pb had a negative correlation with soil Ca and this have also been reported previously

Table 5
Scoring of the rice varieties in terms of Transfer Factor (TF) of As, Pb and essential elements Ca, Mg, K, Fe, Mn, Zn, Cu and Se.

Variety	IRAT_170 (V$_1$)	SIPI_692033 (V$_2$)	ITA_315 (V3)	WITA_4 (V$_4$)	NERICA_L19 (V$_5$)	NERICA_L34 (V$_6$)	NCRO_49 (V$_7$)	ART3_7L (V$_8$)	ART_15 (V$_9$)	Bisalayi (V$_{10}$)
TF (As)	0.12	0.17	0.20	0.22	0.27	0.26	0.20	0.10	0.10	0.18
Score	9	7	6	5	3	4	6	10	10	8
TF (Pb)	0.18	0.09	0.16	0.12	0.10	0.09	0.09	0.13	0.21	0.08
Score	4	9	5	7	8	9	9	6	3	10
TF (Ca)	0.09	0.08	0.10	0.09	0.10	0.08	0.10	0.09	0.09	0.08
Score	9	8	10	9	10	8	10	9	9	8
TF (Mg)	0.49	0.57	0.59	0.53	0.55	0.53	0.59	0.65	0.65	0.56
Score	4	8	9	5	6	5	9	10	10	7
TF (K)	1.65	1.78	1.89	1.75	1.71	1.66	1.90	2.02	2.15	1.60
Score	3	6	7	5	4	2	8	9	10	1
TF (Fe)	0.0014	0.0012	0.0011	0.0011	0.0017	0.0011	0.0014	0.0014	0.0014	0.0035
Score	8	7	6	6	9	6	8	8	8	10
TF (Mn)	0.70	0.62	0.91	0.71	0.66	0.82	0.74	0.69	0.97	0.79
Score	4	1	9	5	2	8	6	3	10	7
TF (Zn)	17.5	14.2	18.1	13.6	14.5	15.3	15.7	16.4	20.6	15.4
Score	8	2	9	1	3	4	6	7	10	5
TF (Cu)	4.38	3.45	4.33	3.82	3.59	3.42	2.93	3.48	5.10	3.91
Score	9	3	8	6	5	2	1	4	10	7
TF (Se)	0.77	0.74	0.77	0.78	0.81	0.80	0.80	0.73	0.78	0.76
Score	7	5	7	8	10	9	9	4	8	6
Total Score	65	56	76	57	60	57	72	70	88	69
Rank	6	9	2	8	7	8	3	4	1	5

Score for As and Pb: Highest score 10 for the variety with lowest TF.
Score for essential elements: Highest score 10 for the variety with highest TF.

(Huang et al., 2021). The addition of soluble Ca with phosphate amendments to Pb-contaminated soils enhances Pb immobilization (Li et al., 2014). Hence, the negative correlation of rice grain Pb with the soil parameters were largely due the fact that the bioavailability of Pb was being regulated by these parameters. Despite, being cultivated in highly Pb contaminated soil, the observed correlation of soil As with other soil parameters (Fig. 3) and rice As with soil physio-chemical properties like positive correlation with the soil As, Pb, Se and Ba and negative correlation with soil CEC, Mn, Zn, Cu, Cr, Sb and Se content (Table 3) were similar to one of the previous study (Mondal et al., 2020; Mandal et al., 2019). Soil As content has a direct relationship with the grain As and these had been reported by several authors (Kumari et al., 2021; Sengupta et al., 2021 and Yaoa et al., 2021). There are both direct and indirect evidences to suggest that As is held in soils by sediments by oxides (e.g. of Fe, Mn, Zn) through the formation of inner-sphere complexes via ligand exchange mechanism (Kumari et al., 2021; Raj et al., 2021). Iron appeared highly efficient to sequester As and to restrict As acquisition by rice (Chowdhury et al., 2018a). The mobility of As in the soil during the flooded period, is largely controlled by the setting of oxic/anoxic interfaces at the surface of soil in contact with flooding water and in the rhizosphere of rice (Herath et al., 2016). The CEC of the soil is the capacity of the soil to adsorb and exchange cations, As being negatively charged (H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$, AsO_4^{3-}), CEC had a negative correlation with As (Ye et al., 2012; Sanyal, 2017). Selenium has an antagonistic effect with As in rice and when Se was added to the soil a reduction in uptake of As was observed (Kaur et al., 2017). The presence of Se could significantly decrease the As concentration in the soil pore water inhibiting the As uptake in rice (Pokhrel et al., 2020). So, a negative association of soil Se with grain As is normally observed, as in this study. Both Sb and As binds to organic matter, silicate clay minerals, oxides and hydroxides of Fe, making it more vulnerable to environmental release when redox conditions change, inducing a competitive relationship between the two elements (Wilson et al., 2010). These supports a correlation between rice As with soil Sb.

The negative correlation of rice As with essential elements (like Zn, Fe, Mn, Cu and Ca) in rice grains observed in this study was previously noted in Peruvian rice (Mn (−0.11), Cu (−0.43) and Zn (−0.59) (Mondal et al., 2020). Negative interaction of As with certain elements in rice has been previously reported, for example, the uptake of Zn to combat the As

in rice (Wu et al., 2020) and use of Fe as a supplement to reduce As stress in rice (Nath et al., 2014). The significant negative correlation of Pb with Se in rice grains, observed in this study was previously reported by Hu et al., (2014) in brown rice (−0.624 at p < 0.05). The significant positive correlation between rice Pb with essential elements: Zn and Ca observed in this study was noted in Indian rice by Satpathy et al., (2014). A close association of the essential elements: Zn, Mn, Ca, Cu, K, Mg in rice grain (seen from the PCA, Fig. 3B) was also reported in Brazilian rice (Lagne et al., 2019) and presence of the essential elements in considerable amounts along with Pb in Nigerian rice was reported by Adedire et al. (2015).

Even though soil Pb levels are extremely high, there is little Pb buildup in rice grains. In comparison to other plant parts, grain had a very low quantity of Pb. Similar findings were reported by Liu et al. (2003), who suggested that the translocation of Pb from root to grain in rice plants would be blocked by all parts along the pathway. Plant roots may take up a lot of Pb from the soil while also limiting the amount of Pb that gets to the aerial portions (Tangahu et al., 2011). Several studies have also found that different plant species have varying Pb uptake and translocation properties (Deng et al., 2004). Variation in Pb accumulation in 35 rice varieties have been previously reported by (Lee et al., 2016).

Among the ten rice varieties, the lowest As uptake was in V$_8$ and V$_9$ (TF = 0.10) and lowest Pb uptake was in V$_{10}$ (TF = 0.08). Nevertheless, V$_9$ had higher concentration of essential elements and TF of Mg, K, Mn, Zn and Cu was highest in this variety. Hence, this rice variety ART-15 (V$_9$) which is an indigenous upland rice with a crop duration of 110–115 days having a pretty good yield potential of 6 t ha^{-1} is promising and can be considered as suitable variety to be cultivated in Zamfara. Further studies using this specific variety to ascertain its effectiveness against Pb contamination through controlled studies addressing the plant physiological, biochemical, and molecular parameters should be conducted in Zamfara. That said, since V$_9$ had a high TF for Pb, the V$_{10}$ rice variety, Bisalayi, of Nigerian origin, similar crop duration (110–115 days) as V$_9$ but better yield (4–8 t ha^{-1}) and possible cultivation in both upland and lowland, and with relatively good essential element TF (highest for Fe) should be considered for food and nutritional security particularly in areas where rice is cultivated in high Pb contaminated agricultural fields. The high TF of Pb and/or As in

other rice varieties was alarming. Cultivation of such varieties in Pb contaminated villages of Zamfara should be done with a caution. Moreover, appropriate mitigation techniques involving the use of soil amendments (both inorganic and organic) to lower Pb bioavailability are necessary. For example, the addition of compost could result in a greater reduction of the harmful effects of heavy metals such as Pb (Bolan et al., 2003). Besides, biochar's significance in decreasing heavy metal toxicities from soil to plants has been established in several research (Hussain et al., 2017; Rizwan et al., 2021). Phosphate additives can immobilize Pb in contaminated soil and could be potential mitigation due to ease in their availability and ecofriendly nature (Fang et al., 2012). These additives induce Pb immobilization primarily via the formation of stable lead phosphate minerals that are stable even at low soil pH (Cao et al., 2013).

Despite the challenges inherent in field research, such as the difficulty of controlling extraneous variables, this study advances understanding of the behavior of ten common Nigerian rice varieties in terms of: (a) As and Pb uptake and resultant contamination/safety considerations when cultivating rice in a Pb polluted environment; (b) the influence of other soil parameters on transfer to rice; and (c) the nutritional quality of rice based on uptake of essential elements. Based on this study, the most appropriate rice varieties for cultivation in Pb polluted agricultural lands of Zamfara state were identified. However, further studies in similar ecological contexts are warranted to evaluate the influence of other factors (e.g. climate stress and the presence of other contaminants) on the transfer to different rice varieties.

5. Conclusion

The varietal influence on As and Pb contamination along with uptake of essential elements in rice grains was investigated to determine candidate rice varieties for local farmers to cultivate in the mining-contaminated farmlands of Dareta village, Zamfara State, Nigeria. Among the ten distinct and popularly farmed Nigerian rice varieties, Bisalayi exhibited lowest TF for Pb as well as highest TF for Fe. Bisalayi is known for its yield, taste, disease resistance and a cultivation potential in both upland and lowland conditions. Though its Pb uptake was lower than the other varieties studied, the rice grain concentration were still above the Codex guidelines. Therefore, Bisalayi cultivation in the high Pb contaminated farmlands of Zamfara must be undertaken with caution and possibly with appropriate remediation measures such as addition of compost and biochar having the capacity to immobilize Pb in soil. Contrary to previous studies, there was a significant negative correlation between the As and Pb levels in rice grains, but the As content in rice grains, including in Bisalayi was far below the Codex recommendation to limit exposure from rice intake. The lowest As uptake was in V_8 and V_9 (TF = 0.10). The TF of essential elements: Mg, K, Mn, Zn and Cu were highest in V_9 (ART_15). Hence this lowland, irrigated African rice variety, ART_15 could be suitable for cultivation in As contaminated areas in Nigeria. To ensure food and nutritional security, in these severely Pb contaminated farmlands, Bisalayi rice variety should be further investigated for overall performance and potential resistance to Pb uptake. Furthermore, though rice is mainly cultivated as a rainfed crop in the region, further investigation should be carried out regarding the mobility of Pb and other contaminants including As with the changes in the water regime. Finally, the positive correlation between rice grain As and soil Pb content suggests that soil intervention studies should be explored to reduce As and Pb uptake in rice when cultivated in Pb-contaminated farmlands.

Credit author statement

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2022.135339.

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