Research Article

Evaluation of Heavy Metals Contamination from Environment to Food Matrix by TXRF: The Case of Rice and Rice Husk

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This paper is devoted to the chemical analysis of contaminated soils of India and the rice grown in the same area. Total reflection X-ray fluorescence spectroscopy is a well-established technique for elemental chemical analysis of environmental samples, and it can be a useful tool to assess food safety. Metals uptake in rice crop grown in soils from different areas was studied. In this work soil, rice husk and rice samples were analyzed after complete solubilization of samples by microwave acid digestion. Heavy metals concentration detected in rice samples decreases in the following order: $Mn > Zn > Cu > Ni > Pb > Cr$. The metal content in rice husk was higher than in rice. This study suggests, for the first time, a possible role of heavy metals filter played by rice husk. The knowledge of metals sequestration capability of rice husk may promote some new management practices for rice cultivation to preserve it from pollution.

1. Introduction

Heavy-metal pollution of soil affects the quality of the environment leading to serious consequences. Heavy metals group includes Ag, Ba, Cd, Co, Cr, Mn, Hg, Mo, Ni, Pb, Cu, Sn, Tl, V, Zn, and some metalloids such as As, Sb, Bi, and Se. Arsenic, for example, is often considered as a heavy metal due to the similarity of its chemical properties and behavior with the other heavy metals. Heavy metals accumulation in soil, and in the environment in general, may be related to the phenomenon of bioaccumulation ability of living organisms, that is, increasing the concentration at human organism due to industrial activities and the food chain. The main sources of heavy-metal pollution in soil are irrigation, especially with sewage; solid-waste disposal, for example, sludge and compost refuse; the use of pesticides and fertilizers; and atmospheric deposition [1].

Plants acquire the necessary nutrients, such as N, P, and K, from the environment. However, they may also accumulate unnecessary and toxic metals, such as Pb and Cd. Several plants have the ability to accumulate high metal concentrations [2]. Many studies have reported data for the transfer of

heavy metals from soil to plants and vegetables through roots and shoot [3]. Therefore, toxic metals such as As, Cd, and Pb can be taken up from cereal crops and transferred to their grains [4]. Toxic metals may be classified according to their capability of being transferred from soil to plants in mobile metals, such as Cd, and poorly mobile metals, such as Pb. This property may affect their bioaccumulation in plants [5].

Rice is one of the most important and widespread cereals in the world. It is the staff of life for 3 billion people, mainly in Asia [6], contributing over 70% of the energy and 50% of the protein provided by their daily food intake. In the last report of EU Commission, India was presented as the first country for rice production with 19% of export. India is followed by Cambodia and Thailand. United States and Vietnam are the countries with less amount of imported rice [7]. About 80% of the rice production of Europe takes place in Italy and Spain, with a further 12% in Greece and Portugal.

On this basis the presence of toxic heavy metals in rice, which may raise the metal daily intake, should be strongly avoided in order to prevent negative effects on human health. The following elements are considered macronutrients in rice and their content is usually in some %: P, S, K, Ca, and Mg.

Other elements, like Mn, Fe, Cu, Zn, Se, and Ni, are classified as micronutrients and they are present in lower amount, while As, Cr, Pb, and Cd are undesirable elements because of their toxic effects even in very low quantity. As a consequence, it is crucially necessary to reduce possible accumulation effects in rice grains from the environment for safe food production. Great efforts are necessary to remediate polluted sites. Other approaches could be developed to reduce metals accumulation in edible parts of plants. For instance, favorable agronomic practices and chemical regulators may decrease plant heavy metals uptake. In this context it is important to identify which parts of the plant accumulate more toxic substances.

Rice husk (RH) is the external protecting covering of each rice grain. The chemical composition of RH varies from sample to sample depending on rice variety, climate, and origin. Organic compounds and water are the main components of RH (about 74%), followed by amorphous silica (between 15 and 22%) and other inorganic compounds (about 4%) such as Al_2O_3 , Fe_2O_3 , CaO , and MgO [8]. Omatola and Onojah [9] reported the following list of elements detected by X-ray fluorescence (XRF) in RH: K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, Sr, Br, I, As, and Cl. These elements, owing to their low concentrations, are considered as impurities. Sun and Gong reported that the main application of RH [10] is the production of thermal energy, due to its high calorific value, about 13607 kJ/kg. Several other destinations of RH were reported, such as livestock for the cattle, agricultural fertilizer, ingredient for substrates in floriculture and horticulture, and simple fertilizer for plants. RH was also used for the production of biodegradable pots, instead of using oil.

It is also known that the produced byproduct of rice husk is called rice husk ash (RHA). RHA is widely used by the steel industry in the production of high quality flat steel for automotive body panels [11]. Owing to its insulating properties, RHA has been used in the manufacture of refractory bricks, which are exposed to extreme temperatures in furnaces, such as the blast furnaces employed for producing molten iron, and in the production of cement clinker. The Indian Space Research Organization has successfully developed the technology for producing high purity precipitated silica from RHA, which has a potential use in the computer industry [12, 13]. American and Brazilian scientists also developed new ways to extract and purify silicon from RHA to use it in semiconductor manufacture. Other uses have been explored. In the frame of the COSMOS-RICE project, RHA is employed as metals stabilizer for municipal solid waste incineration fly ash treatment [14, 15].

It is very interesting to verify the higher capability of heavy accumulation by RH with respect to rice. This can play a fundamental role in the management of rice cultivation.

Elemental chemical analysis of rice is usually performed by normative techniques such as FAAS [16]. In this study we used total reflection X-ray fluorescence (TXRF) to analyze the chemical composition of rice, RH, and soils of two different areas of India. The aim was the evaluation of metal uptake from soil to rice and the investigation of possible sources of environmental pollution in the studied areas. Moreover this work aims to highlight the possible role of RH in preserving rice from bioaccumulation of heavy metals.

TABLE 1: Type of samples and their corresponding numbers sampled from the studied areas.

City	Samples	Number of samples
Raipur	Soil	
Raipur	A	5
Raipur	B	5
Raipur	Rice husk (RH)	5
Raipur	Rice	5
Korba	Soil	5
Korba	Rice husk (RH)	5
Korba	Rice	5

2. Materials and Methods

2.1. Study Areas. Elemental chemical analysis of soils coming from the central-east area of India, where soil contains high concentration of heavy metals, was performed. The state of Chhattisgarh (India) is rich in minerals such as iron, limestone, dolomite, coal, bauxite, garnet, quartz, marble, alexandrite, and diamonds. Because of the huge production of rice, Chhattisgarh district nickname is “rice bowl of Central India.” Industrial activities in this area increased a lot in the last years. In fact, the construction of new coal-fired power plants has increased up to 50% the production of ashes, which exposes the human and the environment to high pollution risks. Therefore, Raipur and Korba were chosen as the target cities of this study. Raipur is located at $21^\circ 13' 60''$ N and $81^\circ 37' 60''$ E, and hundreds varieties of rice grow. Different studies have already confirmed the presence of heavy metals in soils from this area, demonstrating a degradation of the environmental quality [17–19]. Meanwhile, Korba is located at $22^\circ 21' 0''$ N and $82^\circ 40' 60''$ E and, as well as Raipur, it is also a “victim” of the industrial growth, especially of cement industry. Soil and rice samples from each city region were collected in 5 different areas. Samples in Raipur were collected in duplicate to check the homogeneity of its composition. The two samples, named as A and B in Table 1, were collected in the same area at a distance less than 1 km from each other.

2.2. Samples Preparation Procedure. Soil samples were homogenized through a mortar and dried for 90 min at 90°C . Samples were weighed before and after this process in order to determine their humidity. Rice samples were transported from India as they were collected. Rice grains were inside their husk. The separation of each rice grain from its outer shell (husk) was carried out manually in the first step of sample preparation. Some differences were noticed at a glance. Rice samples had different husk colors, from green to yellow, and crop dimensions.

2.3. Digestion of Samples. About 0.5 g soil sample was added to 9 mL of nitric acid 65% (Fluka), 3 mL of hydrofluoric acid (Fluka), and 2 mL of hydrochloric acid 37% (Fluka) in Teflon vessels. HF was necessary to perform total solubilization of soil, probably due to the high content of silicates. This procedure was performed according to US-EPA 3050B method

FIGURE 1: TXRF spectra of soil samples from Korba (black) and Raipur (grey).

[20]. Smaller quantities of RH and rice samples were used for digestion. About 0.30 g of rice and rice husk was weighed, transferred inside the vessel, and mixed with 10 mL of nitric acid 65% (Fluka). A magnetic shaker was inserted in each vessel and then the vessel was closed with a cap provided with a hole to allow the leakage of gases formed during the digestion. A CEM microwave digestion device was used to digest the samples at 200°C and 400 Psi. After complete sample solubilization, the solutions were transferred to 25 and 10 mL volumetric flasks, respectively, for soil and rice/RH and filled with MilliQ water to the exact volume.

2.4. TXRF Analysis of Soils, Rice Husk, and Rice Samples. Chemical analysis of the solutions, obtained by digestion, was performed by means of TXRF spectroscopy. Quantitative analysis was performed by the internal standard addition procedure [21], using Ga as internal standard element, because it was not present in all the original samples. 10 μ L of Ga (1 g/L) was added to 990 μ L of soil samples in order to obtain a final Ga concentration of 10 mg/L. Ga concentration in rice and RH solutions was 1 mg/L. 10 μ L of each sample solution was deposited on a three-quartz glass sample carrier, cleaned and siliconized, and then dried on a hot plate at 50°C. TXRF measurements were performed by Bruker S2 Picofox, equipped with Mo tube, operating at 50 kV and 750 μ A, and Silicon-Drift Detector. Live time for each measurement was 600 seconds.

3. Results and Discussion

3.1. TXRF Analysis of Soils. Humidity in Raipur soils was higher than in Korba samples. It ranges from 1.4 to 6.7%, while in Korba soils humidity was in the interval from 1.7 to 2.9%.

TXRF spectra of soil samples from Korba and Raipur are shown in Figure 1. Signals of Al, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Rb, Ba, Pb, and Sr are clearly identified in all the samples of both cities region. Bi was present only in the soils from Raipur, suggesting possible anthropogenic causes.

Regarding the nonmetals, signals of S, Cl, and Br were always identified.

TXRF measurement was performed in air; for this reason it is not possible to give an accurate estimation of the content of lighter elements such as Al, P, and S. Their concentration may be underestimated and higher standard deviations may occur (about 20% in the case of Al). The content of Fe is higher compared to the other elements. For this reason, fitting of TXRF spectra was performed considering the pile up peak of Fe $K\alpha$. However, as it was demonstrated in a recent publication, TXRF is a successful technique to perform quantitative analysis of soils [22]. Background levels were kept to a minimum with the use of quartz sample carriers, reducing at minimum their contact time with HF.

Results of quantitative analysis of soil samples are reported in Table 2. Heavy metals content is higher in Raipur soil samples compared with Korba samples. Almost all the elements concentrations are 4-5 times higher in Raipur than in Korba. Relative standard deviation (RSD) is used to evaluate the precision of the measurements. RSD for most of the elements (Mn, Fe, Ni, Cu, and Zn) is in the range from 1 to 6.4%. Slightly higher RSD values are observed for V, 9.4%, and for Ba, from 6.5 to 24.6%, due to the reasons already discussed [22]. The highest RSD values are observed for Bi probably due to its low concentration, which is near the lowest limit of detection (LLD).

Descriptive statistics of elemental content in soil samples is reported in Table 3. Concentration of Bi is significantly lower compared to other elements in soils. Mn is the element with the widest range of concentrations and the largest differences in the two studies areas. Zn concentration is almost the same in both cities, while Cr and Pb are significantly higher in all the Raipur samples, highlighting the possible adverse effects of the metallurgy industry in Raipur. The data of soils collected in the same area of Raipur, in two different points, do not show any significant difference. This result figures out a homogeneous distribution of metals in the studied regions.

A comparison of our results with the guidelines and limits proposed for the determination of heavy metals pollution

TABLE 2: Elemental concentration (mg/kg) in soil samples from Korba and Raipur. Results are expressed as the average $\pm$ standard deviation.

Sample	Elements concentration (mg/Kg)											Sr	Pb	Bi	
	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	As				Ba
Korba															
S 1_K	4524 ± 203	2560 ± 297	1550 ± 85	14 ± 1	22 ± 1	254 ± 12	7071 ± 309	9 ± 1	11 ± 1	52 ± 3	4 ± 1	152 ± 18	28 ± 2	11 ± 1	n.d.
S 2_K	3829 ± 175	1448 ± 463	1562 ± 68	17 ± 2	25 ± 1	230 ± 10	8409 ± 379	10 ± 1	10 ± 1	58 ± 3	3 ± 1	76 ± 9	14 ± 2	12 ± 1	n.d.
S 3_K	5705 ± 447	1101 ± 417	1572 ± 72	15 ± 2	19 ± 1	83 ± 4	5676 ± 246	10 ± 1	6 ± 1	14 ± 1	4 ± 1	57 ± 8	3 ± 0.1	10 ± 1	n.d.
S 4_K	5031 ± 239	421 ± 25	1350 ± 59	15 ± 1	24 ± 1	102 ± 4	7257 ± 316	12 ± 1	7 ± 1	15 ± 1	5 ± 1	117 ± 13	11 ± 1	11 ± 1	n.d.
S 5_K	6217 ± 511	441 ± 34	1293 ± 63	11 ± 1	15 ± 1	143 ± 7	5781 ± 254	7 ± 1	6 ± 1	22 ± 1	5 ± 1	136 ± 10	15 ± 1	13 ± 1	n.d.
Raipur															
S 1A_R	7617 ± 391	2660 ± 1637	4337 ± 197	61 ± 6	112 ± 6	1455 ± 66	38863 ± 1737	39 ± 2	34 ± 2	60 ± 4	15 ± 1	166 ± 28	23 ± 6	64 ± 5	4 ± 1
S 1B_R	8117 ± 356	786 ± 57	4893 ± 213	55 ± 4	120 ± 5	1055 ± 46	39578 ± 1716	45 ± 2	37 ± 2	60 ± 2	12 ± 2	162 ± 12	16 ± 1	55 ± 5	5 ± 1
S 2A_R	6172 ± 318	1088 ± 228	4610 ± 222	65 ± 5	111 ± 5	973 ± 46	38183 ± 1671	45 ± 3	34 ± 2	60 ± 5	13 ± 2	160 ± 22	20 ± 3	46 ± 5	5 ± 1
S 2B_R	4895 ± 226	1199 ± 66	4716 ± 207	60 ± 4	127 ± 6	463 ± 20	37942 ± 1647	49 ± 2	34 ± 1	51 ± 2	15 ± 2	158 ± 18	21 ± 1	46 ± 5	5 ± 1
S 3A_R	9251 ± 477	837 ± 151	5246 ± 248	107 ± 10	145 ± 7	1855 ± 81	32937 ± 1437	80 ± 4	43 ± 2	60 ± 3	21 ± 3	170 ± 42	16 ± 2	55 ± 8	5 ± 2
S 3B_R	9149 ± 400	786 ± 42	5959 ± 258	116 ± 7	121 ± 5	1389 ± 61	27203 ± 1331	75 ± 3	46 ± 2	50 ± 2	26 ± 1	147 ± 22	11 ± 2	44 ± 2	4 ± 1
S 4A_R	5318 ± 233	1078 ± 115	4993 ± 218	74 ± 4	131 ± 6	1304 ± 58	42808 ± 1863	55 ± 2	36 ± 2	54 ± 7	18 ± 2	191 ± 13	17 ± 1	54 ± 5	5 ± 2
S 4B_R	5497 ± 270	824 ± 137	5270 ± 254	116 ± 11	122 ± 6	1984 ± 90	31119 ± 1360	80 ± 5	49 ± 14	56 ± 3	30 ± 3	129 ± 30	11 ± 4	55 ± 6	4 ± 1
S 5A_R	7477 ± 510	1275 ± 594	4672 ± 205	127 ± 8	174 ± 8	2597 ± 113	43853 ± 2203	79 ± 4	44 ± 2	54 ± 6	36 ± 3	261 ± 116	17 ± 6	69 ± 3	5 ± 1
S 5B_5	8599 ± 422	2557 ± 237	5285 ± 232	111 ± 6	155 ± 7	1701 ± 75	40033 ± 1767	71 ± 3	43 ± 2	55 ± 2	24 ± 3	427 ± 54	31 ± 3	67 ± 6	8 ± 1

TABLE 3: Descriptive statistics results of elemental chemical analysis for Korba and Raipur soils.

	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	As	Ba	Rb	Sr	Pb	Bi
Korba																
Mean	5061.10	1195.82	1465.22	14.38	20.78	162.39	6838.82	9.54	7.96	32.20	4.20	107.51	23.62	14.24	11.35	n.d.
SD	942.97	880.66	133.32	2.29	4.10	76.01	1136.39	1.90	2.29	21.11	0.64	39.98	7.20	8.98	1.20	n.d.
Min	3829.12	420.76	1292.66	11.08	14.56	82.90	5676.19	6.54	5.95	14.15	3.38	56.99	13.81	3.16	9.85	n.d.
Max	6216.60	2559.93	1571.93	17.32	24.68	253.70	8409.31	11.62	10.84	58.18	4.86	171.60	30.73	27.82	12.80	n.d.
Raipur																
Mean	7209.17	1309.09	4988.11	89.34	131.88	1477.54	37201.98	61.84	39.59	55.86	20.96	197.05	26.24	18.45	55.45	5.11
SD	1628.34	707.36	471.33	28.31	20.11	596.58	5189.52	16.60	5.91	3.86	8.05	88.00	16.64	6.32	8.94	1.18
Min	4895.48	785.77	4336.85	55.44	111.48	462.53	27202.51	39.34	31.09	50.03	11.90	129.43	10.23	10.76	43.55	3.83
Max	9251.30	3659.98	5958.69	126.84	173.61	2579.07	43354.00	79.93	48.51	60.11	35.68	427.57	71.32	32.75	69.21	8.15

[23] indicates that all the soil samples of Korba are not contaminated, while soils from Raipur are contaminated by Ni, Cu, Cr, As, and Ba.

A more detailed comparison of our data with those obtained in other studies of soil contamination in the same area reveals a good agreement. The comparison with data reported by Kabata Pendias for uncontaminated soils (Cr 0.4–29 mg/kg, Mn 25–8000 mg/kg, Ni 3–150 mg/kg, Cu 0.5–135 mg/kg, Zn 1–750 mg/kg, and Pb 0.6–63 mg/kg) [24] suggests that Cr and Pb contamination is present in Raipur. More recent studies by Srinivasa Gowd et al. [25] and Patel et al. [26] reported higher content of Pb, Zn, and Cr. Thus, only contamination by Cr would be present. However, it should be considered that Pb, Zn, and Cr concentration increased easily during the industrial activity, particularly in the mining areas. So the increasing in metal concentration in these soils may be a consequence of anthropogenic influence.

Statistical analysis was used to evaluate the correlation of the elements present in soil. Cluster analysis was used to highlight the differences between soils from Korba and Raipur. Hierarchical division was performed using the Ward method, which is based on the analysis of variances instead of distances. The varimax rotation with Kaiser normalization method was used for factor analysis. By extracting the eigenvalues, the number of significant factors was determined. Data treatment was performed using the JMP 10 software. Results of cluster analysis are reported in Figure 2. The dendrogram clearly points out the division of the samples in two clusters corresponding to the different sampled areas of Korba and Raipur. Considering that the two studied cities belong to the same region of India, and supposing the same crustal composition, this result suggests a different degree of pollution.

Results of factor analysis show that the three eigenvalues explain 90.18% of the variance. Therefore, they were selected for further factor analysis. The loadings of elements with respect to each one of the three identified factors are reported in Table 4. All the elements with high loadings for the same factor may have a common origin in soils. The first factor is responsible for 56.3% of the total variance and it includes K, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Pb, and Bi. Considering the nature of these elements and their simultaneous presence this suggests their anthropogenic origin. The second factor

FIGURE 2: Dendrogram of cluster analysis for Korba (red) and Raipur (green) samples.

accounts for 17.09% of the total variance and it includes Ca and Sr. Ca and Sr are included in the list of the eight most abundant rock forming elements of biosphere, which may be added to the soil from wind dispersion of dust from mine tailing and wastes tips [27, 28]. The third principal component represented 16.79% of the total variance and it includes Al, Rb, and Ba. The presence of Al would suggest a crustal origin. Indeed, Al acts as a natural marker element, while its anthropogenic origin is still unknown. Al is a conservative element and is contained in aluminosilicates as is reported by Vodyanitskii [29]. However, the crustal origin of Rb and Ba is not assessed.

3.2. TXRF Analysis of Rice and Rice Husk. TXRF spectra of rice and rice husk are shown in Figure 3. Signals of Mg, Al, P, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Ba, Rb, Pb, Br, and Sr are identified in both rice and RH samples. After spectra deconvolution, concentration of each was determined except

FIGURE 3: Spectra of rice husk (black) and rice (gray) sample 2 from Korba measured by S2 Picofox.

TABLE 4: Rotated component matrix for soil samples.

Variables	Rotated factor		
	1	2	3
Al	0.4877	0.3792	0.7279
K	0.5859	-0.0676	0.5477
Ca	0.0419	0.9249	0.1358
Ti	0.9527	0.1259	0.0972
V	0.9167	0.0068	0.3339
Cr	0.9421	0.1997	0.203
Mn	0.8834	0.0792	0.2768
Fe	0.8929	0.3231	0.0015
Ni	0.9423	-0.0077	0.2811
Cu	0.9715	0.1256	0.1389
Zn	0.6599	0.5904	-0.1872
As	0.8862	-0.04	0.29
Rb	0.0402	0.147	0.9675
Sr	0.0761	0.9325	0.2809
Ba	0.4065	0.5243	0.6689
Pb	0.9163	0.287	0.1481
Bi	0.8439	0.3457	0.2535

Factor	Variance explained by each factor		
	Variance	Percent	Cum. percent
Factor 1	9.5731	56.313	56.313
Factor 2	2.9045	17.085	73.398
Factor 3	2.8535	16.785	90.183

for elements lighter than K. Quantification of the detected low Z elements is not reported because our measurements were performed in air, and vacuum conditions are recommended in this case [30]. Results of quantitative analysis of rice and rice husk samples are reported in Table 5.

Elemental composition of rice husk and rice is similar for all the studied samples, even if Ca, Ti, Mn, Fe, and Pb are higher in RH with respect to rice. The concentration of metals in the two matrices is usually correlated. In the samples from Korba the highest concentrations of Ti, Fe, and Zn were detected in sample 3 for both the analyzed matrices (3R_K and 3RH_K) and the highest concentration of Ca and Mn in sample 1 (1R_K and 1RH_K). In the samples from Raipur the highest concentrations of Fe and Zn are found in sample 3 (3R_R and 3RH_R), while the highest content of Mn was in sample 4 (4R_R and 4RH_R). Rice husk samples of Korba contain Cr that is not detected in rice, while Cr is present in both the matrices collected in Raipur, with the usual correlation. This can be due to the higher concentration of Cr in Raipur than Korba soils. The correlation observed for the other elements is not present in the case of Pb. Indeed, the highest value of Pb for rice husk samples is present in sample 5RH_K, while the highest value of Pb for rice is present in sample 2R_K. A similar behavior is observed for Ca and Ti in the samples from Raipur.

Descriptive statistics of elemental content in rice and rice husk samples is reported in Table 6. The comparison of heavy metals concentration in rice grain from the two studied areas shows no significant differences among K, Ca, Ti, Ni, Cu, and Zn. Other elements such as Cr, Fe, and Pb are higher in Raipur samples, while Mn and Rb are higher in Korba samples. Concentration of heavy metals detected in rice samples decreases in the following order: Mn > Zn > Cu > Ni > Pb > Cr.

Metal uptake is higher for plants germinated in soils enriched with metals from anthropogenic factors. Therefore, bioaccumulation ability of plants is one of the most critical problems faced in agriculture and environmental studies. Transfer factor (TF) is an indicator of the plant species ability or tendency to uptake a certain element from the soil [31]. TF is obtained by dividing the element concentration in the plant by its concentration in soil, according to (1) where C_p is the metal concentration in plant and C_s is the metal

TABLE 5: Elemental concentration in rice (R) and rice husk (RH) samples from Korba and Raipur.

Sample	Elemental concentration (mg/Kg)												
	K	Ca	Ti	Cr	Mn	Fe	Ni	Cu	Zn	Rb	Sr	Ba	Pb
Korba													
1 R_K	2179 ± 122	267 ± 67	1.9 ± 0.4	0.0 ± 0.0	44 ± 2	18 ± 3	0.4 ± 0.1	2.2 ± 0.2	29 ± 1	18.6 ± 1.0	0.67 ± 0.14	n.d.	0.27 ± 0.01
2 R_K	2911 ± 160	225 ± 19	0.5 ± 0.3	0.0 ± 0.0	29 ± 1	19 ± 2	0.9 ± 0.1	2.4 ± 0.1	30 ± 1	35.2 ± 1.7	0.33 ± 0.05	n.d.	0.51 ± 0.03
3 R_K	2603 ± 184	227 ± 17	4.0 ± 0.3	0.0 ± 0.0	32 ± 1	21 ± 1	0.5 ± 0.1	3.0 ± 0.2	39 ± 2	4.2 ± 0.3	0.52 ± 0.03	n.d.	0.25 ± 0.02
4 R_K	1604 ± 111	223 ± 20	1.4 ± 0.4	0.0 ± 0.0	27 ± 1	13 ± 1	2.0 ± 0.6	3.0 ± 0.2	22 ± 1	5.7 ± 0.3	0.29 ± 0.02	n.d.	0.08 ± 0.02
5 R_K	2162 ± 113	175 ± 11	0.7 ± 0.2	0.0 ± 0.0	24 ± 1	15 ± 1	0.4 ± 0.1	2.5 ± 0.1	24 ± 1	22.5 ± 1.0	0.33 ± 0.01	n.d.	0.13 ± 0.01
1 RH_K	4152 ± 303	1500 ± 68	2.8 ± 0.9	0.4 ± 0.1	325 ± 15	93 ± 4	0.6 ± 0.1	2.0 ± 0.1	32 ± 1	22.3 ± 1.2	4.76 ± 0.22	32 ± 2	0.41 ± 0.04
2 RH_K	3894 ± 311	1277 ± 61	7.3 ± 2.4	0.0 ± 0.0	174 ± 8	161 ± 11	3.3 ± 0.2	1.8 ± 0.4	26 ± 1	28.7 ± 2.0	2.68 ± 0.13	15 ± 1	0.47 ± 0.03
3 RH_K	2277 ± 152	1485 ± 106	59.9 ± 45.6	0.9 ± 0.2	210 ± 9	409 ± 26	1.0 ± 0.1	2.1 ± 0.2	33 ± 3	3.7 ± 0.3	4.49 ± 0.23	26 ± 2	0.70 ± 0.07
4 RH_K	4441 ± 196	1072 ± 47	6.0 ± 2.4	0.2 ± 0.1	213 ± 9	184 ± 9	2.6 ± 0.1	2.2 ± 0.1	28 ± 1	11.1 ± 0.5	2.24 ± 0.10	25 ± 1	0.43 ± 0.02
5 RH_K	3782 ± 167	948 ± 61	2.3 ± 0.3	0.0 ± 0.0	206 ± 9	93 ± 4	0.6 ± 0.1	1.9 ± 0.1	27 ± 2	23.4 ± 1.1	2.89 ± 0.15	30 ± 1	1.02 ± 0.05
Raipur													
1 R_R	3021 ± 221	395 ± 54	2.4 ± 1.1	0.3 ± 0.1	21 ± 1	33 ± 22	0.6 ± 0.1	3.4 ± 0.4	30 ± 2	0.6 ± 0.03	0.31 ± 0.03	n.d.	0.38 ± 0.02
2 R_R	2201 ± 101	232 ± 12	0.8 ± 0.2	0.0 ± 0.0	20 ± 1	13 ± 1	0.2 ± 0.1	1.7 ± 0.1	19 ± 1	3.2 ± 0.2	0.38 ± 0.02	n.d.	0.45 ± 0.04
3 R_R	2621 ± 120	347 ± 98	3.2 ± 0.4	0.3 ± 0.1	33 ± 1	24 ± 1	0.4 ± 0.1	2.3 ± 0.2	31 ± 2	1.1 ± 0.1	0.55 ± 0.04	n.d.	0.40 ± 0.03
4 R_R	2441 ± 134	345 ± 40	2.2 ± 0.5	0.2 ± 0.1	35 ± 2	22 ± 1	1.4 ± 0.1	3.1 ± 0.2	30 ± 5	6.7 ± 0.3	0.49 ± 0.02	n.d.	0.26 ± 0.02
5 R_R	2295 ± 119	453 ± 182	1.7 ± 0.7	1.6 ± 0.7	26 ± 1	32 ± 2	1.8 ± 0.1	2.3 ± 0.1	25 ± 4	4.9 ± 0.3	0.59 ± 0.12	n.d.	0.24 ± 0.04
1 RH_R	6134 ± 284	1407 ± 237	24.8 ± 7.7	1.7 ± 0.9	159 ± 7	747 ± 43	0.9 ± 0.3	3.1 ± 0.3	32 ± 3	1.3 ± 0.1	2.89 ± 0.15	5 ± 1	4.04 ± 0.18
2 RH_R	5088 ± 320	1727 ± 284	11.6 ± 2.8	1.0 ± 0.2	155 ± 8	601 ± 32	0.8 ± 0.4	2.2 ± 0.1	38 ± 8	4.8 ± 0.3	4.24 ± 0.56	5 ± 1	1.04 ± 0.12
3 RH_R	5474 ± 273	2165 ± 284	6.8 ± 0.7	0.8 ± 0.1	263 ± 12	589 ± 26	0.5 ± 0.1	2.4 ± 0.1	34 ± 2	1.8 ± 0.4	5.63 ± 0.26	8 ± 2	0.76 ± 0.05
4 RH_R	4866 ± 214	1367 ± 113	11.4 ± 0.7	43.3 ± 2.3	398 ± 18	957 ± 50	38.0 ± 1.9	2.9 ± 0.2	33 ± 3	9.2 ± 0.4	3.13 ± 0.19	14 ± 1	1.05 ± 0.07
5 RH_R	5930 ± 341	1441 ± 220	42.7 ± 11.5	8.4 ± 0.5	232 ± 10	918 ± 167	13.0 ± 0.6	2.7 ± 0.8	33 ± 4	7.1 ± 0.3	3.62 ± 0.23	6 ± 1	0.87 ± 0.34

TABLE 6: Descriptive statistics results of elemental chemical analysis for rice and rice husk from Korba and Raipur.

	K	Ca	Ti	Cr	Mn	Fe	Ni	Cu	Zn	Rb	Sr	Ba	Pb
Korba													
Rice													
Mean	2291.61	223.52	1.71	0.00	31.19	17.25	0.85	2.61	28.92	17.24	0.43	n.d.	0.25
SD	495.62	32.67	1.41	0.00	7.63	3.14	0.67	0.36	6.64	12.79	0.16	n.d.	0.17
Min	1603.61	175.06	0.47	0.00	23.97	13.20	0.39	2.22	22.18	4.18	0.29	n.d.	0.08
Max	2910.56	2671.3	4.02	0.00	43.67	20.86	2.01	3.00	39.09	35.19	0.67	n.d.	0.51
RH													
Mean	3709.19	1256.24	15.67	0.32	225.62	188.03	1.62	2.01	29.49	17.85	3.41	25.62	0.61
SD	839.90	245.48	24.83	0.09	57.67	130.03	1.22	0.13	3.22	10.18	1.14	6.45	0.26
Min	2277.06	947.76	2.30	0.00	174.33	92.74	0.62	1.85	25.87	3.69	2.24	15.40	0.41
Max	4440.80	1499.97	59.92	0.90	325.00	408.97	3.25	2.17	33.31	28.69	4.76	31.96	1.02
Raipur													
Rice													
Mean	2515.78	354.45	2.09	0.47	26.85	24.73	0.88	2.56	27.07	3.29	0.46	n.d.	0.34
SD	323.75	81.34	0.88	0.11	6.91	8.24	0.66	0.71	5.09	2.56	0.12	n.d.	0.09
Min	2200.82	231.92	0.84	0.00	19.66	12.67	0.22	1.66	19.09	0.58	0.31	n.d.	0.24
Max	3020.55	452.90	3.24	1.60	34.50	32.61	1.77	3.44	31.36	6.69	0.59	n.d.	0.45
RH													
Mean	5498.53	1621.25	19.48	11.02	241.33	762.37	10.64	2.66	34.12	4.84	3.90	7.67	1.55
SD	538.45	335.42	14.63	18.30	99.08	172.01	6.21	0.35	2.13	3.39	1.09	3.86	1.39
Min	4866.02	1366.79	6.83	0.80	155.14	588.74	0.52	2.19	32.18	1.31	2.89	4.67	0.76
Max	6134.38	2165.07	42.73	43.26	397.79	956.78	38.05	3.08	37.65	9.21	5.63	14.17	4.04

concentration in soil. The variation observed in TFs for the same species may be due to several factors such as the age of the plant, the tissue, and the environment in which the plant is grown. It was demonstrated that the absorption of minerals and their distribution in the plant hang on the bioavailability of the minerals in soil, root structure, and shoot system [32]. Moreover, the bioavailability of elements from soil to plants is determined by other factors including pH, redox conditions, speciation, soil texture and mineralogy, organic matter content, and the presence of competing ions.

TFs calculated for rice and RH using the average values of elemental concentration in rice, RH, and soils of Korba and Raipur are shown in Figure 4. In our study, TFs for RH were always higher than rice samples for both the studied areas. TFs of K, Mn, Cu, Zn, Rb, and Ba are higher in Korba samples compared to those of Raipur. Elements such as Ca and Cr show TFs higher in Raipur samples, while Ti, Fe, Ni, and Pb were in the same range. Our results clearly show that the bioaccumulation is higher in RH than in rice:

$$TF = \frac{C_p}{C_s} \quad (1)$$

A comparison with the literature data [33] for the content of As, Ba, Cu, Pb, Ni, Mn, and Cr in rice is reported in Table 7. The average values, calculated as the arithmetic mean, for Korba and Raipur are reported separately. The literature reports that geometric means (GM) illustrate more exact distribution of the element concentrations in rice samples, but comparison with many other studies is difficult due to the lack of information on GM [33]. As and Ba are not present

FIGURE 4: Transfer factors calculated for rice and rice husk samples with respect to soil samples from Korba and Raipur.

in our samples. Our values of Cu and Ni are aligned mainly with those from Vietnam. The concentrations of Pb and Mn are aligned, respectively, with commercial rice from China

TABLE 7: Concentration of hazardous elements in rice samples reported in different literature studies: (a) arithmetic means; (b) arithmetic standard deviations; (c) [34]; (d) [35]; and (e) [36].

Element	Area	N	AM (a)	ASD (b)	MIN	MAX
Cu	Taizhou	13	4260	826	3037	5184
	Commercial rice, China	5	3326	774	2812	4478
	Vietnam (c)	31	2600	—	1100	5800
	Bangladesh (d)	—	—	—	—	—
	Hangzhou (e)	—	—	—	—	—
	Raipur	5	2560	710	1662	3438
	Korba	5	2610	360	2222	2995
Pb	Taizhou	13	2042	2070	256	2602
	Commercial rice, China	4	356	267	167	745
	Vietnam (c)	—	—	—	—	—
	Bangladesh (d)	3	2370.0	1980.0	2010.0	2400.0
	Hangzhou (e)	5	131	103	45	308
	Raipur	5	340	90	235	452
	Korba	5	250	170	78	514
Ni	Taizhou	13	761	391	339	1134
	Commercial rice, China	4	476	276	201	818
	Vietnam (c)	31	869	—	<100	2022
	Bangladesh (d)	—	—	—	—	—
	Hangzhou (e)	—	—	—	—	—
	Raipur	5	880	660	216	1770
	Korba	5	850	670	387	2009
Mn	Taizhou	13	28640	5570	21977	37490
	Commercial rice, China	4	9363	3288	5804	12708
	Vietnam (c)	31	9900	—	5900	16300
	Bangladesh (d)	—	—	—	—	—
	Hangzhou (e)	—	—	—	—	—
	Raipur	5	2685	6910	19700	34500
	Korba	5	31200	7600	24000	43700
Cr	Taizhou	13	107	83	6	279
	Commercial rice, China	4	199	157	62	424
	Vietnam (c)	—	—	—	—	—
	Bangladesh (d)	3	740	340	650	830
	Hangzhou (e)	—	—	—	—	—
	Raipur	5	470	110	0	1600
	Korba	5	n.d.	n.d.	n.d.	n.d.

and Taizhou. The content of Cr in the samples of Raipur is exceptionally high.

Despite all the reported data of metal content in rice, according to the national standard for safety milled rice criteria [37] (NY5115-2002), the maximum allowable concentrations (MAC) of As and Pb are 0.50 and 0.20 $\mu\text{g/g}$, respectively. Moreover, the World Health Organization (WHO) provides 0.20 mg/Kg as the safe limit for Pb in rice [38], but it does not report any limit for other analyzed metals. In the present study, Pb concentration is much higher than the reported limit in many samples both from Raipur and Korba, even if the average value is aligned with that of WHO. Even it is known as a toxic element, Cr safe limit from WHO/FAO is

not determined. Since rice is the common food for the Asian continent and especially in China, the MAC criteria determine the same limit for some metals such as Cu 10 mg/Kg, Zn 50 mg/Kg, Cr 1 mg/Kg, and Pb as that decided by WHO [39].

Statistical analysis does not show any significant difference between rice and rice husk samples of the two areas of interest.

Figure 5 shows the concentration of selected elements in all samples, classified by species: soil, rice husk, and rice. This figure highlights the possible transfer and/or accumulation of elements from soil into the other two matrices. In some cases, rice husk seems to act as a barrier for some heavy metals such

FIGURE 5: Concentration of elements in soil, rice husk, and rice samples from Korba and Raipur.

as Cr, K, Fe, and Pb. The possible barrier role of rice husk is interesting, and it can be hypothesized also for Mn, Ba, and Sr. Unfortunately, it is not clear in the case of Cu, Ni, Zn, Rb, Bi, Ti, and V.

4. Conclusions

This work reports the chemical composition study of soils, rice, and rice husk, from Korba and Raipur (India), by means

of TXRF. Results show some metals uptake from soil to rice, in particular Pb and Cr from the Raipur region. The novelty of this study is the chemical characterization of rice, made in parallel with the analysis of soils and corresponding rice husk. A detailed analysis of all the data shows that rice husk accumulates more heavy metals than rice, suggesting a possible barrier effect of the husk. Despite that, dedicated studies should be done to verify the clear role of husk and other parameters, such as rice species, soils characteristics (pH, clay content, and organic matter), and other variables. Based on the extremely interesting results obtained in this study, some approaches may be developed to promote low metals accumulation in rice.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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