Energy-Dispersive X-ray (EDX) fluorescence based analysis of heavy metals in marble powder, paddy soil and rice (Oryza sativa L.) with potential health risks in District Malakand, Khyber Pakhtunkhwa, Pakistan

Asghar Khan*, Muhammad Saleem Khan*, Fazal Hadi*, Ghulam Saddiq* and Abdul Naeem Khan*

*Department of Botany, Islamia College Peshawar, Pakistan; **Department of Biotechnology, University of Malakand, Malakand, Pakistan; ***Department of Physics, Islamia College Peshawar, Peshawar, Pakistan; ****National Center of Excellence in Physical Chemistry, University of Peshawar, Peshawar, Pakistan

ABSTRACT

Rice is staple food of Asian countries including Pakistan. Contamination of paddyfields with marble waste containing toxic metals has emerged as a key public health concern. Current study aimed to analyze heavy metal concentrations in marble powder, paddy soil and rice crop to estimate probable human health risks in District Malakand of Pakistan. Triplicate dry samples were analyzed through Energy Dispersive X-ray Fluorescence spectroscopy (ED-XRF). The marble waste increased the concentration of metals in paddy soil, subsequent increase in metals accumulation was found in rice grains. In grains the maximum concentration (mg/kg) of Fe (50.70), Cu (17.60), Mn (7.49) and Al (6.80) exceeded the permissible limits of FAO/WHO. The cumulative hazard index (HI) value from heavy metals through consumption of rice was greater than unity (HI > 1) indicating potential health risks. The results of Pearson correlation, Principal component analysis (PCA), and cluster analysis (CA) for metals were consistent.

INTRODUCTION

Urbanization and rapid growth of the industrial sector introduce a mass of contaminants into the environment that causes severe heavy metal (HM) pollution in soil, disruption in the geochemical cycle of ecosystem, and adversely affect human health [1,2]. Globally, millions of tons of marble waste are produced daily in marble quarrying and processing units comprise of fine powder and fragmented rocks which is dumped in roads, riverbeds, empty pits, agriculture land that causes a wide range of environmental pollution [3,4]. Dispersion of particulate matter from marble quarries and processing units causes widespread accumulation of Magnesium and Calcium compounds in different media of the earth systems significantly affects the quality of water, air, soil and biodiversity [5,6].

Heavy metals contamination of water, soil and food crops emerged as a critical global concern having detrimental influences on plant growth, food safety and water purification [7]. Heavy metals accumulate in food chain through the application of agrochemicals, organic and inorganic manures, sewage, and industrial wastewater are used for higher agricultural yield [8]. Metals like zinc (Zn) and copper (Cu) are essential for enzymatic activities and have DNA binding domains [9]. However, the majority of heavy metals enter the food chain, bioaccumulate, and induces cancers and various diseases by the mechanism of production of reactive oxygen species led to oxidative stress, endocrine disruption, carcinogenicity, neurotoxicity, genomic instability, impaired psycho-social behavior, and immunological problems [10–12]. Heavy metals are detrimental for their high bioaccumulation potential, long half-lives, and non-biodegradable nature [13]. Heavy metal (HM) contamination in rice has mostly come from the soil in which it is cultivated [14]. Unfortunately, the industrial sector in Pakistan produces about 1.309 × 10^9 m^3 wastewater annually and discharge into freshwater resources or agricultural land that cause contamination of the water bodies [15,16]. Hence, the farmers in the country are reluctant to use contaminated water to meet the water requirement of the crops [17]. So, it is essential to know the possible risks to human health by studying heavy metals buildup in soil-rice systems [18].

Energy-dispersive X-ray fluorescence spectroscopy (ED-XRF) is a rapid, non-destructive, and easy handling analytical technique widely used for fast mineral analysis in the cement industry, archeology, mining, geology, forensic and food sciences [19–21]. ED-XRF has a specific, multi-elemental detection capacity that involves no sample pre-treatment. It is an alternative to the traditional atomic spectroscopic methods being time-consuming that requires highly skilled staff for...
digestion of the sample with toxic reagents and daily calibration of the instrument using a standard solution for routine analysis. Moreover, EDXRF is a powerful green technology that quickly results and makes data analysis effectively [19,22–25]. The instrumental analysis worked on the principle that each element emits secondary ‘fluorescent’ X-rays of typical energy when exposed to X-rays of appropriately high quanta from an X-ray tube. The energy with the intensity of these emitted X-rays is measured and used for the determination of elemental composition and its concentration in the sample through the detection system [26,27]. Generally, elements with higher atomic weight required higher energy for fluorescence emission and subsequently higher energy of fluorescence easily detects fluorescence. The elemental concentration in the analytical sample is estimated by calibration standards that are used to correlate the intensity of emitted X-ray for each element with its previously known concentration already detected via ICP-OES [21,28]. The current study aimed (i) to analyze essential and toxic elements of marble waste powder, and their subsequent accumulation in paddy soil and rice plants (ii) to determine the potential sources of elements in paddy soil, and rice plants through multivariate statistical techniques (iii) and to assess the potential human health-related risks for the local population via the dietary intake of rice grains.

Materials and methods

Study area

Malakand is the gateway to District Swat, Dir, Chitral, and ex-federally administered tribal areas (Bajaur, Mohmand) which are most famous for tourist spots. District Malakand occupies a total of 952 Km² area with a population density of 475 people/Km² [29]. Precious mineral reserves such as Malakand granite, Dargai chromite, marble, mica, quartz, and other valuable mineral resources have been reported in various geographical points at District Malakand [30]. Malakand is a major rice-producing district in Khyber Pakhtunkhwa ranked 4th in terms of rice production. The total irrigated paddy land in district Malakand in 2016–17 was 4991 hectares and produced 10,773 tons during the same year [31,32]. The current research study was conducted near the marble industrial area located between Batkhela and Thana village of district Malakand as presented in (Figure 1). The marble

Figure 1. Pictorial representation of sampling sites of the study area of District Malakand, Pakistan.
industrial effluents contain harmful compounds, toxic metals, and suspended solids, which are non-biodegradable in nature [33]. Discharge of these untreated marble industry effluents to water bodies and agricultural land causes water and soil pollution [16].

**Sampling of marble industry powder**

The sampling of marble powder, paddy soil, and rice crop were carried out during Aug-Dec 2019. The dried marble powder was collected in triplicate (each with 0.25 kg) from nine marble/granite processing plants adjacent to paddy fields, and kept in labeled, clean polythene bags, and were brought to the laboratory of Botany Department Islamia College Peshawar for further analysis. The collected powder sample from at least three marble industry was then combined, thoroughly mixed, sieved with 2 mm mesh to obtain a composite sample of each with 2.2 kg [34]. For analysis of multi-elements in marble powder through (EDXRF-7000), a total of nine (09) samples were prepared and stored in labeled clean polythene bags.

**Rice and paddy soil sampling**

Rice plants at the reproductive stage were uprooted in triplicate along with soil (0.5 kg) at a depth of 0–20 Cm using steel shovel from the three sites (i) Upstream sites: unpolluted, located 400 meters away from the marble industry taken as control (ii) industrial sites: where marble dust and effluents were directly discharged into paddy fields (iii) Downstream site: located 400 meters behind of marble factories where effluents of all marble factories were collected and used directly for irrigation of the paddy crop [35]. The soil particles were removed on the spot from the roots of rice plants. The collected samples of both soil and rice plants were kept in separate, labeled, clean polythene bags and brought to the laboratory of Botany Department Islamia College Peshawar.

**Preparation of soil and rice plant samples**

The soil samples were mechanically ground, air-dried, and passed through a sieve up to 2 mm, and stored in labeled polythene bags at ambient temperature for further analysis [36]. The rice plants were washed three times with tap water and rinsed with distilled water to remove soil and airborne pollutants. The surface water was absorbed through Whatman filter paper no. 42. The rice plant tissues such as roots, straws, leaves, and panicles were separated and oven-dried at 70°C for 24 hours to remove moisture content [37]. Each rice grain from its outer shell was separated manually. Through an electric grinder, the rice plant tissues such as root, straw, leaves, and grains were ground into a fine powder. A composite sample of the root, straw and leaves powder were prepared. All the samples including rice grains were stored in labelled clean polythene bags for multi-elemental analysis.

**Energy dispersive X-ray fluorescence analysis**

Prepared samples of marble powder, soil, and rice plant tissues were transported to the Centralized Resource Laboratory (CRL), University of Peshawar. The samples were quantified using energy dispersive X-ray fluorescence spectrometer (EDX-7000, Na-U, Shimadzu, Japan) with loose powder method, calibration with Al-Cu standard [38–40]. One-gram powder from the samples of marble, paddy soil, and rice plant in replication of three were placed over a thin film lined a 10 mL Polypropylene cup and then mounted inside the EDX-7000 spectrometer [41]. The instrument is equipped with an X-ray tube using Rhodium (Rh) target and a high-performance silicon drift detector (SDD), operated with a maximum of 50 kV and 1000 μA and a PCEDX-Navi software. The elemental composition of all samples was detected under an air-based atmosphere. The analytes were then assessed with a collimator of 10 mm in diameter with a live acquisition time of the 60s [40,42].

**Health risks assessment**

**Estimated daily intake (EDI) of Heavy metals through consumption of rice**

The potential health risks via consumption of contaminated rice grains with heavy metals were assessed by using the following equation adopted by [43,44].

$$\text{EDI} = \frac{C_{\text{metal}} \times IR}{BW}$$  

(1)

Where EDI is the estimated daily dose (mg/kg/person/day)

- $C_{\text{metal}}$ is the concentration of metal in rice grains (mg/kg dry mass)
- IR is the daily ingestion rate of rice which is 0.120 kg/person/day [45]
- BW is the average body weight which is 73.3 Kg [46]

**Hazard quotient (HQ)**

The hazard quotient is a ratio of the estimated daily intake (EDI) and reference dose (RfD). HQ value less than one indicates no health risk whereas an HQ > one demonstrates detrimental health risk and can be calculated by following [44].

$$\text{HQ} = \frac{\text{EDI}}{\text{RfD}}$$  

(2)
The oral reference doses (RfD) value for Al, Cr, Cu, Fe, Mn, Ni, and Zn are 1.00, 0.003, 0.04, 0.7, 0.14,0.02, and 0.3 mg/kg/day respectively [47–49].

Hazard index (HI)
Hazard index (HI) was used for the estimation of overall non-carcinogenic human health risks via the consumption of multiple elements in food crops [50]. The hazard index (HI) is the sum of the hazard quotients and can be calculated as follows

\[ HI = \sum_{n=1}^{n} (THQ) n \]  

Whereas HI less <1.0, indicate negligible noncarcino- genic adverse effect due to the exposure pathway.

Statistical analysis
Descriptive statistics such as mean, standard deviation, standard error of mean, minimum, and maximum were calculated for the elements present in marble powder, paddy soil, and rice plant using Excel software 2016. For finding an association between metals and their potential sources in marble powder, soil, and rice plant, Pearson correlation, Principal component analysis (PCA), and Cluster analysis (CA) were carried using a statistical software package, SPSS Version 25. Pearson correlation, a bivariate correlation used to calculate pairwise relationships for a set of variables and is helpful for the determination of the strength and direction of the relationship between two variables [51]. The principal component analysis is designed for the transformation of the original variables into new (uncorrelated) variables called principal component. In the PCA the principal component that is eigenvalue (>1) was extracted whereas factor analysis was performed with varimax rotation with Kaiser normalization method [42,52]. Cluster analysis (CA) is adopted for the classification of metals into groups on a similarity basis so that similar metals come together in the same class for variable space [53]. Before the execution of cluster analysis, the raw data was standardized with the Z score. The cluster analysis (CA) was performed with dendrogram using Wards algorithmic method [52].

Results and discussions
Quantification of heavy metals in marble industry powder, paddy soil and rice plants
A total of sixteen elements were quantified for marble powder and paddy soil including eleven elements for rice plants and its grains through the energy-dispersive x-ray fluorescence (ED-XRF) analysis (Tables 1, 2).

Heavy metals concentrations in marble industry powder
Table 1(a) showed mean highest concentrations (mg/kg) for Ca (759.3 ± 110.6) followed by Si (324.4 ± 53.6), Fe (111.9 ± 18.0), Al (90.5 ± 4.0), K (486.6 ± 9.9) and Ti (16.9 ± 3.6) respectively. Concentrations of Mn and Vanadium (V) was maximum with mean values of (5.2 ± 1.9 mg/kg) and (3.8 ± 1.0 mg/kg). Mean metal contents for Strontium (Sr), Chromium (Cr), Nickel (Ni) and Rubidium (Rb) were found to be (3.4 ± 2.0 mg/kg), (3.3 ± 1.3 mg/kg), (3.1 ± 1.4 mg/kg), and (3.0 ± 2.4 mg/kg), respectively. Similarly, mean level for Zr (2.5 ± 0.7 mg/kg), Zn (2.3 ± 1.6 mg/kg), Cu (2.3 ± 1.6 mg/kg), and Y (2.2 ± 1.4 mg/kg). The essential and trace heavy metals in marble powder were found to be in the order of Ca > Si > Fe > Al > K > Ti > Mn > V > Sr > Cr > Ni > Rb > Zr > Zn > Cu > Y. In a similar study [16] reported heavy metal level in marble stones of District Buner, Pakistan with mean values of Fe (125.0 µg/g), Pb (1.12 µg/g), Mn (0.98 µg/g), Zn (0.29 µg/g), Cr (0.26 µg/g), Cu (0.22 µg/g) and Ni (0.06 µg/g) respectively. Therefore, strongly support our current results. Moreover, in current study the concentrations of essential and trace metals in marble industry powder were within the permissible limits of world average shale value proposed by [54,55]. It was further reported that in marble processing plants, dust and effluents from crushing of the marble stone were released into the surroundings that contain heavy metals which is a major possible source of water and soil pollution [3,56].

Heavy metals content level in paddy soil
Concentrations of essential and trace heavy metals of the selected paddy soil sites (Figure 1) were summarized in (Table 1(b)). Among macronutrients, mean maximum concentration was observed for Ca (413.0 ± 65.5 mg/kg) at downstream followed by K (52.3 ± 12.5 mg/kg) at upstream (Table 1(b)). According to (Ali et al., 36) macronutrients exist in higher proportions in the upper horizons of the earth core are comprised of main elements in parent rock. Moreover, these elements are vital for plant growth due to its mobile nature, transformed easily by liberating cations and insignificantly change soil pH and are commonly not categorized as hazardous elements. The concentrations of Ca and K in current soil samples was found lower than the average world shale values reported by [54]. In other study [57] also reported a higher concentration of Ca (36,675.5 mg/kg), K (18,927 mg/kg) in soil sample of Peshawar valley Pakistan [42]. reported an average higher Ca and K level for the soil of Chhattisgarh (India), suggests a higher volume of Ca and K in earth crust. The heavy metal distribution in paddy soil was found to be in the
| Pollutants | Unit-I Alif sons, Azan, Makkah Mean | Min SD | Max SE | Mean Min | SD SE | Max Min | SD SE | Mean Min | SD SE | Max Min | SD SE | Mean Min | SD SE | Max Min | SD SE | Mean Min | SD SE | Max Min | SD SE |
|-----------|-----------------------------------|-------|-------|----------|--------|--------|--------|--------|----------|--------|--------|--------|----------|--------|--------|--------|----------|--------|--------|--------|
| Cr        | 0.40                              | 0.30  | 0.50  | 0.60     | 0.40  | 0.30  | 0.50  | 0.60  | 0.40     | 0.30  | 0.50  | 0.60  | 0.40     | 0.30  | 0.50  | 0.60  | 0.40     | 0.30  | 0.50  | 0.60  |
| Ni        | 31.10                             | 22.70 | 48.00 | 7.30     | 4.00  | 23.40 | 35.30 | 100.40 | 100.40   | 100.40 | 100.40 | 100.40 | 100.40   | 100.40 | 100.40 | 100.40 | 100.40   | 100.40 | 100.40 | 100.40 |
| Mn        | 5.20                              | 1.40  | 5.20  | 5.20     | 1.40  | 5.20  | 1.40  | 5.20  | 1.40     | 5.20  | 1.40  | 5.20  | 1.40     | 5.20  | 1.40  | 5.20  | 1.40     | 5.20  | 1.40  | 5.20  |
| K         | 1.10                              | 1.10  | 1.10  | 1.10     | 1.10  | 1.10  | 1.10  | 1.10  | 1.10     | 1.10  | 1.10  | 1.10  | 1.10     | 1.10  | 1.10  | 1.10  | 1.10     | 1.10  | 1.10  | 1.10  |
| Fe        | 26.50                             | 6.20  | 18.00 | 11.90    | 2.20  | 40.80 | 38.60 | 24.60  | 24.60    | 24.60  | 24.60  | 24.60  | 24.60    | 24.60  | 24.60  | 24.60  | 24.60    | 24.60  | 24.60  | 24.60  |
| Cu        | 2.80                              | 1.90  | 1.90  | 1.90     | 1.90  | 1.90  | 1.90  | 1.90  | 1.90     | 1.90  | 1.90  | 1.90  | 1.90     | 1.90  | 1.90  | 1.90  | 1.90     | 1.90  | 1.90  | 1.90  |
| K         | 1.40                              | 1.00  | 1.40  | 1.40     | 1.00  | 1.40  | 1.00  | 1.40  | 1.00     | 1.40  | 1.00  | 1.40  | 1.00     | 1.40  | 1.00  | 1.40  | 1.00     | 1.40  | 1.00  | 1.40  |
| Sr        | 1.70                              | 1.00  | 1.70  | 1.70     | 1.00  | 1.70  | 1.00  | 1.70  | 1.00     | 1.70  | 1.00  | 1.70  | 1.00     | 1.70  | 1.00  | 1.70  | 1.00     | 1.70  | 1.00  | 1.70  |
| Ti        | 1.30                              | 1.50  | 1.30  | 1.30     | 1.50  | 1.30  | 1.50  | 1.30  | 1.50     | 1.30  | 1.50  | 1.30  | 1.50     | 1.30  | 1.50  | 1.30  | 1.50     | 1.30  | 1.50  | 1.30  |
| V         | 1.40                              | 1.50  | 1.40  | 1.50     | 1.40  | 1.50  | 1.40  | 1.50  | 1.40     | 1.50  | 1.40  | 1.50  | 1.40     | 1.50  | 1.40  | 1.50  | 1.40     | 1.50  | 1.40  | 1.50  |
| Y         | 1.40                              | 3.70  | 1.40  | 3.70     | 1.40  | 3.70  | 1.40  | 3.70  | 1.40     | 3.70  | 1.40  | 3.70  | 1.40     | 3.70  | 1.40  | 3.70  | 1.40     | 3.70  | 1.40  | 3.70  |
| Zn        | 0.70                              | 0.50  | 0.70  | 0.50     | 0.70  | 0.50  | 0.70  | 0.50  | 0.70     | 0.50  | 0.70  | 0.50  | 0.70     | 0.50  | 0.70  | 0.50  | 0.70     | 0.50  | 0.70  | 0.50  |
| Zr        | 0.10                              | 0.60  | 0.10  | 0.60     | 0.10  | 0.60  | 0.10  | 0.60  | 0.10     | 0.60  | 0.10  | 0.60  | 0.10     | 0.60  | 0.10  | 0.60  | 0.10     | 0.60  | 0.10  | 0.60  |

Table 1. Heavy metal concentrations (mg/kg) of the various marble processing units (a) and paddy soil (b) of District Malakand (n = 09).

(a) Marble processing units

Statistic: Mean, SD, Min, Max

(b) Soil

Statistic: Mean, SD, Min, Max

Average shale value (mg/kg)

80,000 22,100 90 45 47,200 26,600 850 68 140 73,000 300 4600 130 26 95 160

Average shale values were taken as background concentration for metals as proposed by 54.
order of $\text{Si} > \text{Fe} > \text{Al} > \text{Ti} > \text{Mn} > \text{Sr} > \text{Zr} > \text{Zn} > \text{Cu} > \text{Ni} > \text{V} > \text{Nb} > \text{Y} > \text{Cr}$. The data presented in (Table 1b) obviously demonstrated mean higher concentration for $\text{Fe} (146.7 \pm 15.3 \text{ mg/kg})$, $\text{Al} (125.0 \pm 18.0 \text{ mg/kg})$, $\text{Ti} (42.3 \pm 11.2 \text{ mg/kg})$, $\text{Mn} (3.63 \pm 0.70, \text{ mg/kg})$ $\text{Sr} (3.17 \pm 1.04 \text{ mg/kg})$, $\text{Zr} (3.03 \pm 1.27 \text{ mg/kg})$, $\text{Zn} (2.60 \pm 0.85 \text{ mg/kg})$, $\text{Cu} (2.50 \pm 1.32 \text{ mg/kg})$, $\text{Ni} (2.2 \pm 1.47 \text{ mg/kg})$, $\text{V} (2.13 \pm 1.10 \text{ mg/kg})$, $\text{Nb} (2.03 \pm 1.27 \text{ mg/kg})$, $\text{Y} (2.0 \pm 1.32 \text{ mg/kg})$ and $\text{Cr} (1.86 \pm 1.57 \text{ mg/kg})$ at downstream. The main reason for the elevated mean metal/metalloids contents at the downstream paddy soil is due to the buildup of marble industry effluents at this site [16,35]. However, the mean highest concentration of $\text{Si} (514.7 \pm 31.1 \text{ mg/kg})$ in upstream soil may be due to the weathering of river sediments and usage of river hull residues [58,59]. The contents of $\text{Cr} (1.86 \text{ mg/kg})$, $\text{Cu} (2.50 \text{ mg/kg})$, $\text{Ni} (2.2 \text{ mg/kg})$, and $\text{Zn} (2.60 \text{ mg/kg})$ in the paddy soil near the marble industry was relatively higher than the adjacent agricultural fields as reported by [11] for $\text{Cr} (0.48 \text{ mg/kg})$, $\text{Cu} (1.48 \text{ mg/kg})$, $\text{Ni} (0.50 \text{ mg/kg})$ and $\text{Zn} (0.414 \text{ mg/kg})$. In another study [11] reported higher metal contents of $\text{Cr} (724 \text{ mg/kg})$, $\text{Cu} (55.64 \text{ mg/kg})$, $\text{Fe} (23,720 \text{ mg/kg})$, $\text{Mn} (760 \text{ mg/kg})$, $\text{Ni} (406 \text{ mg/kg})$ and $\text{Zn} (44.74 \text{ mg/kg})$ in nearby mining affected soil of district Malakand [60]. also reported a mean higher level of $\text{Cr} (19.3 \text{ mg/kg})$, $\text{Ni} (21.8 \text{ mg/kg})$, $\text{Cd} (1.4 \text{ mg/kg})$, $\text{Pb} 22.7 \text{ mg/kg}$ in fish collected from river swat that irrigate most the paddy fields in study area. The literature study revealed that mining activities significantly affect the profile of agricultural lands of the study area [61].

Heavy metal content level in rice plants and rice grains

Mean concentrations of essential and trace elements of rice crop raised in vicinity of the marble industry were summarized in (Table 2). Mean concentration of $\text{K} (370.9 \pm 178.6 \text{ mg/kg})$ and $\text{Ca} (181.1 \pm 126.2 \text{ mg/kg})$ was found higher in rice plant samples collected from marble industry and downstream sites. Proportion of $\text{Si} (355.1 \pm 130 \text{ mg/kg})$, $\text{Fe} (126.4 \pm 208.7 \text{ mg/kg})$, $\text{Cu} (3.86 \pm 3.30 \text{ mg/kg})$, $\text{Cr} (3.15 \pm 1.46)$, $\text{Zn} (1.182 \pm 0.625 \text{ mg/kg})$, $\text{Rb} (0.42 \pm 0.37 \text{ mg/kg})$ and $\text{Ni} (0.89 \pm 0.06)$ was maximum in rice plant samples of the downstream and marble industry sites (Table 2a). $\text{Al}$ and $\text{Mn}$ showed mean higher concentration of $(43.1 \pm 18.90 \text{ mg/kg})$ and $\text{Mn} (11.39 \pm 6.51 \text{ mg/kg})$ in rice plant samples collected from upstream site (Table 2a). In case of the rice grains mean higher concentration for $\text{K} (441.9 \pm 6.60 \text{ mg/kg})$, $\text{Fe} (50.7 \pm 9.79 \text{ mg/kg})$, $\text{Cu} (17.6 \pm 1.05)$, $\text{Mn} (7.49 \pm 2.21 \text{ mg/kg})$, $\text{Al} (6.80 \pm 0.90)$, $\text{Zn} (4.96 \pm 3.43 \text{ mg/kg})$, $\text{Rb} (4.56 \pm 2.18 \text{ mg/kg})$, $\text{Ni} (0.90 \pm 0.08)$ and $\text{Cr} (0.70 \pm 0.10)$ was reported at the downstream site respectively (Table 2b). Mean maximum concentration for $\text{Ca} (297.4 \pm 4.90 \text{ mg/kg})$ in rice
grains was recorded near marble industry site (Table 2b). In rice grains mean maximum concentrations of Fe (50.7 ± 9.80 mg/kg), Cu (17.6 ± 1.05 mg/kg), Mn (7.49 ± 2.21 mg/kg) and Al (6.80 ± 0.90 mg/kg) exceeded than the permissible limits of 17, 3.0, 5.0 and 1.0 mg/kg set by [62] (Table 2b). Mean elevated concentration of Ca (297.4 ± 4.90 mg/kg), K (441.9 ± 6.60 mg/kg), Zn (4.96 ± 3.43 mg/kg), Ni (0.90 ± 0.08 mg/kg) and Cr (0.70 ± 0.10) in rice grains were within the respective permissible limits of [62] which is (1000 mg/kg for Ca), (3500 for K, 20 for Zn), (10 mg/kg for Ni), and (2.3 mg/kg for Cr) respectively (Table 2b). Silicon (Si) showed mean higher content of (355.1 ± 130 mg/kg) in rice plants while in grains accumulation of Si was not observed from respective study sites (Table 2a, b).

According to [64] potential mineral uptake of plant is a function of mineral contents in soil, its cation exchange capacity, pH, content of organic matter, age, and genetic makeup of the plants [65]. reported that elevated levels of K and Ca in the rice plants and rice grains are possibly owing to the statistics that such elements are extremely mobile and easily translocated among the plant tissues. According to [66] higher Ca and K concentrations may be due to the utilization of organic and inorganic fertilizers rich in these minerals. Our current results are supported by the study of [11] who observed a lower background concentration for Cu (0.19 mg/kg), Mn (0.44 mg/kg) and Zn (0.13 mg/kg) in rice plants of adjacent area without the influence of marble industry. Likewise [67], also reported comparatively mean lower concentration of Zn (1.9 mg/kg), Mn (1.6 mg/kg), Fe (1.4 mg/kg) and Cu (0.2 mg/kg) in Malagasy rice species. A slightly elevated level of Cu (4.9 mg/kg) in Chinese rice near the electroplating plant was reported by [68]. [69] reported a higher concentration of Cu (25 ppm), Zn (19 ppm), and Cr (14 ppm) in rice grains irrigated by paper mills effluents in Karnataka, India. A relative mean higher content of Fe (2525.364 mg/kg) and Cu (10.4 mg/kg) was investigated by [70] in rice plants cultivated near Tajan river. The literature study revealed that the accumulation of metals in edible tissues of rice is due to the cultivation of crops on or near polluted soils [15]. Moreover, the elevated level of K, Ca, Fe, and Mn in the media like soil, plant, grains represented their origin of twins, bioavailability and influence its order in the media [71,72]. reported that the mobility of metals from anthropogenic sources is comparatively more than lithogenic or pedogenic ones. In current study except Si and K, concentrations of the remaining metals in paddy soil near marble industry and downstream were comparatively higher than the upstream site (Table 1b). Therefore, resulted higher metal concentration in rice plants and its grains of the respective study sites (Table 2a, b)).

### Potential Human Health Risk Assessment through consumption of rice

Rice is one of the most stable staple foods in most countries consumed in routines in households, and especially in wedding functions in Pakistan [73]. For the assessment of health risks owing to pollutants, estimation of exposure level is mandatory through quantification of the exposure routes of a toxin to a target organism [74]. Many pathways like inhalation, ingestion, dermal contact led to human exposure to toxic metals. However, consumption of rice has been recognized as one of the main pathways of toxic metals that trigger harm to human health [69]. To evaluate the potential human health risk, the EDI, HQ and HI of the eight elements (Al, Cr, Cu, Fe, Mn, Ni, Rb, Zn) were evaluated according to its average concentration in rice followed by the respective consumption rate in adults (Table 3(a, b)).

### Estimation of daily intake (EDI) (mg/ kg/person/day)

Estimated daily intake is a common index used for transfer of metal from plants to human [75]. (Table 3a) showed estimated daily intake (EDI) of the trace elements through consumption of rice for adults. The average daily consumption of rice in Pakistan is 0.120 kg/person/day [45]. The average estimated daily intake (EDI) were in the order of Fe (8.29E-02) > Cu (2.88E-02) > Mn (1.23E-02) > Al (1.12E-02) > Zn (8.11E-03) > Rb (7.46E-03) > Cr (1.22E-03) > Ni (1.48E-03) mg/kg/person/day respectively (Table 3a). It was observed that the EDI of the eight elements (Al, Cr, Cu, Fe, Mn, Ni, Rb, Zn) for adults were lower than the provisional tolerable daily intake values (PTDI) as suggested by [62,76,63]. The EDI of Al, Cr, Cu, Fe, Mn, Ni, and Zn were 0.87, 0.43, 5.17, 9.26, 2.63, 16.99 and 0.70% of the safe values which showed that the levels of Al, Cr, Cu, Fe, Mn, Ni and Zn were not that lower than reported in the rice grains (Table 3a, Table 2b). Similar low EDI for Cr, Cu, Fe, Mn, Ni and Zn in rice grains has also been reported by [77–79]. The EDI of the potential toxic metals via the consumption of rice followed the order: Fe > Cu > Mn > Al > Zn > Rb > Cr > Ni. The order agrees with the reports of [77,78,80].

### Hazard quotient (HQ)

The hazard quotient (HQ) is another useful factor for risk assessment which is linked with the intake of metal contaminated food crops [81]. The hazard quotient of potential toxic elements for a 73.3 kg adult from rice consumption showed the order of Cu (6.46E-01) > Cr (2.90E-01) > Fe (1.06E-01) > Mn (6.76E-02) > Ni (4.25E-02) > Zn (2.32E-02) > Al (8.70E-03) respectively (Table 3b). HQ for Rubidium (Rb) was not calculated
due to unavailability of reference data in the literature. The hazard quotient (HQ) of all the individual studied elements was found less than unity, indicating no health risk from individual metal.

**Hazard index (HI)**

The hazard index (HI) is an indicator used to evaluate the combined noncarcinogenic effects of multiple elements [48,82]. In current study the hazard index (HI) for multiple elements through consumption of rice was greater than 1 in downstream (HI = 1.45) and marble industry (HI = 1.23) sites (Table 3b). This indicates that adults that consume rice from these field might experience antagonistic health effect much later with bio accumulation of heavy metals over a period of time [77]. A similar results were obtained by [48] for rice and vegetables grown in the industrial areas of Bangladesh. The contribution of potential toxic metals to hazard index (HI) were in the order of Cu (55%) > Fe (25%) > Mn (6%) > Ni (4%) > Zn (2%) > Al (1%) respectively. This assessment only represents the ingestion of toxic metals through rice consumption. Besides, individuals of the local population are also subjected to other food sources that contain heavy metals such as vegetables, fish, milk, Chocolate powder, wheat, maize, fruit, and medicinal herbs [11,56,83–86]. Hence, a regular monitoring of heavy metals in nutritional components is required to prevent the buildup of these metals in food chain.

**Potential sources of the targeted heavy metals**

The potential source of targeted heavy metals in marble powder, paddy soil, rice plants and in its grains were identified by the application of Pearson correlation coefficient (PCC), Principal component analysis (PCA), and Cluster analysis (CA). The Pearson correlation coefficient matrix values are presented in (Tables 4–6). PCA was validated in view of (p < 0.001) in KMO and Bartlett sphericity test (Table 7).

Principal component analysis (PCA) has received predominant attention for the determination of the source of heavy metals among the researchers [87]. Two principal components were extracted for the targeted heavy metals of paddy soil using Varimax rotation with Kaiser normalization. The PCA of heavy metals of paddy soil showed a total variance of 71.466% with eigenvalues greater than 1.0 (Table 7). The cluster analysis of soil samples (Figure 2a) classified these metals into four distinct clusters. The principal component one (PCI) accounted for a total variance of 61.214% and was dominated by high factor loadings of Rb (0.9054), Zr (0.940), V (0.918), Zn (0.862), and Ti (0.825). These elements are released in the form of dust from marble and granite rocks during mining activities, sculpturing, and making slices for the beautification of buildings, and are controlled by atmospheric process [16]. According to [88] coal mining was the major pollution source for Rb, Ti, and Zn in agricultural soil of Bangladesh [89], reported that the origin of Rb and Zr may be from natural sources while V was recognized as the main element of petroleum. The current paddy fields of the study area are irrigated by the river Swat, which is a large sink for a variety of contaminants of various industrial sectors and community sewage [90]. Therefore, the source of the metals Rb, Zr, V and Zn in our study sites may be better described as anthropogenic.

Rubidium (Rb), Zr, V, Zn, and Ti exhibited a significantly strong positive correlation (p < 0.05) with r = 0.955 for Rb and V, r = 0.951 for Rb and Zr, r = 0.853 for Rb and Zn, r = 0.830 for Rb and Ti, r = 0.941 for V and Zr, contribute to a common origin. Moreover,
Table 4. Pearson Correlation coefficient matrices between metal concentrations of paddy soil of District Malakand.

|      | Al   | Ca   | Cr   | Cu   | Fe   | K    | Mn   | Ni   | Rb   | Si   | Sr   | Ti   | V    | Y    | Zn   | Zr   |
|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| Al   | 1    |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |
| Ca   | 0.246| 1    |      |      |      |      |      |      |      |      |      |      |      |      |      |      |
| Cr   | 0.148| 0.651| 1    |      |      |      |      |      |      |      |      |      |      |      |      |      |
| Cu   | 0.216| 0.637| 0.337| 1    |      |      |      |      |      |      |      |      |      |      |      |      |
| Fe   | 0.031| 0.271| -0.205| 0.329| 1    |      |      |      |      |      |      |      |      |      |      |      |
| K    | -0.392| -0.721*| -0.177| -0.712*| -0.227| 1    |      |      |      |      |      |      |      |      |      |      |
| Mn   | 0.751*| 0.769*| 0.487| 0.662| 0.089| -0.755*| 1    |      |      |      |      |      |      |      |      |      |
| Ni   | 0.180| 0.635| 0.845**| 0.654| -0.093| -0.445| 0.566| 1    |      |      |      |      |      |      |      |      |
| Rb   | 0.079| 0.499| 0.437| 0.857**| 0.105| -0.442| 0.526| 0.567| 1    |      |      |      |      |      |      |      |
| Si   | -0.047| -0.937**| -0.580| -0.482| -0.397| 0.556| -0.572| -0.450| -0.436| 1    |      |      |      |      |      |      |
| Sr   | 0.218| 0.695*| 0.396| 0.941**| 0.377| -0.790*| 0.650| 0.661| 0.811**| -0.583| 1    |      |      |      |      |      |
| Ti   | 0.432| 0.783*| 0.555| 0.837**| 0.083| -0.712*| 0.687**| 0.662| 0.830**| -0.641| 0.798**| 1    |      |      |      |      |
| V    | 0.298| 0.534| 0.507| 0.798**| 0.150| -0.410| 0.651| 0.563| 0.955**| -0.472| 0.763*| 0.874**| 1    |      |      |      |
| Y    | 0.236| 0.589| 0.381| 0.652| 0.057| -0.548| 0.604| 0.329| 0.825**| -0.570| 0.724*| 0.768*| 0.823**| 1    |      |      |
| Zn   | 0.268| 0.703*| 0.582| 0.896**| 0.150| -0.739*| 0.712*| 0.793*| 0.853**| -0.565| 0.953**| 0.874**| 0.832**| 0.743*| 1    |      |
| Zr   | 0.133| 0.456| 0.462| 0.821**| 0.066| -0.345| 0.551| 0.606| 0.951**| -0.366| 0.701*| 0.841**| 0.941**| 0.663| 0.782*| 1    |

** Correlation is significant at the 0.01 level (2-tailed).
* Correlation is significant at the 0.05 level (2-tailed).
the results of cluster analysis were consistent with the PCA and correlation coefficient matrix. These metals are included in cluster one (Figure 2a) and may share a common source. The principal component two (PC II) accounted for an eigenvalue of 1.640 with high factor loadings for Ca (0.739), Mn (0.714). Calcium and Mn also showed a strong positive correlation (p < 0.001) with r = 0.751 and included in cluster three (Figure 2a), and therefore indicated their common source of origin. According to [91] marble typically contains chemical compounds i.e. CaO, MgO, Al2O3, Na2O, Fe2O3, P2O5, TiO2, and SiO2 [92]. reported that due to frequent discharge of marble effluents into irrigation canals resulted contamination of water and soil as these effluents contain heavy metals like Mn, Fe, Zn, Cr, Cd, and Pb respectively [92]. The higher concentration of Ca in surface water near marble quarrying of North Central Nigeria was anthropogenic as reported by [93].

Similarly, for finding potential sources of heavy metals in rice plants, the principal component analysis via Varimax rotation with Kaiser normalization accounted for a total variance of 60.77% with an eigenvalue of 4.179 (Table 7). Similar to soil, the cluster analysis (CA) grouped the trace metals into three clusters (Figure 2b). The first principal component (PCI) associated with a total variance of 39.374% and was dominated by Zn, Fe, Al and Rb, holding a factor loading of 0.924, 0.908, 0.872 and 0.802 (Table 7). Hence, showed a strong inter-relationship among the metals [94], reasoned presence of Mn and Fe in fertilizers used for agricultural purposes. Likewise, a positive correlation (p < 0.01) was observed for Fe, Zn, Al and Rb with r value of 0.952 for Fe and Zn, r-value of 0.840 for Zn and Al, r-value of 0.825 for Fe and Al and r-value of 0.628 for Rb and Fe (Table 5a). The result of cluster analysis (Figure 2b) also included (Al, Fe, Zn, Rb) into cluster one, indicated a common source of these elements. The second principal component (PC II) was dominated by Ca and Mn that accounted for 21.395% of variance with factor loading of 0.814 and 0.581 (Table 7). The correlation coefficient between Ca and Mn was (r = 0.390), signifies a slight positive correlation at P < 0.01 level (Table 5a) and was included in cluster two (Figure 2b). Therefore, suggested a shared source of these elements.

It is quite essential to assess the quality of rice grains for total metal contents as rice is consumed worldwide on large scale [95]. The principal component analysis (PCA) accounted for a cumulative variance of 70.759% with an eigenvalue greater than 1 [96]. The cluster analysis of rice grains categorized the metals into three different clusters (Figure 2c). The principal component I (PC I) received a major contribution for Zn, Mn, Rb, Cu and Fe with a total variance of 43.185%, and with high loading factors of 0.941, 0.923, 0.905, 0.871 and 0.801 respectively (Table 7). Thus, indicated a strong association between these metals. A strong significant positive correlation (p < 0.01) was observed...
Table 5. Pearson Correlation coefficient matrices between metal concentrations of (a) rice plants and (b) rice grains (n = 09) near marble industry District Malakand.

(a) Rice plant

|        | Al  | Ca  | Cr  | Cu  | Fe  | K   | Mn  | Ni  | Rb   | Si  | Zn  |
|--------|-----|-----|-----|-----|-----|-----|-----|-----|-------|-----|-----|
| Al     | 1   |     |     |     |     |     |     |     |       |     |     |
| Ca     | 0.094 | 1   |     |     |     |     |     |     |       |     |     |
| Cr     | 0.040 | −0.179 | 1   |     |     |     |     |     |       |     |     |
| Cu     | −0.304 | 0.135 | −0.303 | 1   |     |     |     |     |       |     |     |
| Fe     | 0.823** | 0.385 | −0.184 | 0.001 | 1   |     |     |     |       |     |     |
| Mn     | −0.392 | −0.725* | 0.054 | −0.168 | −0.653 | 1   |     |     |       |     |     |
| Ni     | −0.312 | 0.390 | −0.002 | −0.347 | −0.306 | −0.136 | 1   |     |       |     |     |
| Rb     | 0.482 | −0.037 | −0.302 | −0.236 | 0.628** | 0.046 | −0.263 | 0.299 | 1   |     |     |
| Si     | −0.764 | −0.129 | 0.197 | 0.205 | −0.635 | −0.013 | 0.295 | 0.085 | 0.139 | 0.660 | −0.620 | 1 |
| Zn     | 0.840** | 0.230 | −0.205 | −0.193 | 0.952** | −0.574 | −0.328 | −0.139 | 0.660 | −0.620 | 1   |     |

(b) Rice grains

|        | Al  | Ca  | Cr  | Cu  | Fe  | K   | Mn  | Ni  | Rb   | Si  | Zn  |
|--------|-----|-----|-----|-----|-----|-----|-----|-----|-------|-----|-----|
| Al     | 1   |     |     |     |     |     |     |     |       |     |     |
| Ca     | 0.060 | 1   |     |     |     |     |     |     |       |     |     |
| Cr     | 0.646 | 0.215 | 1   |     |     |     |     |     |       |     |     |
| Cu     | 0.039 | 0.184 | 0.613 | 1   |     |     |     |     |       |     |     |
| Fe     | 0.496 | 0.155 | 0.773* | 0.667* | 1   |     |     |     |       |     |     |
| K      | 0.243 | −0.858* | 0.249 | 0.224 | 0.178 | 1   |     |     |       |     |     |
| Mn     | 0.048 | −0.158 | 0.540 | 0.818** | 0.750* | 0.424 | 1   |     |       |     |     |
| Ni     | 0.595 | −0.186 | 0.878** | 0.470 | 0.583 | 0.586 | 0.440 | 1   |       |     |     |
| Rb     | 0.069 | −0.006 | 0.263 | 0.695* | 0.653 | 0.198 | 0.816** | 0.146 | 1   |     |     |
| Zn     | −0.065 | −0.077 | 0.287 | 0.707* | 0.726* | 0.234 | 0.889** | 0.152 | 0.899** | n/c | 1   |

** Correlation is significant at the 0.01 level (2-tailed).
* Correlation is significant at the 0.05 level (2-tailed).
nc = not counted

Table 6. Correlation (Pearson) coefficient matrices between metal levels in soil (s) versus rice plants (p) and its grains (g), and rice plants (p) versus grains (g) (n = 09).

| Elements | Al (s) | Ca (s) | Cr (s) | Cu (s) | Fe (s) | K (s) | Mn (s) | Ni (s) | Rb (s) | Si (s) | Zn (s) |
|----------|--------|--------|--------|--------|--------|-------|--------|--------|--------|--------|--------|
| Al (p)   | 0.179  | −0.139 | −0.426 | −0.050 | 0.117  | 0.082 | 0.123  | −0.389 | −0.068 | 0.135  | −0.291 |
| Ca (p)   | −0.362 | −0.094 | −0.255 | 0.596  | 0.097  | −0.225 | −0.078 | 0.078  | 0.639  | 0.129  | 0.408  |
| Cr (p)   | 0.386  | 0.383  | 0.403  | 0.181  | −0.114 | −0.300 | 0.523  | 0.462  | 0.153  | −0.301 | 0.474  |
| Cu (p)   | −0.049 | 0.230  | 0.257  | 0.168  | 0.563  | 0.212  | −0.233 | 0.051  | 0.233  | −0.478 | 0.166  |
| Fe (p)   | −0.131 | 0.084  | −0.169 | 0.262  | 0.121  | 0.049  | 0.115  | −0.102 | 0.278  | 0.084  | −0.050 |
| K (p)    | 0.504  | 0.189  | 0.056  | −0.234 | 0.184  | −0.204 | 0.215  | −0.020 | −0.505 | 0.132  | −0.128 |
| Mn (p)   | −0.351 | −0.514 | −0.306 | −0.081 | −0.302 | 0.044  | −0.471 | 0.045  | −0.212 | 0.624  | −0.077 |
| Ni (p)   | 0.209  | 0.934  | 0.751  | 0.473  | 0.267  | −0.529 | 0.630  | 0.681  | 0.305  | −0.879 | 0.560  |
| Rb (p)   | 0.277  | 0.265  | 0.006  | 0.291  | 0.133  | −0.118 | 0.361  | 0.145  | 0.013  | −0.093 | 0.041  |
| Si (p)   | −0.436 | −0.035 | 0.497  | −0.240 | −0.404 | 0.223  | −0.336 | 0.305  | 0.015  | 0.059  | 0.116  |
| Zn (p)   | −0.025 | −0.004 | −0.161 | 0.097  | −0.120 | 0.142  | 0.123  | −0.167 | 0.156  | 0.038  | −0.182 |

For Rb and Zn with an r-value of 0.899, Mn and Zn with an r-value of 0.899, Cu and Mn with an r-value of 0.818, Mn and Rb with an r-value of 0.816 (Table 5b), Fe also showed a significant positive correlation (p < 0.05) with Mn (r = 0.750) and Zn (r = 0.726). Similarly, Cu was strongly positive correlated (p < 0.05) with Zn (r = 0.707), and Fe (r = 0.667) (Table 5b). Therefore, all these metal pairs fell in cluster one (Figure. 2c) and evidenced a common source of these metal pairs. The principal component II (PC II), accounts for 27.574% of
variance and was dominated by Ni, Al, Cr, and K with high loading factor of 0.901, 0.726 and 0.720 (Table 7).

Result of strong positive correlation for Cr with Ni ($r = 0.878$), Al with Ni ($r = 0.595$) and K with Ni ($r = 0.586$) at ($p < 0.01$, $P < 0.05$) (Table 7) indicate common source of these metal pairs and were included in cluster three (Figure. 2c). K showed a strong negative correlation with Ca ($r = -0.858$) at ($p < 0.01$) and included in cluster two (Figure. 2c).

To link up marble industry as a source of heavy metal contamination in paddy soil, and paddy crops, PCA was performed for the classification of metals in marble powder. Two principal components with eigenvalues greater than 1 were extracted that accounted for a total variance of 68.783%. Principal component one (PC I) accounts for 37.678 of variance (Table 7) and was dominated with high factor loadings of Cr (0.842), K (0.832), Ni (0.787), Cu (0.773), Sr (0.739). The result of the PCA was consistent with the cluster analysis which indicated a strong association between these metal pairs in marble powder. The principal component two (PC II) with a total variance of 31.105% was dominated by Fe, Al, Mn, with factor loading of 0.941, 0.876, 0.800 (Table 7). The cluster analysis included these metals in one cluster (Figure 2d), implying the same source of origin. It was found that in paddy soil and marble powder, Cr are grouped with Ni, Fe with Si and Cu with Sr. Whereas in paddy plants and grains Fe, Rb and Zn were grouped together. These suggest that these metals might also share a common source and derived from the marble industry waste.

The correlation coefficient matrix for the elements of paddy soil, plants, and rice grains showed a slight positive correlation between Cr contents in the three media i.e. soil versus plant, soil versus grains and plant versus grains (Table 6) showing that elevated Cr levels in rice plants originates from their increased levels in the soil. Similarly, the positive correlation between Cr of plants and Cr of grains (Table 6) indicated that higher metal content led to absorption of Cr from the soil and then translocated to the grains [95]. Ni contents also showed significant positive correlation in the three media (Table 6), evidencing that the source of elevated level in plants and rice grains originates from the particular level of soils which can then be translocated to edible parts [95]. The Cr and Ni concentrations in rice grains were within the permissible limits of [62] (Table 8). However, prolonged exposure to these metals via consumption of rice might cause health hazard among the people [96]. The essential elements like Ca, Fe and Mn displayed a slight positive correlation in soil versus rice grains, indicating translocation of the metals from soil to plant followed by their accumulation in rice grains. Unlike, the metalloid (Si) showed negative correlation with other studied metals in soil versus plant and soil versus grains indicating no translocation from soil to grains.

### Conclusion

The key findings of the current study demonstrated that paddy fields near marble industry were highly enriched with essential and nonessential elements in the decreasing order of Ca > K > Si > Fe > Al > Ti > Mn > Sr > Zr > Zn > Cu > Ni > V > Rb > Y > Cr. The concentration of these elements in paddy soil was within the permissible limits set by the [54]. Likewise, the average metal level in rice grains for Fe, Cu, Mn and Al were higher than the permissible limits of [62]. The cumulative hazard index (HI) of the heavy metals exceeded than one (HI > 1) which showed a probable noncancerogenic risk for the local population. From the current study, it was concluded that direct or indirect discharge of marble industrial waste into irrigation
canals, agricultural field result heavy metal contamination of the soil, and subsequent accumulation of the heavy metals in rice plant tissues and may pose probable health risks for Human and livestock. The contamination source for paddy soil and rice plant of the study area was found to be predominantly anthropogenic.

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Disclosure statement

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.

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