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Research article

Assessment of potentially toxic and mineral elements in paddy soils and their uptake by rice (*Oryza sativa* L.) with associated health hazards in district Malakand, Pakistan

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ABSTRACT

Rice, a primary food source in many countries of the world accumulate potentially harmful elements which pose a significant health hazard to consumers. The current study aimed to evaluate potentially toxic and mineral elements in both paddy soils and rice grains associated with allied health risks in Malakand, Pakistan. Rice plants with intact root soil were randomly collected from paddy fields and analyzed for mineral and potentially toxic elements (PTEs) through inductively coupled plasma optical emission spectrometry (ICP−OES). Through deterministic and probabilistic risk assessment models, the daily intake of PTEs with allied health risks from consumption of rice were estimated for children and adults. The results of soil pH (< 8.5) and electrical conductivity ($EC > 400$ μs/cm), indicated slightly saline nature. The mean phosphorus concentration of 291.50 (mg/kg) in soil samples exceeded FAO/WHO permissible limits. The normalized variation matrix of soil pH with respect to Ni (0.05), Ca (0.05), EC (0.08), and Mg (0.09), indicated significant influence of pH on PTEs mobility. In rice grains, the mean concentrations (mg/kg) of Mg (463.81), Al (70.40), As (1.23), Cr (12.53), Cu (36.07), Fe (144.32), Mn (13.89), and Ni (1.60) exceeded FAO/WHO safety limits. The transfer factor >1 for K, Cu, P and Zn indicated bioavailability and transfer of these elements from soil to rice grains. Monte Carlo simulations of hazard index >1 for Cr, Zn, As, and Cu with certainties of 89.93% and 90.17%, indicated significant noncarcinogenic risks for children and adults from rice consumption. The total carcinogenic risk (TCR) for adults and children exceeded the USEPA acceptable limits of 1×10^{-6} to 1×10^{-4}, respectively. The sensitivity analysis showed that the ingestion rate was a key risk factor. Arsenic (As) primarily influenced total cancer risk (TCR) in children, while chromium (Cr) significantly impacted adults. Deterministic cancer risk values slightly exceeded probabilistic values due to inherent uncertainties in deterministic analysis. Rice consumption poses health risks, mainly from exposure to Cr, Ni and As in the investigated area.

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1. Introduction

Agricultural soil, a finite natural resource, plays a critical role in sustaining human civilization and ecosystems by providing habitat for soil organisms and a growth medium for crops [1,2]. Worldwide, soil quality is often compromised by industrial and agronomic actions that can disperse PTEs into the soil environment, initiating undesirable impacts on both ecosystems and human wellbeing [3,4]. PTEs like Cr, Hg, Ni, As, V, Cd, Pb, and Se are hazardous contaminants exhibit toxicity, persistence, and bioaccumulative characteristics in environmental media [5,6]. PTEs occur naturally in ecosystems. However, anthropogenic actions such as mining, industrial waste, power generation and vehicle emissions further contribute to unsafe levels of PTEs in water, soil, forage, and food crops [7,8]. PTEs enter the environment and are deposited in the soil, where they accumulate within clay particles and various organic compounds [9,10]. PTEs can also bind to hydrated states of manganese (Mn) and iron (Fe) oxides [11]. In addition, PTEs are temporarily deposited in soil particles and eventually reach surrounding water bodies [12]. Contaminated water used for irrigation deposits PTEs in agricultural fields, and accumulate in vegetables and food crops, posing a threat to humans through food chain contamination [13,14]. Therefore, conducting a thorough evaluation of soil chemical, fertility, and physical characteristics is essential for formulating reclamation strategies. Moreover, precise scientific data guides the amendment of undesirable soil attributes, ultimately leading to increased productivity [15].

Rice (*Oryza sativa* L.) is a major cereal crop, serving as an essential food for over 3.5 billion individuals globally, with approximately half of the world's population consume it daily as dietary component [16–18]. Pakistan ranks as the world's tenth-largest rice producer, with an output of around 6.8 million tons and is the fourth largest rice exporter after India, Thailand, and Vietnam. Additionally, it contributes to nearly 8.2% of the world's paddy rice exports [19,20]. In Pakistan, the industrial sector generates approximately 1.309×10^9 m^3 of wastewater yearly and is used as a substitute source of irrigation due to insufficient freshwater availability for irrigating agricultural land [21,22]. Furthermore, numerous brick kilns in the country employ low-grade coal for crafting handmade bricks, resulting in the release of PTEs such as Cu, As, Fe, Cd, Pb, Zn, and Hg into the surrounding ecosystem as byproducts of coal combustion [23]. Rice fields along rivers accumulate suspended solids through irrigation, flooding, and the use of fertilizers, agrochemicals, and sewage sludge [24]. In arable lands, such activities lead to the transfer of PTEs to agricultural crops, especially to rice, as rice easily absorbs PTEs and accumulates in edible parts [25]. Various pathways exist for potentially toxic elements (PTEs) to enter the human body. However, the main route of human exposure is through food consumption [26,27]. Consumption of unsafe foods can significantly contribute to various diseases, including cancer, diarrhea, birth defects, heart disease, and numerous kidney diseases [28]. Hence, it is crucial to oversee and limit accumulation of potentially toxic elements (PTEs) in crop from their surroundings. To achieve this objective, it is essential to investigate the transferability of PTEs from soil to plants. Furthermore, the assessment of PTEs is of great significance in human health risk assessment, with emphasis on nutritional intake through consumption of plants [29].

The appraisal of potential hazards to human health due to exposure to PTEs has become a common practice, estimate the likelihood and severity of health issues in people [30–33]. These estimations have improved over the years through different assessment frameworks and established models through studying patterns of diseases and their causes, toxic effects of environmental pollutants and exposure frequency that contribute to health problems [34–36]. The deterministic model utilizes empirical formulas which are intended to attribute a distinct representative value to individual input factor within the risk equation [37]. Ultimately, this process yields a singular output value representing the overall risk [38]. Implementing such a traditional deterministic risk calculation method is complicated due to the variability of input factors that cannot be treated as fixed point values [39]. Assigning various values to each input factor in the risk equation leads to multiple estimates of risk [40]. The uncertainties associated with risks can lead to either underestimation or overestimation of the potential dangers [41]. In response to the complicated nature of human health risk assessments and the need for comprehensive refinement, a newly developed probabilistic method has been widely implemented [36,39,42]. The probabilistic risk analysis integrates probability distributions through stochastic methods, like the Monte Carlo Simulation (MCS) [37]. This involves simulating multiple input parameters in the risk equation to determine the probability distribution of the resulting risk [39]. MCS generates random numbers adhering to a specific rule, added to a risk model for quantitative estimation of probabilities of adverse biological effects, revealing uncertainty and variability in the risk assessment [41,43]. Therefore, probabilistic risk analysis approach provides greater information compared to the deterministic method in health risk assessment [44]. In line with the above perspective, the present study aimed (i) to evaluate PTEs concentrations in paddy fields and rice grains considering plant transfer factor (TF) and (ii) to evaluate health risks for individuals exposed to PETs through rice consumption using deterministic and probabilistic models.

2. Material and methods

2.1. Background of study area

The current study was carried out between April 2018 and September 2019 on paddy soils irrigated by the Swat River in Malakand District, Khyber Pakhtunkhwa, Pakistan (Fig. 1). In Khyber Pakhtunkhwa, most of the rice growing area is in high altitude mountain valleys, such as the Malakand and Hazara divisions. The Malakand district holds a significant role in rice production, ranking fourth after the Swat, DI Khan, and Dir districts [45]. The rice cultivation area in Malakand district was 4991 ha in 2016–17, and the production in the same year was 10,773 tons [46].

Geographically, located between longitude 34.3718°N and latitude 72.2420°E, Malakand District is the entry point to districts of Dir, Chitral, Swat, Buner, Shangla, and the currently merged tribal areas of Mohmand and Bajaur. The District spans 952 km^2 with population density of 475 individuals per square km [47]. The land of Malakand District is fertile and surrounded by mountains with

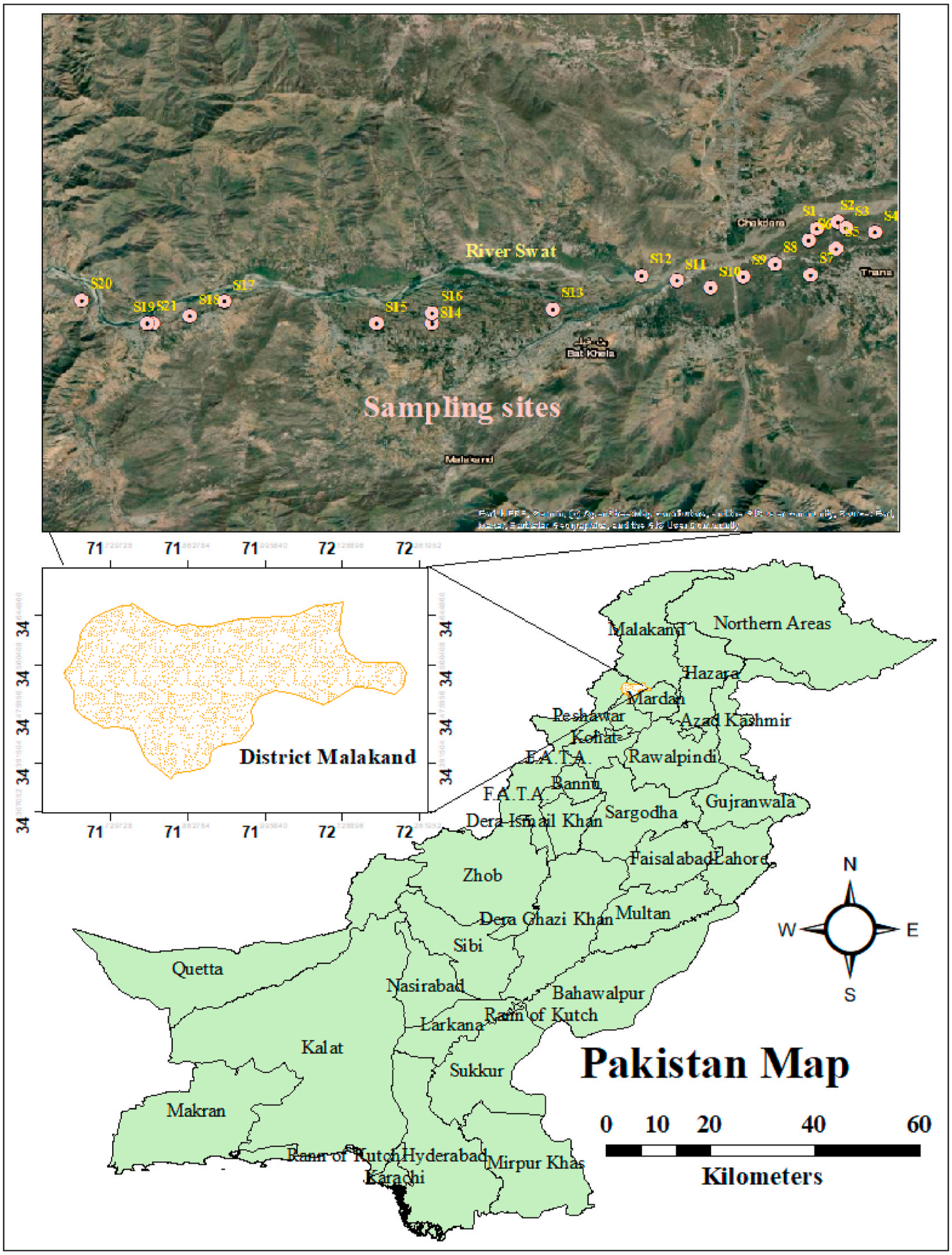


Fig. 1. Study area map presenting sampling sites.

rich biodiversity. The winter season experiences extremely cold temperatures, dropping to −2 °C in January. The summers are hot, and the temperature reaches 41 °C in June-July [48]. The yearly average rainfall ranges from 600 to 650 mm [49].

2.2. Sampling and analytical methods

Fully grown rice plants with undisturbed soil from 0 to 20 cm depth, were randomly collected by hand auger from designated locations (Fig. 1) employing a quincunx sampling design [24,50]. After removing the root soil, the rice grains were securely sealed in labeled, clean plastic bags and transported to the laboratory of Botany Department, Islamia College Peshawar for analysis [9]. Soil samples were dried in microwave oven, mechanically ground, passed through a 2 mm sieve, and then stored at room temperature [51, 52]. The rice grains were subjected to oven drying at 70 °C for 24 h to eliminate moisture [53]. The outer husk from rice grain was manually removed, and finely ground into powder via a ceramic mortar and pestle [54].The sampling points' coordinates were recorded using a Global Positioning System (Garmin eTrex 10).

2.3. Analysis of physicochemical properties of soil samples

A suspension was formulated with a soil to water ratio of 1:2.5 in double deionized water, followed by stirring and centrifugation at 3000 rpm for 4 h. Electrical conductivity (EC) and pH of soil solution were analyzed using a portable meter (Model WT01 China) [55].

2.4. Soil and rice samples acid digestion

0.5 gm powder of each dried soil samples were placed in triplicate into 50 mL volumetric flasks. The samples were subjected to treatment with a 26 mL triacid mixture (HNO_3, HCl, and HF) at a ratio of 9:3:1 and stored overnight [56]. Similarly, 0.25 gm powder of dried rice grains were placed into 50 mL volumetric flasks and treated by 6.5 mL of triacid mixture of $HClO_4$, H_2SO_4, and HNO_3 in a ratio 0.5:1:5 [57]. All the samples were completely digested on hot plate at 155 °C until white dense fumes appeared [58]. After cooling, the digested samples were diluted to 50 mL using distilled water. Filtration of the samples were carried out through Whatman filter paper (0.45 μm) into a clean volumetric flask and kept at room temperature [59]. Concentration of mineral elements and PTEs in all samples were analyzed via Inductively Coupled Plasma Optical Emission Spectroscopy (ICP−OES) (model iCAP 6500 from Thermo Scientific, UK).

2.5. Quality assurance and quality control

Considerable attention was retained on the approved analytical quality control methods for sample collection, preparation, preservation, and laboratory analysis [60–62]. The analytical reagents employed in laboratory analysis were of high purity. Calibration curves were generated utilizing standard reference materials (SRMs) from Thermo Fisher Scientific, USA. The calibration standards included elements that exhibited strong linear relationships (correlation coefficient >0.999). Calibration was verified against Specpure standards and EPA limits (recoveries between 95 and 105%). Accuracy of ICP−OES procedures were confirmed through NIST SRM 1568b, GBW10043, and IAEA-Soil-7 reference materials (Tables S1–S2). The detection limits (LODs) were determined based on five blank samples. Triplicate analyses for each sample produced a mean value with minimum (2.0%) relative standard deviation (RSD) for the analyzed elements (Tables S1–S2).

2.6. Transfer factor (TF)

The transfer of elements from soil to a plant system is known as transfer factor, indicates risk level linked to consumption of vegetabes and food crops [63]. TF can be computed using the formula below [64]:

$$TF = \frac{C_{\text{rice grain}}}{C_{\text{soil}}}$$

where, $C_{\text{rice grains}}$ signifies concentrations of elements (mg/kg) of rice grains, and C_{soil} denotes concentrations in paddy soil.

2.7. Methods for health risk assessment

The health risk assessment models are a valuable tool for evaluating potential risks to humans arising from pollutants. Probabilistic and deterministic risk models were employed to define probable noncarcinogenic and carcinogenic health hazards associated with pollutants [65,66].

2.7.1. Deterministic health risk estimation

The estimated daily intake (EDI), hazard quotient (HQ) and hazard index (HI) were used to appraise the probable noncarcinogenic health risks linked with prolong exposure to PTEs via rice ingestion [67]. The EDI relies on the daily consumption of food and the body tolerance to pollutants, determined by the concentration of metals in the diet. Estimation of EDI was conducted through the below equation [68,69]:

$EDI = \frac{C \times IR \times ED \times EF_r}{BW \times AT}$ where, EDI represents projected daily dose (mg/kg/person/day), C signify elemental dry weight concentration in rice grains (mg/kg), IR shows daily ingestion rate of rice (kg/day), ED indicates exposure duration (year), EFr denotes frequency of exposure(day/year) to PTEs, BW represents body average weight (kg) and AT shows average exposure time (days) [14,70]. The associated input values and units of the parameters were presented in Table S3.

2.7.2. *Hazard quotient (HQ)*

Potential noncarcinogenic risk from PTEs exposure via rice consumption was evaluated using HQ and the USEPA region III risk based concentration table [71,72]. HQ is the exposure ratio to a specific toxicant over a defined period compared to the reference dose for that substance within a similar exposure timeframe [73]. The subsequent equation was employed to calculate HQ:

$$\mathrm{HQ} = \frac{\mathrm{EDI}}{\mathrm{Rfd}}$$

where, HQ represents the hazard quotient, and RfD denotes the oral reference dose (mg/kg/day). The Rfd values for Fe (0.7), Ni (0.02), Zr (0.0004), Cr (0.003), Al (1.0), Cu (0.04), Sr (0.6), Mn (0.14) and As (0.0003). A population is considered at risk of exposure when the HQ ratio equals or exceeds one [73,74].

2.7.3. *Hazard index (HI)*

HI assesses combined noncarcinogenic health effects of diverse elements and is developed following guidelines for assessing health risks linked with chemical mixtures [73,75]. HI is the sum of HQs and can be computed through below equation [26]:

$$\mathrm{HI} = \sum_{K=1}^{n} \mathrm{HQ} = \mathrm{HQ}_1 + \mathrm{HQ}_2 + \ldots\ldots + \mathrm{HQ}_n$$

2.7.4. *Estimation of cancer risk (CR)*

Cancer risk is the likelihood of developing cancer with exposure to potential carcinogens throughout a person lifetime [76,77]. The probability of cancer risk to PTEs through rice consumption were assessed by the following equation [29]:

$$\mathrm{CR} = \mathrm{EDI} \times \mathrm{CSF}$$

where, EDI represents the estimated daily intake of the carcinogenic elements (mg/kg bw/day), and CSF represents slope factor of carcinogen. The CSF for Ni, As and Cr are 91, 1.5 and 0.5 mg/kg/day, respectively [78]. The acceptable range for cancer risk is 1×10^{-6} to 1×10^{-4} [79].

The exposure assessment to several carcinogenic PTEs through rice consumption was conducted utilizing the given risk equation [77]:

$$\sum_{1}^{n} = \mathrm{CR1} + \mathrm{CR2}\ldots\ldots\ldots\mathrm{CRn}$$

2.7.5. *Evaluation of probabilistic health risk and sensitivity analysis*

The probabilistic assessment of health risk employs deterministic health risk model as foundation and Monte Carlo Simulation (MCS) as framework [42].

MCS is conducted to reveal the uncertainty involved in estimating potential ecological risks based on individual point values of element concentrations [80]. The measured concentrations of individual PTEs in rice grains served as a dataset of random variables conforming to a particular probability distribution. Following the establishment of a deterministic model, point estimates were substituted with assumed probability distributions, and the resulting output distribution was projected [81]. After 10,000 iterations, a stable exposure distribution was achieved. The assessment of probabilistic risk was conducted using the values at the 95th percentile of the exposure distribution [70]. Sensitivity analyses were conducted to assess the impact of exposure factors on the results. A positive value indicates a positive association between the exposure factor and health risks, while a negative value suggests a negative association [36]. The details of the input parameters to the Monte Carlo simulation were listed in Table S3.

2.8. *Statistical analysis*

The data was collected in the MS Excel 2016 for initial preparation and then proceeded with descriptive statistical analyses, involving computation of mean, median, and standard deviation (SD). The covariance biplot (Fig. 2) and normalized variation matrix (Table 2) were generated using the R package 'compositions' and CoDaPack software version 2.03.01 [82,83]. Health risk probabilities through best fitting distribution for individual parameters and sensitivity analysis from exposure to PTEs were evaluated by MCS using Crystal Ball software (version 11.1). The distribution map of sampling points and associated graphs for the data were created using ArcGIS 10.2.2, Oracle Crystal Ball, and Excel 2016 software [14,80].

3. Results and discussion

The current research explored the concentrations of potentially toxic and mineral elements in paddy soil. It examined their interrelationships with physicochemical variables, pinpointed contamination sources, and assessed the transfer of these elements to rice grains. Furthermore, an evaluation was conducted on the health risks linked to exposure to PTEs through the consumption of rice, considering both children and adults (Tables 1–7).

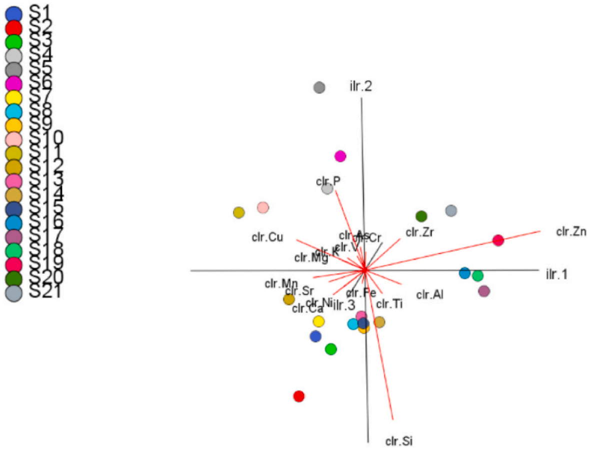


Fig. 2. Centered log ratio (clr) biplots displays clustering of elements on PCI versus PCII.

Table 1
Statistics of physicochemical parameters and potential toxic elements concentrations (mg/kg) in paddy soil.

Variable	Unit	Statistics							Permissible limits		
		Min	Q1	Median	Q3	Max	Mean	SD	[a]Shale	[b]Earth crust	[c]FAO
pH		7.10	7.40	8.70	8.90	9.10	8.30	0.70	–	–	6.5–8.5
ECe	µs/cm	190.00	268.50	390.00	450.50	779.00	374.60	133.10	–	–	400
Al	mg/kg	5100.0	8250.0	9150.0	12575.0	23250.0	10914.30	4893.30	80000	25000	–
As	mg/kg	2.00	3.50	4.50	6.80	10.00	5.30	2.30	1.60	0.80	15
Ca	mg/kg	12650.0	14800.0	19050.0	24675.0	29250.0	19881.0	5331.70	22100	39100	–
Cr	mg/kg	8.80	21.30	29.00	32.80	40.00	26.60	8.10	90	35.0	100
Cu	mg/kg	6.40	10.00	17.50	27.50	40.50	20.0	10.60	45	28.0	100
Fe	mg/kg	1075.0	2877.80	4835.0	5900.0	13200.0	4699.70	2544.0	47200	9800	50000
K	mg/kg	734.50	1342.80	1760.0	2932.30	3990.50	2105.70	951.60	26600	10700	–
Mg	mg/kg	2438.50	4515.50	5100.0	6675.0	8050.0	5420.70	1676.10	15000	7000	–
Mn	mg/kg	68.50	90.50	131.50	216.0	315.50	149.30	73.40	850	1100	2000
Ni	mg/kg	12.50	15.00	18.50	21.0	27.0	18.40	4.10	68.0	47.0	20–60
P	mg/kg	65.50	145.80	199.00	426.80	805.50	291.50	207.30	125.0	84.0	–
Si	mg/kg	1.50	7.00	12.50	16.0	25.50	12.50	7.00	73000	24000	–
Sr	mg/kg	13.50	25.30	35.50	44.50	60.50	35.10	13.40	142.0	320	200
Ti	mg/kg	125.50	334.30	512.0	747.30	1471.0	600.50	378.90	4600	1500	–
V	mg/kg	16.50	33.80	38.0	46.80	59.0	39.20	12.50	130.0	97.0	100
Zn	mg/kg	0.50	1.50	2.50	11.0	19.0	5.80	6.20	95.0	67.0	200
Zr	mg/kg	0.40	1.80	3.00	3.80	4.50	2.80	1.10	160	193.0	–

[a] [86].

[b] [84].

[c] [85], SD = Standard deviation.

3.1. Evaluation of physicochemical characteristics and elemental concentration in paddy soil

The electrical conductivity (EC), pH and elemental concentration of paddy soil were evaluated against the permissible limits (Table 1) proposed by Refs. [84–86]. The soil exhibited a pH range of 7.10–9.10, (mean 8.30), indicating a slightly alkaline nature. Similar pH findings (7.96–8.19) reported in Toshka, Egypt, by Ref. [15] are attributed to the characteristics of the parent material. According to Ref. [87], soil alkalinity is driven by carbonate and bicarbonate anions, which elevate the pH above 8.0 and are linked with ion depletion and toxicity. The EC of the soil water suspension varied between 190 and 779, with an average of 374.60 µs/cm. The maximum EC value of 779 µs/cm exceeded the permissible limit of 400 µs/cm set by Ref. [88], signifying marginal salinity and the existence of dissolved inorganic solutes in the aqueous phase of the soil [89]. Similarly, the EC values (77.7–1021.5 µs/cm) reported by Ref. [90] are consistent with our results. According to Refs. [91,92], soil quality indicators like pH < 8.5 and EC > 400 µs/cm suggest saline soil conditions and are linked with elevated concentrations of Na, Mg and Ca in soil solution. Elevated soil salt levels hinder plant water uptake by lowering osmotic potential, increasing the difficulty of water absorption. Additionally, increased salt levels can induce specific ion toxicity, disrupt nutrient balance, and lead to reduced crop yield [93,94].

The paddy soil elemental concentrations were compared with the Earth shale and Earth upper crust [84,86] (Table 1). Earth shale was chosen due to the absence of background concentration data for the study area. The average concentrations (mg/kg) of Ca (19881), Mg (5420.70), and K (2105.70) in the soil samples fell within the acceptable limits of the world average shale. Similarly, the

Table 2
Normalized variation matrix of the data in table (1).

	pH	Ec	Al	As	Ca	Cr	Cu	Fe	K	Mg	Mn	Ni	P	Si	Sr	Ti	V	Zn	Zr
pH	0.00																		
Ec	**0.08**	0.00																	
Al	0.15	0.19	0.00																
As	0.16	0.16	0.27	0.00															
Ca	**0.05**	0.14	0.21	0.17	0.00														
Cr	0.11	**0.09**	0.10	0.12	0.12	0.00													
Cu	0.29	0.23	0.43	0.28	0.20	0.20	0.00												
Fe	0.27	0.32	0.19	0.35	0.23	0.18	0.33	0.00											
K	0.16	0.17	0.35	0.30	0.18	0.21	0.36	0.34	0.00										
Mg	**0.09**	0.10	0.18	0.12	**0.08**	0.10	0.20	0.18	0.20	0.00									
Mn	0.20	0.28	0.29	0.22	0.10	0.19	0.17	0.21	0.35	**0.09**	0.00								
Ni	**0.05**	0.13	0.17	0.10	0.03	**0.09**	0.23	0.19	0.19	**0.06**	0.11	0.00							
P	0.49	0.38	0.61	0.44	0.57	0.42	0.56	0.74	0.49	0.38	0.54	0.55	0.00						
Si	0.59	0.95	0.64	0.90	0.59	0.85	1.21	0.83	0.93	0.81	0.83	0.63	1.41	0.00					
Sr	0.13	0.16	0.33	0.15	0.10	0.18	0.31	0.36	0.17	0.14	0.22	**0.09**	0.59	0.77	0.00				
Ti	0.33	0.38	0.30	0.50	0.44	0.35	0.71	0.39	0.50	0.38	0.53	0.37	0.92	1.01	0.50	0.00			
V	0.11	0.10	0.16	0.10	0.13	**0.06**	0.21	0.22	0.27	**0.07**	0.18	**0.08**	0.52	0.88	0.15	0.38	0.00		
Zn	1.04	0.97	0.63	0.87	1.14	0.79	1.48	0.98	1.07	1.00	1.33	1.04	1.38	1.51	1.22	1.07	0.88	0.00	
Zr	0.27	0.26	0.22	0.21	0.28	0.17	0.44	0.27	0.35	0.23	0.35	0.21	0.69	1.09	0.39	0.48	0.18	0.60	0.00

Table 3

Concentration and transfer factor (TF) of potential toxic elements (mg/kg) in rice grains in district Malakand.

Elements	Concentration (mg/kg)						Transfer factor (TF)				
	Mean	Min	Max	Median	SD	[a]FAO limit	Mean	Min	Max	Median	SD
Al	70.40	8.90	165.70	65.80	52.86	1.00	0.006	0.001	0.017	0.006	0.004
As	1.23	0.40	3.15	1.20	0.65	0.1	0.268	0.06	0.788	0.228	0.174
Ca	903.83	60.70	2451.30	420.30	892.90	1000	0.048	0.003	0.133	0.027	0.049
Cr	12.53	4.50	50.40	8.80	10.75	2.3	0.463	0.207	1.26	0.356	0.286
Cu	36.07	12.40	56.60	38.30	12.60	2–3	2.305	0.693	8.708	1.938	1.709
Fe	144.32	20.80	480.40	46.50	171.18	15	0.033	0.003	0.13	0.014	0.038
K	2585.93	1410.60	4202.60	2500.40	840.93	3500	1.483	0.515	4.599	1.436	0.881
Mg	463.81	126.50	860.80	498.40	213.89	350	0.095	0.024	0.273	0.079	0.06
Mn	13.89	2.70	30.50	12.80	7.57	2–3	0.114	0.02	0.349	0.084	0.088
Ni	1.60	0.50	3.50	1.40	0.91	0.5	0.089	0.024	0.184	0.081	0.048
P	2396.70	1544.40	3524.60	2348.30	519.37		12.751	3.31	29.038	11.356	8.396
Sr	27.03	2.40	58.80	26.30	16.46		0.862	0.102	2.719	0.672	0.675
Ti	35.70	3.40	74.50	36.30	22.44		0.075	0.011	0.26	0.07	0.064
Zn	7.63	2.60	13.40	7.70	2.73	60	3.258	1.4	11.25	2.667	2.097

[a] [85,179,180], SD = Standard deviation.

Table 4

Ratios of maximum to minimum element concentrations in rice and paddy soils and ratios of TF along the River Swat.

Variables	Cr	Ni	Zn	K	P	Mg	As	Cu	Mn	Al	Ti	Sr	Fe	Ca
Rice grains	11	7	5	3	2	7	8	5	11	19	22	25	23	40
Paddy soil	5	2	11	5	12	3	5	6	5	5	12	4	12	2
Transfer Factor (TF)	6	8	8	9	9	11	13	13	17	23	23	27	42	43

Table 5

Statistics of estimated daily intake (mg/kg body wt/day) for individual PTEs due to consumption of rice irrigated by River Swat.

Elements	EDI Adult				EDI Children				
	Mean	Mini	Max	SD	Mean	Mini	Max	SD	[a]PTDI
Al	3.94E-02	2.15E-02	6.23E-02	1.33E-02	4.68E-02	2.55E-02	7.39E-02	1.58E-02	1.00E+00
As	1.78E-03	8.82E-04	3.23E-03	8.10E-04	2.11E-03	1.05E-03	3.84E-03	9.61E-04	3.00E-04
Cr	1.76E-02	7.79E-03	5.00E-02	1.47E-02	2.09E-02	9.24E-03	5.93E-02	1.75E-02	3.00E-03
Cu	5.22E-02	2.25E-02	7.74E-02	1.88E-02	6.19E-02	2.67E-02	9.19E-02	2.23E-02	5.00E-01
Fe	2.11E-01	3.53E-02	6.66E-01	2.64E-01	2.51E-01	4.18E-02	7.90E-01	3.13E-01	8.00E-01
Mn	1.95E-02	7.35E-03	2.79E-02	8.79E-03	2.31E-02	8.72E-03	3.31E-02	1.04E-02	1.40E-01
Ni	2.30E-03	1.08E-03	4.26E-03	1.20E-03	2.72E-03	1.28E-03	5.06E-03	1.43E-03	2.00E-02
Sr	3.70E-02	4.41E-03	7.74E-02	2.68E-02	4.39E-02	5.23E-03	9.19E-02	3.18E-02	6.00E-01
Zn	1.08E-02	8.82E-03	1.47E-02	2.19E-03	1.28E-02	1.05E-02	1.74E-02	2.60E-03	6.00E+01

PTDI values (in mg/kg body wt/day) of all the metals were based on the data suggested by the Joint FAO/WHO Expert Committee on Food Additives [171], SD = Standard deviation.

[a] The PTDI value of Cr and Sr was based on the reference dose (RfD) of Cr (VI) and Sr established by USEPA [72].

Table 6

Statistics of individual and cumulative non-cancer risks of PTEs due to rice consumption along river Swat in Malakand district.

Elements	HQ Adult				HQ Children			
	Mean	Mini	Max	SD	Mean	Mini	Max	SD
Al	3.94E-02	2.15E-02	6.23E-02	1.33E-02	4.68E-02	2.54E-02	7.39E-02	1.58E-02
As	5.17E+00	1.62E-03	1.08E+01	3.53E+00	6.13E+00	1.92E-03	1.28E+01	4.18E+00
Cr	3.50E+00	5.00E-02	6.51E+00	1.96E+00	4.15E+00	5.93E-02	7.73E+00	2.33E+00
Cu	1.04E+00	7.74E-02	1.64E+00	5.69E-01	1.23E+00	9.19E-02	1.95E+00	6.75E-01
Fe	2.61E-01	5.04E-02	7.41E-01	3.04E-01	3.10E-01	5.98E-02	8.79E-01	3.60E-01
Mn	1.18E-01	2.45E-02	1.99E-01	7.32E-02	1.39E-01	2.91E-02	2.37E-01	8.69E-02
Ni	8.49E-02	4.26E-03	1.79E-01	5.47E-02	1.01E-01	5.06E-03	2.12E-01	6.49E-02
Sr	5.43E-02	7.35E-03	9.55E-02	3.49E-02	6.45E-02	8.72E-03	1.13E-01	4.14E-02
Zn	2.17E+01	1.47E-02	2.94E+01	1.01E+01	2.57E+01	1.74E-02	3.49E+01	1.20E+01
HI	**3.19E+01**	9.78E-01	**4.66E+01**	1.49E+01	**3.79E+01**	**1.16E+00**	**5.53E+01**	1.77E+01

Table 7
Cancer risks for individual PTEs due to consumption of rice grown along the Swat river in Malakand district.

Variable	Adult			Children		
	Mean	Mini	Max	Mean	Mini	Max
As	2.67E-03	1.32E-03	4.85E-03	3.17E-03	1.57E-03	5.75E-03
Cr	1.59E-02	3.89E-03	7.49E-02	1.89E-02	4.62E-03	8.89E-02
Ni	2.09E-03	9.81E-04	3.88E-03	2.48E-03	1.16E-03	4.60E-03
TCR	2.07E-02	6.54E-03	8.12E-02	2.27E-02	7.75E-03	8.36E-02

Note: The [181] safe limit for carcinogenic risk is 1×10^{-6} and 1×10^{-4}.

mean concentrations (mg/kg) of Al (10914.30), Fe (4699.70), Ti (600.50), Mn (149.30), V (39.20), Sr (35.10), Cr (26.60), Cu (20), Ni (18.40), Si (12.50), Zn (5.80) and Zr (2.80) also dropped within the acceptable thresholds of both world average shale and the Earth's crust. However, concentrations (mg/kg) of phosphorus (291.50) and As (5.30) surpassed permissible limits of worldwide average shale (125–1.60 mg/kg) and Earth's crust (84–0.80 mg/kg) (Table 1). Similar results for elevated concentrations (mg/kg) of phosphorus (4700) and As (18.5) were recorded by Refs. [45,95] in DI Khan and Chitral regions of Pakistan. Phosphorus enrichment in paddy soils, often resulting from phosphate fertilizer application, has direct effects on rice root health [96]. The application of phosphorus (P) in paddy fields contaminated with arsenic (As) leads to the formation of iron plaques, which enhances the adsorption of As species and lowers the As content in rice. This implies that phosphorus can be considered as a viable alternative for mitigating arsenic-induced toxicity [97,98]. Agrochemicals like insecticides, hormones, and fungicides serve as significant contributors of arsenic (As), leading to an augmentation of its concentration in the soil [99]. Arsenic mobilization in paddy soils is dependent upon dynamics of iron, pH, organic matter and the speciation of arsenic [100]. The current study revealed that accumulation of PTEs in nearby paddy soils is a consequence of human activities, notably the extensive fertilizer application in agriculture, and utilization of domestic sewage and industrial effluents for crop irrigation [9,13,14,101]. This situation poses a substantial threat to public health.

3.2. *Looking for associations and contamination sources in paddy soil*

Potentially Toxic Elements (PTEs) exhibit intricate geochemical behavior, and their concentrations are compositional as their attributes vary together [102]. Therefore, it is essential to identify any anomalous patterns that could be associated with the sources of PTEs pollution in a given area [102,103]. Compositional data (CoDa) techniques, such as variation matrices, biplots or CoDa dendrograms, have proven to be powerful tools for determining pollution sources [102,104]. The normalized variation matrix indicates a linear relationship among the subcomposition components within a dataset of compositions [105]. Variations below 0.2 indicate proportionality or a linear relationship, whereas variations exceeding 1.0 signify an absence of proportionality or linear association within the compositional dataset [102]**.** In the present study, the contributions of less than 0.2 for Ca, Mg, Ni, Al, As, Cr, K, Sr, and V to pH and EC (Table 2) indicate that these pairs are proportional and explain that soils where these elements are available are formed from basic rocks and the mobility of PTEs is influenced by high pH [106,107]. Similarly, the lowest inputs to the ratios of Mg to Ca (0.08), Ni to Cr (0.09) and Mg (0.06), Mn to Mg (0.09), Sr to Ni (0.08) and V to Cr (0.06), and Mg (0.07) and Ni (0.08) (Table 2) show associations between pairs of elements. This relationship is further exemplified by the observation that soils containing magnesium (Mg) also exhibit richness in calcium (Ca). Similarly, this pattern holds true for other combinations like Ni, Cr and Mg, Mn–Mg, Sr–Ni, as well as V, Cr, Mg and Ni [108]. The validity of the normalized variation matrix findings was confirmed through a biplot (Fig. 2), revealing that As, Cr, V, and P share the same ray direction and have closely arranged vertices. This distinct association is likely linked to the lithospheric composition and the influence of fertilizers [109,110]. Similarly, a close association was observed between Mg–Cu–K and Ca–Ni–Mn–Sr which is evident from their closely positioned vertices and shared ray direction (Fig. 2). This association could stem from a combination of both anthropogenic and geogenic factors [110]. Distinct associations are formed by Fe, Si, Al, and Ti, as their vertices closely cluster together, and rays pointing in same direction. These associations are likely attributed to riverbed erosion [111]. Zinc (Zn) and Zr exhibit a robust association due to the alignment of rays in the same direction and the proximity of their vertices. This association suggests the input of impurities from smelters and chemical industries [112,113].

3.3. *Evaluation of potentially toxic and mineral elements in rice grains*

The contamination of rice by PTEs is one of the main health concern which received greater attention worldwide [114–116]. In this study, Table 3 shows great variations in concentrations of minerals and PTEs in rice grains. Concentrations of Ca (60.70–2451.30), P (1544.40–3524.60) and K (1410.60–4202.60), with mean values of 903.83, 2396.70 and 2585.93 mg/kg, dropped within the acceptable limits [117]. However, concentration of Mg (463.81 ± 213.89) surpassed the approved limit of 350 mg/kg (Table 3). The concentrations of Sr (2.40–58.80), Ti (3.40–74.50) and Zn (2.60–13.40), with mean values of 27.03, 35.70 and 7.63 mg/kg, remained within the acceptable limits (Table 3). Whereas, mean concentrations (mg/kg) of Al (70.40), As (1.23), Cr (12.53), Cu (36.07), Fe (144.32), Mn (13.89) and Ni (1.60) exceeded the allowable limits [117] (Table 3). Similar results were also recorded by Refs. [9,24] for Cd, Fe, Cu, Mn and Al, with mean concentrations of 0.2, 50.70, 17.60, 7.49, and 6.80 mg/kg, surpassing the permissible limits [117]. Similarly, mean concentration (mg/kg) of Al (143.66) in the Iranian code six rice variety was twice that in our current study [118]. Overall, the concentrations in rice grain samples were in increasing order of As < Ni < Zr < Cr < Mn < Sr < Ti < Cu < Al < Fe < Mg < Ca < P < K. Moreover, the results of this study are consistent with those of [9,26,52,119–121], who also reported higher concentrations of Cu, Ni, Mn, As, Al, and Cr in rice grains. Therefore, investigation of the dietary concentration of PTEs is essential, as they were identified above the limit of detection (LOD) in all samples. According to Refs. [122,123], the smaller ionic radius and weaker soil binding of magnesium (Mg) make it more mobile in soil than Ca, K, or Na, influencing plant Mg nutrition. Mg is essential for plant growth and contributes to chlorophyll synthesis, enzyme activation, ribosome subunit aggregation for protein synthesis, and cadmium accumulation mitigation in rice plants [124–126]. However, increased Mg intake is linked to decreased systemic inflammation, reduced blood pressure, and a decreased risk of metabolic syndrome [127,128].

Similarly, aluminum (Al) lacks a significant role in the human body, and its introduction can harm the nervous system, potentially leading to Alzheimer's disease [129,130]. Arsenic (As) poisoning results in severe health issues, including kidney, bladder, prostate, skin, and lung cancer; restrictive respiratory and ischemic heart disease; melanosis; hyperkeratosis; diabetes mellitus; gangrene; hypertension; and peripheral vascular disease [99,118,131]. Chromium (Cr) improve cognitive function, regulate blood sugar, and facilitate the breakdown of carbohydrates and lipids, all crucial for maintaining overall health [132]. An overabundance of dietary chromium (Cr) intake can lead to gastrointestinal discomfort and hypoglycemia [133]. Moreover, Cr over supplementation can damage the liver, kidneys, and nerves, possibly leading to an irregular heartbeat [134,135]. Copper (Cu) plays an essential role in sustaining organ development and normal fetal growth [136]. However, high copper consumption is linked to impaired development and reproduction, as indicated by preclinical study findings in the literature [137,138].

Iron (Fe), a vital nutrient, is indispensable for the activity of enzymes and proteins, especially hemoglobin and myoglobin, facilitating the transportation of oxygen. Iron deficiency leads to anemia, impacting around 1.2 billion people worldwide [139]. However, Fe toxicity stems from its capacity to generate free radicals, which serve as crucial growth factors for various infectious organisms and neoplastic cells [140]. Likewise, manganese (Mn), a vital trace element, acts as a cofactor for numerous enzymes but is neurotoxic and prone to excessive cellular accumulation [141]. Prolonged exposure with higher manganese (Mn) levels, whether environmental or in occupational settings, results in manganism, a neurodegenerative condition with Parkinsonian symptoms similar to Parkinson's disease (PD) [142,143]. Within the central nervous system, toxicity from manganese (Mn) triggers apoptosis and gliosis in particular brain regions, including the substantia nigra pars reticulata, striatum and globus pallidus. Mn also elicits rapid responses from astrocytes and microglia, contributing to its impact [141,144]. Apart from nickel carbonyls, almost all nickel compounds are considered non-toxic when ingested orally, primarily owing to their minimal absorption from the gastrointestinal (GI) tract [145]. Elevated serum nickel levels, however, can induce coronary vasoconstriction in individuals with angina pectoris and myocardial infarction [146]. Therefore, the current study provides significant findings regarding the manifold interactions among the studied elements, revealing their essential roles, health complications, and environmental considerations.

3.4. *Transfer of mineral nutrients and potentially toxic elements into rice grains*

Transfer factor (TF) denotes a plant's capacity to transport ions from its roots to aboveground portions. TF is a convenient technique for measuring element concentrations in plant tissues relative to its concentrations in soil [26]. A TF greater than one (TF > 1) signifies enhanced elemental uptake from the soil by the plant, indicating its suitability for phytoremediation. Conversely, lower TF values (TF < 1) indicate a reduced plant response to element absorption, indicating that the plant is suitable for human consumption [147]. Table 3 summarizes the soil−rice grain transfer factor (TF) and PTEs concentrations. A TF < 1 for Cr, Al, Mg, As, Ca, Ni, Fe, Mn, Ti, and Sr in rice grains suggests their suitability for human consumption. In Fig. 3, high TF > 1 for P, Cu, K, and Zn, show increased elemental uptake from soil to rice grains [148]. A high transfer factor of phosphorus (P) is vital for crop productivity. However, humans and non-ruminants, such as fish, poultry and swine, cannot digest the main form of phosphorus (phytate) in grains due to its binding to mixed salts of phytic acids, which requires enzymatic dephosphorylation for availability [149,150]. A decrease in phosphorus accumulation in grains would promote sustainable and biologically friendly agriculture (Yamaji et al., 2017). Likewise, copper (Cu)

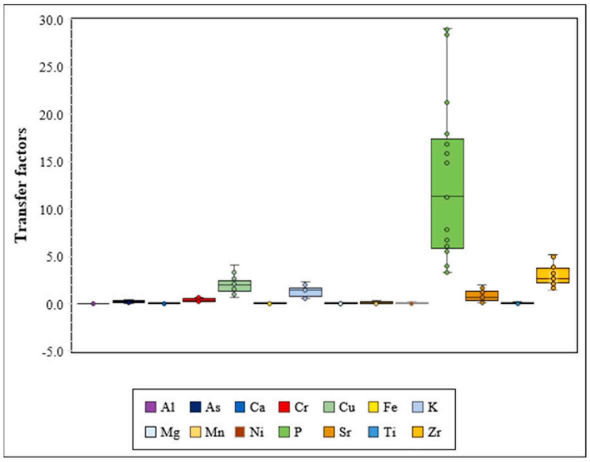


Fig. 3. Comparative account of Transfer factor (TF) of elements.

plays a vital role in plant growth, and toxic at high concentrations. The accumulation of Cu in rice grains is directly linked to the safety considerations for both rice and humans [67,151]. Zinc, an essential cofactor, can be toxic when present at elevated levels. Ingestion of high doses of zinc sulfate and concentrated zinc chloride can lead to acute toxicity, due to their direct corrosive effects, characterized primarily by gastrointestinal symptoms such as hematemesis [152,153]. Similarly, potassium (K), the most prevalent cation in plants, confers tolerance to biotic, abiotic stresses including extreme temperatures, drought, diseases, and insect pests [154]. According to Ref. [155], insufficient K intake increases the risk of rise blood pressure, mainly when coupled with high Na intake. Conversely, sufficient ingestion of potassium help in lowering blood pressure, partly by promoting improved vasodilation and increased urinary sodium excretion [156]. Therefore, a higher TF > 1 for potassium is considered safe for human health.

To enhance understanding of the primary factors governing soil to plant transfer in the study region, Table 4 shows the maximum to minimum concentration ratios of elements in paddy soils and rice grains with corresponding TF ratios. There were slight variations in concentration ratios of K, Al, Mg, Ni, Ca, Mn, As, Zn, Ti and Sr between rice grains and TF. A significant variations exhibited by Fe, Cr, P and Cu concentration ratios of rice with transfer factor. Likewise, iron (Fe), Cr, Ti, Mn, As, and Mg concentration ratios in rice grains were almost twofold those observed in the soil (Table 4). For Ni, Al, Sr, and Ca, the concentration ratios in the rice grains were 3–5 times and 17 times higher than those in the soil, respectively. However, soil K, P and Zn concentrations were higher than in rice grains (Table 4). Concentration patterns of elements in rice grains (Table 4) were explained from soil concentrations (Table 1) or by the linear relationships between pH and EC and between Ca, Mg, Ni, Al, As, Cr, K, and Sr (Table 2). This suggests that these pairs exhibit proportionality and influence the mobility of PTEs [106,157]. Moreover, factors such as nutrient requirements, rice cultivar, genetic composition, and climatic conditions further impact the absorption of elements [10].

3.5. Daily intake of PTEs through rice

For evaluation of people diets, dietary intake is a consistent method, provides important insight into potential nutrient deficiencies or exposure to food contaminants [158,159]. The EDI (mg/kg/person/day) serves as a primary method for evaluating probable health risks linked to PTEs intake through vegetables and cereal crops consumption [160]. The people of Pakistan widely incorporate rice into their diet as a fundamental source of dietary energy [161]. However, rice holds considerable potential for the accumulation of PTEs [116]. Therefore, it is highly important to obtain information on the extent to which useful and toxic elements are absorbed through rice consumption.

In the current study, the EDI values of PTEs for children and adults from rice consumption were calculated and presented in Table 5. For adults, mean EDI values (mg/kg/person/day) of Al (3.94E-02), Cu (5.22E-02), Fe (2.11E-01), Mn (1.95E-02), Ni (2.30E-03), Sr (3.70E-02) and Zn (1.08E-02) were within the PTDI safe limits (Table 5). Similarly, for children mean EDI values (mg/kg/person/day) of Al (4.68E-02), Cu (6.19E-02), Fe (2.51E-01), Mn (2.31E-02), Ni (2.72E-03), Sr (4.39E-02) and Zn (1.28E-02) were also within the PTDI safe limits (Table 5).

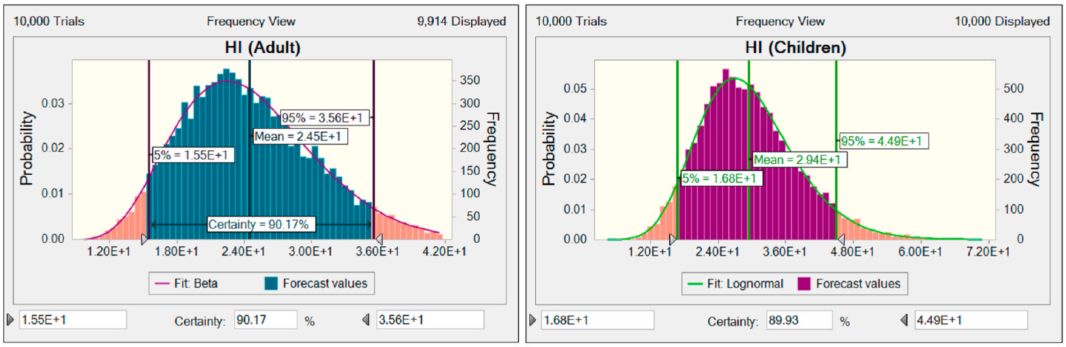
The mean EDI values of As (2.11E-03) and Cr (2.09E-02) for children, and for adults As (1.78E-03) and Cr (1.76E-02) exceeded the recommended safety limits of PTDI (Table 5), indicating health risks. Likewise, mean high EDI values of As and Cr for children than in adults, signifying high risk for children. In the current study, high EDI values for As, Cr and Ni align with findings reported by Ref. [73] for individuals in Bangladesh. In northern Pakistan [162], reported similar results, with higher EDI for Cr, As, Ni, and Cd in children and adults, suggested potential health risks linked with contaminated food consumption. Similarly [163], reported elevated concentrations of As in various rice varieties and rice based food products in India, suggests contamination of food supply chain and aligns with our current results.

3.6. Assessment of noncarcinogenic risk

The noncarcinogenic risk from exposure to PTEs for children and adults were assessed using deterministic and probabilistic approaches. Hazard quotient (HQ > 1) for exposure to As, Cr, Cu, and Zn through rice ingestion in both children and adults suggest probable health risks (Table 6). The HQ values for As (6.13E+00), Cr (4.15E+0), Zn (2.57E+01), and Cu (1.23E+0) were higher in children compared to adults. This suggests a higher susceptibility to noncarcinogenic risks in children. The high HQ values for individual elements result from intensive agricultural practices, smelting, mining, and the discharge of industrial effluents into water resources used for irrigating agricultural land [164]. [165,166] reported that HQ > 1 indicates unsafe ingestion of food material and poses a high risk to consumers. In the current study, HQ values for Cr, As, Zn, and Cu surpassed the acceptable limit of one (HQ > 1). This suggests that regular rice consumption is unsafe and not recommended for the population.

Similarly, hazard index (HI) quantifies cumulative noncarcinogenic effects associated with ingestion of multiple elements by food crops [73]. HI above 1.0 signifies a potential noncarcinogenic health risk, whereas HI below 1.0 suggests nonappearance of health hazard [167]. In the current study, HI > 1 for children (3.79E+01) and for adults (3.19E+01) (Table 6), demonstrate vulnerability to noncarcinogenic risks in both population groups. Moreover, the contribution rates of Cr, Zn, Cu, and As to the hazard index (HI) exceeded those of Al, Mn, Ni, and Sr (Table 6). According to Ref. [70], HI > 1 indicates a potential health risk for humans and is of great concern. Similarly, HI > 1 for Pb, Co and Cd exposure through riin individuals of the Tangail district population of Bangladesh, indicated probable adverse health risk and strongly support our current study results [165]. reported HI > 1 for Pb, Co and Cd exposure linked to rice consumption in the Bangladesh population, indicating likely adverse health risks that strongly align with the findings of our present study.

In Figures (4a-b), the Monte Carlo simulation presenting probability distributions for hazard index (HI) in both children and adults. The HI values exceeded 1.0 at mean, 5th and 95th percentiles, with confidence levels of 90.17% and 89.93% for adults and children,



(a) (b)

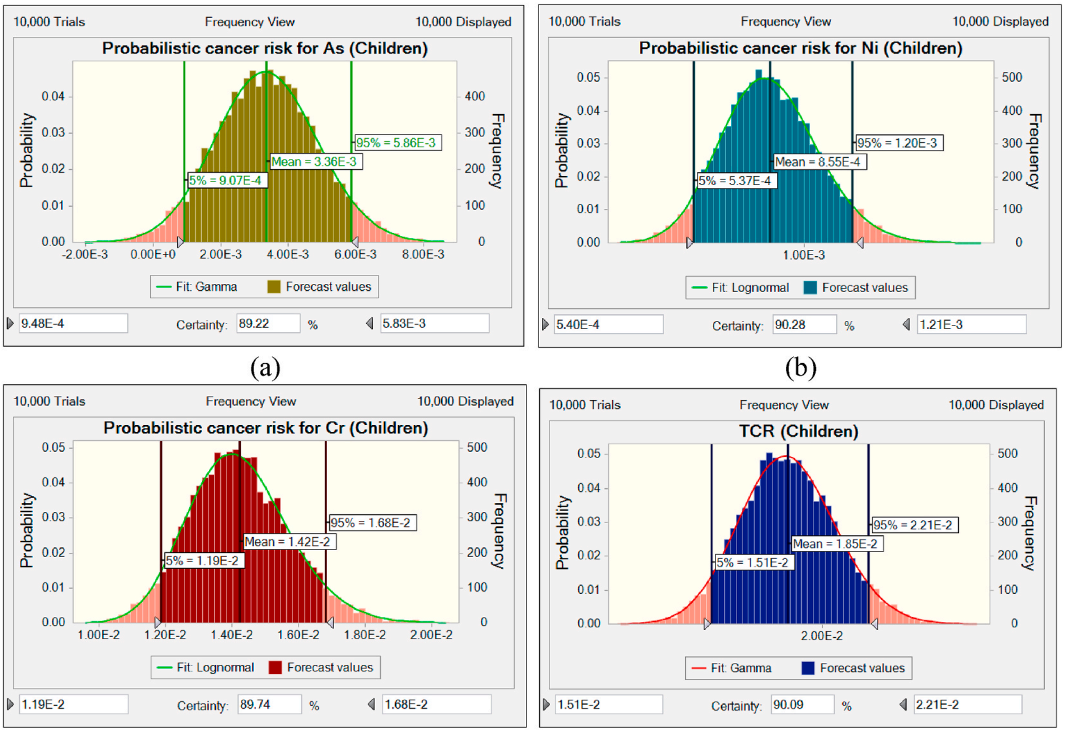
Fig. 4. Probability distribution of hazard index (HI) for (a) adult (b) children.

respectively. This finding suggested that the adults and children face substantial noncarcinogenic hazards from dietary exposure to PTEs through rice consumption. Additionally, the current study demonstrated that the probability distribution of HI (Fig. 4a–b) was slightly greater than that of the deterministic values (Table 5). This variation proposes that the probabilistic assessment method considers all potential scenarios, even the extremes that the deterministic approach might overlook [39].

3.7. Assessment of carcinogenic risk

The carcinogenic risk is the likelihood of developing cancer in individuals at some point in their life from exposure to carcinogens [168]. The values of deterministic and probabilistic cancer risks for Cr, Ni and As resulting from rice consumption in adults and children are presented in Table 7 and Fig. 5a–d.

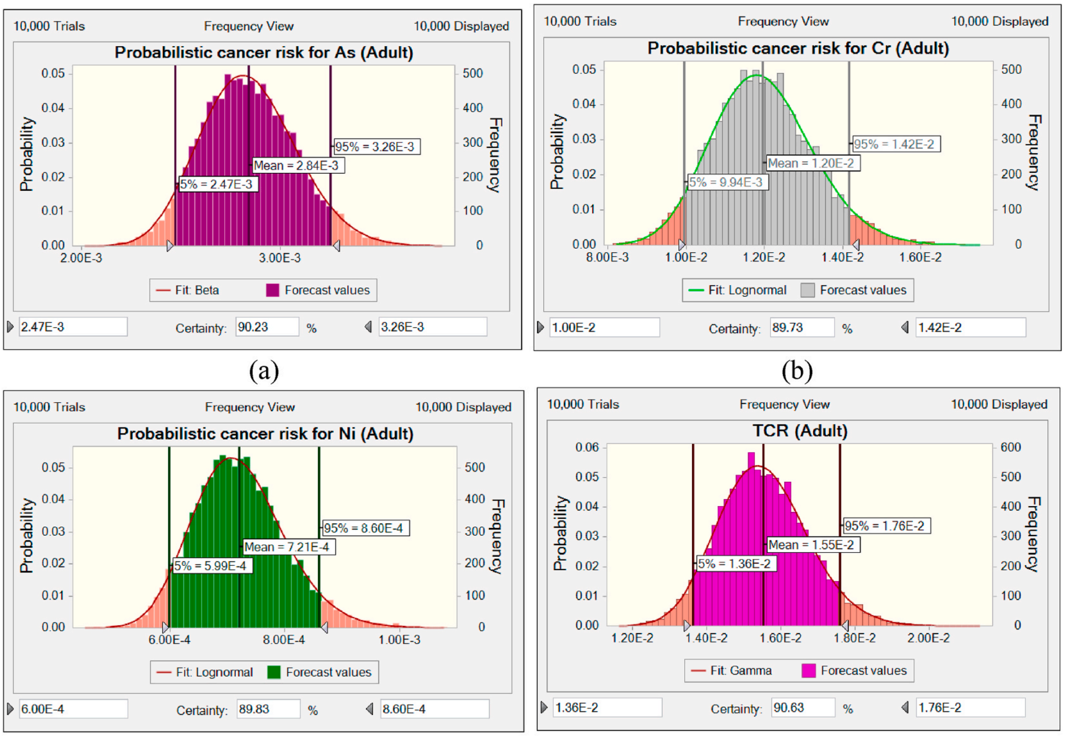
In children, the mean deterministic cancer risks (CR) for As (3.17E-03), Cr (1.89E-02), and Ni (2.48E-03) were slightly greater than those in adults for As (2.67E-03), Cr (1.59E-02), and Ni (2.09E-03) and exceeded the safety limits (Table 7). The total carcinogenic risk



(a) (b)

(c) (d)

Fig. 5. Probability distributions for carcinogenic risk of (a) arsenic (b) nickel (c) chromium (d) total cancer risk in children through rice consumption.



(a) (b) (c) (d)

Fig. 6. Probability distributions for carcinogenic risk of (a) arsenic (b) chromium (c) nickel (d) total cancer risk in adult via rice consumption.

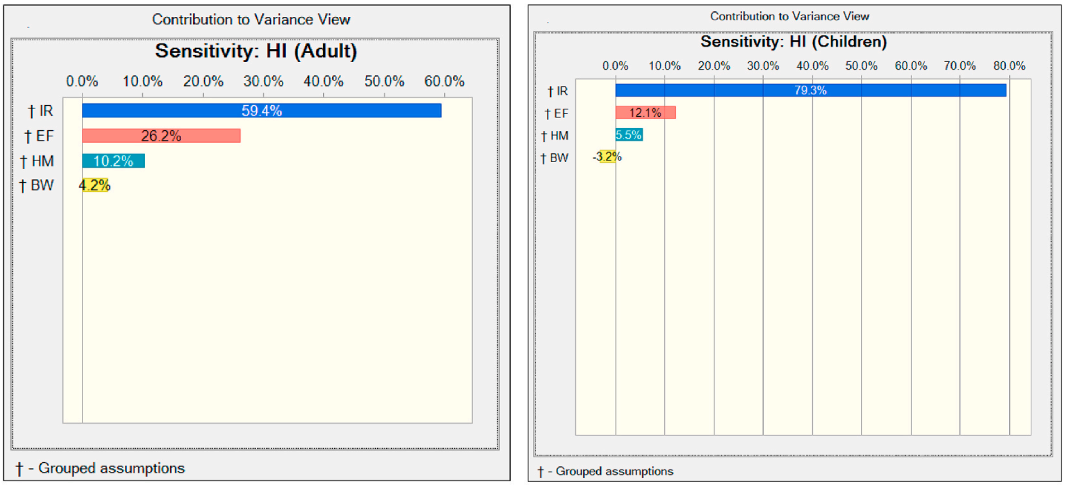
(TCR) values, 2.27E-02 in children and 2.07E-02 in adults, significantly exceeded the acceptable limit of 1 × 10^{-6} and 1 × 10^{-4}. This strongly shows that the cancer risk associated with residents' rice consumption varies, with significantly different risk levels [169].

In addition to the deterministic cancer risk, the probabilistic cancer risk values simulated through Monte Carlo simulation are shown in Fig. 5a–d. This method considered the accurate distribution of parameters, including element concentration, exposure frequency, body weight, ingestion rate, and exposure duration (Tables S–3). The probabilistic cancer risk values for children at the 5th, mean, and 95th percentiles for As (9.07E-4, 3.36E-3, 5.86E-3), Cr (1.19E-2, 1.42E-2, 1.68E-2), and Ni (5.37E-4, 8.55E-4, 1.20E-3), with certainties of 89.22%, 89.74%, and 90.28%, respectively (Fig. 5a–d), exceeded the lower threshold limit of 1 × 10^{-6}. In adults, the probabilistic cancer values for As (2.47E-3, 2.84E-3, 3.26E-3), Cr (9.94E-3, 1.20E-2, 1.42E-2), and Ni (5.99E-4, 7.21E-4, 8.60E-4) at the 5th, mean, and 95th percentiles exceeded the minimum acceptable limits of 1 × 10^{-6} (Fig. 6a–d). Similarly, the probability values of total cancer risk for children (1.51E-2, 1.85E-2, 2.21E-2) and adults (1.36E-2, 1.55E-2, 1.76E-2) at the 5th, mean, and 95th percentiles, with certainties of 90.09% and 90.63%, respectively, were above the acceptable limits of 1 × 10^{-6} and 1 × 10^{-4}. (Fig. 5-d & Fig. 6-d).

Approximately 90.36% of the inhabitants encountered total carcinogenic risk (TCR) exposure exceeding 1 × 10^{-6} (Fig. 5-d & Fig. 6-d). These findings indicate that children and adults face an undesirable cancer risk through the dietary intake of Cr, Ni, and As from rice consumption. In addition, the values of deterministic cancer risk slightly exceeded the probabilistic cancer risk values. This disparity can be ascribed to overestimation of risk resulting from the inherent uncertainties in deterministic analysis [170]. According to Refs. [71,171], cancer risks below 1 × 10^{-6} are negligible, above 1 × 10^{-4} are unacceptable, and from 1 × 10^{-6} and 1 × 10^{-4} are considered acceptable. The current analysis indicates that adults and children in the study area face a higher risk of developing cancer from rice consumption. Similarly [73,118,172], reported comparable outcomes when studying the effects of As and Pb exposure on individuals in Bangladesh and Iran who consumed rice. As indicated by Refs. [173,174], the probable health hazard in the study area is amplified by additional exposures to PTEs through the consumption of fish and vegetables. In the neighboring district (Dir), the cancer incidence rate was 15.04 per 100,000 people. The prevalence of common cancers, including blood, stomach cancers, breast, and skin suggests dietary exposure to PTEs [94].

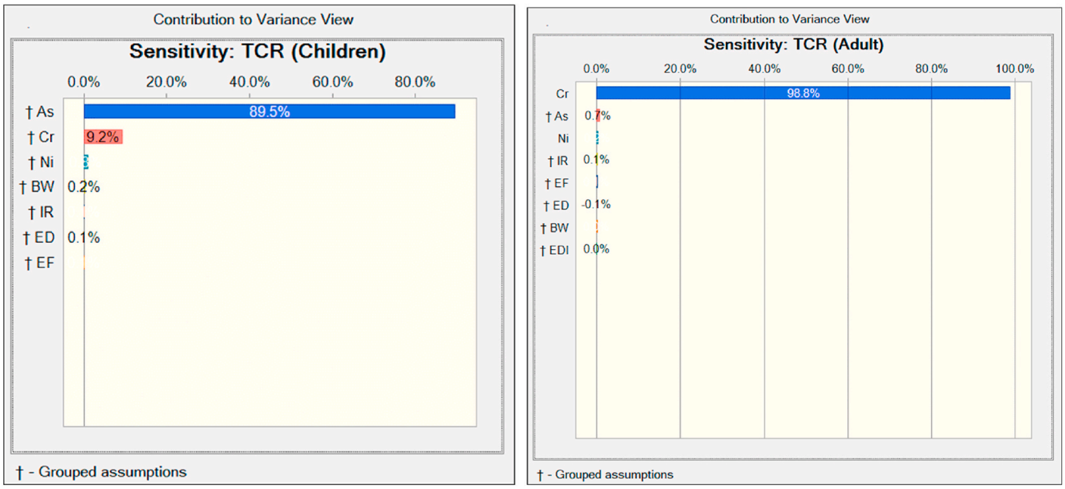
3.8. *Sensitivity analysis*

Sensitivity analysis was conducted to evaluate the importance of variables in estimation of noncarcinogenic and carcinogenic risks [175]. Sensitivity analysis of hazard index (HI) in children indicated significant influence of ingestion rate (79.3%) on hazard index, followed by exposure frequency (12.1%), and PTEs concentration (5.5%), and categorized as key noncancerous risk factors (Fig. 7-a). Likewise, for adults, the key factors for noncancerous risk were ingestion rate (59.4%), exposure frequency (26.2%), PTEs concentration (10.2%), and body weight (4.2%) (Fig. 7-b). The current findings align with those of [70], who also reported ingestion rate as



(a) (b)

Fig. 7. Contribution of exposure factors to hazad index (HI) via rice consumption for (a) adult (b) children.



(a) (b)

Fig. 8. Contribution of exposure factors to total cancer risk (TCR) via rice consumption for (a) children (b) adult.

main influencing factor of health risk, followed by exposure duration and PTEs concentration, while body weight is less influential. In children, the relatively higher contribution of arsenic (89.5%) compared to Cr (9.2%) and Ni (3.0%) to TCR (Fig. 8-a) indicates a more significant impact of arsenic on TCR. Similarly, in adults, a prominent contribution to TCR was simulated for Cr (98.8%). The contribution of arsenic (As) and nickel (Ni) to the total carcinogenic risk due to rice consumption in adults were negligible. The current findings align with [176–178], where it was reported that PTEs like cadmium (Cd), arsenic (As), nickel (Ni) and chromium (Cr) played a predominant role in the overall variance of risk.

4. Conclusion

The current study examined PTEs concentrations in paddy soil, their transfer to rice grains, evaluated potential sources and allied health hazards for individuals through consumption of rice. The soil water suspension exhibited saline nature, with excessive phosphorous (P) concentrations above permissible limits. Various factors resulting from both natural geology and human activities categorized sources of pollution sources as vehicle emissions, industrial effluents, smeltering activities, and unnecessary usage of inorganic fertilizers. The levels of Mg, Ni, As, Cu, Al, Fe, Cr and Mn in rice grains exceeded the safety limits set by FAO/WHO. A high transfer factor (TF) indicated elevated uptake of P, Cu, K, and Zn from the soil to the rice grains. The noncaricnogenic risk exposure to PTEs from rice consumption in children were more significant than for adults. The study identified significant differences in carcinogenic risk among children and adults, primarily attributed to Cr, As and Ni exposure through rice consumption, impacting a considerable portion of the population. Sensitivity analysis pinpointed key noncancerous risk factors for different age groups. Arsenic has emerged as a major contributor to cancer risk in children, while chromium plays a predominant role in adults. This study highlight the importance of addressing probable health hazards associated with consumption of rice raised on contaminated soils. To mitigate potential health risks, it is essential to implement measures for monitoring and controlling the levels of PTEs in water, soil and rice crops. Additionally, educating consumers about safe rice consumption practices is crucial.

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Consent for publication

We declare that this manuscript is original, has not been published before and is not currently being considered for publication elsewhere.

Ethics approval and consent to participate

The current research study was approved by the Institutional Research Committee of Islamia College Peshawar. The article does not include any humans or animals as research objects.

Data availability statement

All the data supporting the results of this study are included in this article.

CRediT authorship contribution statement

Asghar Khan: Writing – original draft, Validation, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Muhammad Saleem Khan:** Writing – review & editing, Supervision, Resources, Project administration, Conceptualization. **Munib Ahmed Shafique:** Writing – review & editing, Visualization, Validation, Resources, Formal analysis. **Qaisar Khan:** Writing – review & editing, Visualization, Validation, Data curation. **Ghulam Saddiq:** Writing – review & editing, Visualization, Validation, Formal analysis.

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.

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Appendix A. Supplementary data

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