Arsenic Speciation in Rice, Mechanisms and Associated Health Risk Through Rice Consumption in Various Districts of Khyber Pakhtunkhwa, Pakistan

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Abstract

Arsenic (As) is one of the toxic metalloids therefore can cause health risk in the consumers through consumption of contaminated food and rice. The current study focused on As speciation in rice, bioavailability, mechanisms and its potential human health risk. For this purpose, rice and soil samples were collected from 16 different districts (non-mining and mining) of Khyber Pakhtunkhwa (Pakistan). Soil physicochemical characteristic such as texture, electrical conductivity (EC), organic matter (OM), pH, iron (Fe) and phosphorus (P) were determined. Total arsenic (As_T) concentrations were analyzed using ICP-MS, while the arsenite (As^{3+}), arsenate (As^{5+}), arsenobetine (BAs), dimethylarsenic (DMA) and monomethyl arsenic (MMA) were determined by HPLC−ICP-MS method. Results showed the highest As_T (0.28 mg/kg) was observed in the rice samples of DI Khan District and lowest (0.06 mg/kg) in Shangla District. However, these findings were found within the permissible limits set by various authorities. Furthermore, results showed higher concentrations of inorganic As (As_i) than organic As (As_o) species in rice. The estimated daily intake (EDI) and incremental lifetime cancer risk (ILTCR) were used to evaluate the potential human health risk for As consumption in rice. Results revealed that the rice samples collected from the district having mining activities had higher value of As (0.28 mg/kg of As_T) as compared to non-mining (0.072 mg/kg of As_T). The highest ILTCR value (0.00196) was observed for rice collected from mining districts. This study revealed that mining activities have great influence on the As contamination of soil and grown rice. This study recommends the soil amendment in districts having mining activities to lower As availability in soil and its bioaccumulation in growing rice that will help to keep lower the potential risk.

Introduction

Arsenic (As) is carcinogenic in nature (Rehman et al. 2019) and considered as one of the most readily available and harmful metalloids (Mitra et al. 2020); Garbinski et al. 2019). It ranked at 20th position in abundance among elements found on our Earth and present in soil, water and living organism (Mitra et al. 2020). The As release into the environment from both the geogenic sources such as denudation of bedrocks and ore deposit (Kumar et al. 2016; Sathe and Mahanta 2019) and anthropogenic activities including mining, agrochemicals, industrial effluents and emission (Muhammad et al. 2010; Gan et al. 2019). Once As is released into the environment, it could easily find ways to water (Rehman et al. 2019). When the water contaminated with As is used for irrigation purposes such as in rice fields it is deposited in soil (Huhmann et al. 2019; Upadhyay et al. 2019). Paddy soils are naturally rich in As (Kato et al. 2019) that further aggravated by contaminated water irrigation (Gan et al. 2019).

The As mobilization and bioavailability were influenced by several factors including speciation, pH, reducing environment (Eh), Fe (iron) (Yamaguchi et al. 2011) and its uptake in the rhizosphere of soil-plant system (Anawar et al. 2018; Kowalczyk and Latowski 2018). Flooded paddies soils had the characteristics that resulted in the mobilization of As, thus enhancing its bioavailability and uptake in rice plant (Yamaguchi et al. 2011). Furthermore, there are a number of characteristics (both biological and physical) of soil and rice, also its chemical characteristics have a great influence on the bioavailability of As in soil. The uptake and toxicity of As varies with varieties of rice (Aqeel et al. 2014; Pravalprukskul et al. 2018). The As_i species may be converted into organic arsenic (As_o) species through methylation governed by microbes' actions in the paddy field (Zhu et al. 2017; Afroz et al. 2019). Tetramethylarsonium (TMA) was mostly found in rice grain of China emanating from the contaminated paddy soil that had average account 5.9% of the total arsenic (As_T) concentration (Meharg and Zhao 2012). It is because of the anoxic environment of the paddies in which rice is grown, rice can uptake

As^{3+} more efficiently than other cereals (Williams et al. 2007). Accumulation capability of rice to store As is almost double than other grain plants like barley and wheat (Su et al. 2010). The contamination of As in rice plant and grains result in food chain contamination and could pose serious public health concern (Lei et al. 2013).

The exposure of As (Long-term exposure) contamination through water and food lead to a wide range of lesions such as melanosis, leucomelanosis and keratosis (Rahman et al. 2009b). Higher As contamination results in high blood pressure, neurological effects, obstetric problems, diabetes mellitus, respiratory diseases and blood diseases such as cancers mostly skin, bladder and lungs (Ahmed et al. 2016). Prolong exposure of As is not only carcinogenic, but it may also disturb nervous system (O'Bryant et al. 2011; Mundey et al. 2013), respiratory system (Parvez et al. 2013; Recio-Vega et al. 2014) also immune system (Martin-Chouly et al. 2011; Srivastava et al. 2013). The excessive As in the body of human may also alter the reproductive system functioning (Davila-Esqueda et al. 2012; Shen et al. 2013).

Earlier research studies have been conducted on the As poisoning in water of Pakistan (Mosood et al. 2019) and Kohistan region of Khyber Pakhtunkhwa (Muhammad et al. 2010) and Dera Ghazi Khan (Malana and Khosa 2011) also Peshawar district (Khan et al. 2015), in rice and wheat (Rasheed et al., 2017) and As speciation in vegetables of southern districts of Pakistan (Rehman et al. 2016). However, no systematic study conducted to investigate the speciation in rice, mechanisms involved in the formation of these species and their uptake by the rice and its associated human health risk. This study will determine As speciation not only in rice but also soil of the same sites so that it shows the mechanisms involved in its bioavailability and uptake by rice plant. This study will also evaluate the potential chronic risk and cancer risk associated with the ingestion of As contaminated rice.

Materials And Methods

2.1 Study area

Khyber Pakhtunkhwa is situated in the NW region of the Pakistan 34.9526° N, 72.3311° E along the international border with Afghanistan (Claus et al. 2003). The climate of Khyber Pakhtunkhwa differs vastly ranging from Dera Ismail Khan, (the hottest place) to skurdo (the coldest place). Due to unlimited diversity in soil and climate, Khyber Pakhtunkhwa produces more than 42 crops; most popular are wheat, maize, rice, barley, tobacco, rape and mustard, sugarcane, groundnut, pulses, fruits and vegetables. Rice production in Khyber pakhtunkhwa according to the 2013-2014 government report is; Peshawar 340, Charsadda 114, Mardan 1739, Swabi 348, Hangu 201, Mansehra 2320, Batgram 1816, Malakand 4960, Swat 5559, Bunir 214, Shangla 1452, Dir lower 4278, Dir uppr 4250, Chitral 1809, DI Khan 12554 and Bannu 2209.

The research work was carried out in the selected districts of Khyber Pakhtunkhwa (Banu, Buner, Battagram, Charsadda, Dera Ismail Khan, Chitral, Hangu, Malakand, Mardan, Mansehra, Swabi, Peshwar, Swat, Shangla, Dir Lower and Dir Upper) which are rice producing areas as shown in the location map (SI). The sites were selected on the basis of rice production in each district and low rice production sites were excluded. Whole study area was divided into two groups mining and non-mining. This was done so as to study the effect of mining activities on the As contamination in both soil and rice.

2.2 Samples collection and pre-treatment

Rice grain samples (1 kg) were collected in polyethene zip-bags from the field having replicates (n=6-10) in each study area district. From base of each uprooted rice, surface soil (0-15 cm) samples were collected in polyethene zip-bags and numbered accordingly. Global position system (GPS, Garman eTrex 30) was used to measure the latitudes and longitudes of each selected sampling points. All rice (n=135) and soil samples (n=135) were taken to laboratory for further analytical procedures.

2.3 Soil characteristics

Physiochemical characteristics including electric Conductivity (EC), pH, Organic Matter (OM), Iron (Fe), Phosphorus (P) and texture were measured according to standard procedures (Table 1). Soil EC and pH were measured in solution of soil and deionized water (1:2.5) with Accumet XL 60 meter equipped both electrodes (pH and EC) (Muhammad et al. 2011). Mastersizer 2000 (Malvern Instruments Ltd, UK) was used to determine the soil particle size (sand, silt and clay) according to operational manual of the instrument. The quantified data was converted into percentage (Li et al., 2018). Weight-loss procedure was used to analyze OM in soil samples (Roper et al., 2019). The concentration of iron (Fe) and phosphourse (P) were measured according to the procedure adopted from the (Kumar et al. 2011) and (Khan et al. 2016).

2.4 Digestion of soil and rice grains

Soil and rice samples were dried in air powdered and passed over 2mm mesh and oven dried. Soil samples were grounded manually with the help of mortar and pestle while rice samples were powdered with Vibrating disc mill (Fritsch, Germany). For the digestion of soil, samples weight 0.2 g were taken and 5 mL HCl (hydrochloric acid (12.0 mol/L)) and 5 mL HNO_3 (nitric acid (15.2 mol/L)) was added, the samples were left overnight at room temperature and then digested with the help of block digester at 100^oC for 1 h, followed by at 120^oC for 1 h, and lastly at 140^oC for 4 h.

Rice samples were digested by taking 0.2 g of rice grain samples and 2 mL of HNO_3 was added and left overnight. Followed by the addition of 2 mL of H_2O_2 (hydrogen peroxide) was added, and the samples were digested using a microwave accelerated reaction system (CEM-Mars,Version 194A05, USA). Initially temperature was raised to 55^0C for 10 min, then raised to 75^0C for 10 min, and lastly to 95^0C for 30 min, and then the samples were cooled at room temperature. The 0.22 µm membrane was used to filter the digested samples and de-ionized water was added to dilute the samples and make it up till 50 mL. ICP-MS (Agilent Technologies, 7500 CX, USA) was used to analyze As_T concentrations while Fe was determined with (AAS atomic absorption spectrometer (Perkin Elmer, AAS-PEA-700) and P was determined with ICP-OES (Perkin Elmer Optima 7000 DV, USA) (Khan et al. 2014).

For the extraction and quantification of As species ((AsIII), (AsV), (DMA), (MMA) and (BAs)), 200 mg of powdered rice samples were placed in 50 ml polypropylene tubes and 10 ml of 1% (v/v) HNO_3 was added to them. For the sample extraction, Microwave assisted digestion technique was used (Jia et al. 2012). Different species of As in the extracts were analyzed with the help of HPLC–ICP-MS. The selected arsenic species were separated with the help of an anion-exchange column (PRP X-100, Hamilton Company, USA) with the mobile phase of 10 mM $(NH_4)_2HPO_4$ and 10 mM NH_4NO_3 (pH 6.2). Total As_i was calculated as the sum of AsIII and AsV, while total As_o was calculated as the sum of MMA, DMA and BAs. The extraction efficiency was 83.8 to 87.9% (SI) of these As species from reference material (mentioned in Sec 2.5) which is considered as satisfactory. The detection limits for As species ranged from 0.1 to 0.3 µg/kg. For the method validation, the sample solution obtained from digestion in microwave oven was selected due to the lesser time consumption involved and the lower blank values. The analytical method validation was performed by considering the LOD. All the analytical methods and validation is carried out according to Magnusson (2014) guidelines.

2.5 Precision and accuracy

For the verification of accuracy of the data standards and blanks run on column at the start and with regular 10 samples interval. Soil and rice flour certified reference materials (GBW07406-GSS-6 and GBW-10045) were used to verify the extraction efficiency and As species stability. These certified reference materials were dried at 50^{o}C for 6 h before microwave digestion. Thus, As content was not affected by the low temperature treatment. HNO_3 (2% of the concentrated acid (65%)) and Milli-Q water were used to wash glass wares and plastic bottles properly. The recovery rates from reference materials were in the range of 92.1 ± 6.3 to 101.3 ± 8.3 %.

2.6 Dietary intake and risk assessment

2.6.1 Calculation of Estimated Daily intake

Estimated daily intake was calculated by the expression suggested by Khan et al. 2014

$$\text{EDI}=\frac{C_m \times IR_{rice} \times EF \times ED}{\text{LE} \times \text{Bw}}$$

Where;

EF = exposure frequency (365 days per year)

ED = exposure duration (70 years)

BW = average body weight (73 Kg) and

LE = life expectancy (25550 days) (Zhuang et al. 2009; Li et al. 2011).

C_m = concentration of the heavy metal i.e As.

IRrice = Rice intake rate (398.3 g/adult person/day) (Zheng et al. 2007).

2.6.2 Incremental Lifetime Cancer risk

The ILTCR (Incremental lifetime cancer risk) for As_i was calculated using the equation (USEPA, 2010; Li et al. 2009):

$$\text{ILTCR} = \frac{\left(\sum_i \text{IRi} \times \text{Ci}\right) \times ED \times EF}{\text{Bw} \times \text{LE}} \times CSF$$

Where;

CSF = Cancer slop factor (1.5 mg/kg/d) (USEPA 2010).

2.7 Statistical analysis

Data were analyzed using computer software's like MS Excel (Office 2013) and SPSS 11.5, Sigma plot 10.0 for figures and Arc GIS ver. 10.5 for maps were used.

Results

3.1 Physical and chemical characteristics of Soil

Results of the texture shows that soil varied from sandy loam to loamy sand (Table 1). Higher EC value was measured for Mansehra (7.53 mS/cm) and lower in Upper Dir (0.77 mS/cm). Highest soil OM was observed in DI Khan (4.7%) and lower in Lower Dir (2.0%). Maximum pH value was observed for Banu (8.1) and minimum for DI Khan (7.4). Low pH of the DI soil could be attributed to higher OM. Higher values of P were found in DI Khan (0.47 g/kg) and lower in Charsadda (0.15 g/kg) and that of Fe were in Upper Dir (3.37 g/kg) and lower in Charsadda (2.06 g/kg).

3.2 Arsenic in soil

Figure 1 represent the values of As_i and As_o found in the soils of Khyber Pakhtunkhwa. Overall results shows that the percentage of As_i is more as compared to As_o while in some areas percentage of the As_o is higher than the As_i. The highest value of As_i was recorded for 79.6% for Buner, while the lowest was 34.6% for Swat district. Also, for As_o, the higher percentage 72.3%, was found in Malakand and the lowest was 20.2% for Buner. This is due to the fact that As^{3+} can be converted into organic forms of As by the process of methylation encouraged by microbial activities in soil paddies (Islam et al. 2004).

In soil the mean As_i ranged from 2.27-4.54 mg/kg, while it was higher in Upper Dir and lower in Banu district. As far as As_o is concerned, it was higher in Swat district (mean=5.73 mg/kg) and lower in Buner (mean=1.11 mg/kg). Similarly, mean As_T was higher in Chitral district (mean=13.72 mg/kg) and lowest in Banu (mean=4.31 mg/kg). The higher values of As in Chitral and swat was due to the mining activities in those areas. All these concentrations were below normal level of As in soil (30 mg/kg) (SEPA 1995). Roychowdhury et al. (2005) reported the highest concentration of As in West Bengal soil (19.4 mg/kg). It is due to the fact that paddy soils are naturally abundant in As (Kato et al. 2019) that further is worsen by contaminated water irrigation (Gan et al. 2019). Flooded paddies soils had the characteristics that resulted in the mobilization of As, thus enhancing its bioavailability and uptake of rice plant (Yamaguchi et al. 2011). Jehan et al. 2019, reported As concentration values in Chitral soil was 10.24 mg/kg, which is much lower as compared to the present study result (13.72 mg/kg). Marin et al. 1992 analyze that bioavailability of As to rice plant shows the following order As^{3+} > MMA >As^{5+} > DMA. All the species of As are taken up through rice roots, however organic form of As is taken up slower than the inorganic form (Abedin et al. 2002).

3.3 Arsenic in rice

The rice samples collected from 16 different districts of Khyber Pakhtunkhwa show variation in As species concentration and are presented in Fig 2 (S10) of SI. The As_i concentration in the rice ranged from 0.05-0.24 mg/kg with high level in DI Khan and low level in Shangla district (Fig 2). Similarly, the As_o ranged from 0.002-

0.02 mg/kg with maximum concentration in Charsadda and minimun in Mardan. Also, the As_T was ranged 0.06-0.28 mg/kg, which was higher in DI Khan and lower in Shangla.

Flooded rice paddies has the characteristics of reducing environment, and this anoxic condition enhances the availability and mobility of As^{3+} as compared to that of As^{5+}, because of the process of dissolution of Fe (Niazi et al. 2011; Shakoor et al. 2018). Earlier studies showed that As_i and DMA were the most common species of As detected in rice (Meharg et al., 2009; Zhu et al. 2008), while MMA occurred rarely with low content (Zhao et al. 2013b). Wu et al. 2019) also found similar result that the concentration of different species of As (As^{3+}, As^{5+}, and DMA) dominates in rice grains, but, no MMA was found in the samples of rice. For As_T the highest concentration was in DI Khan rice 0.28 mg/kg and lower in Shangla rice 0.062 mg/kg, which is much less than the study conducted by Jehan et al. 2019 (3.33 mg/kg). The studies had explained that in Pakistan the rice are cultivated in paddy soils that could possible host higher As concentration (Kato et al. 2019). Also, this contamination increases because of irrigation of soil with As-contaminated water irrigation (Gan et al. 2019). Another reason may be the capacity of rice to accumulate As double than other grains i.e. wheat and barley (Jehan et al. 2019; Mitani et al. 2009; Ma et al. 2008). Selenite and selenate are found to facilitate the arsenate adsorption by paddy soil also they inhibited the uptake of arsenate by rice roots. Further selenate has stronger inhibition on iAs transfer factors than selenite (Pokhrel et al. 2020).

Numerous researches on speciation of As in South and South East Asia found As_i which is highly toxic constitute about 42%-91% of As_T in rice while in America rice, the major specie of As is DMA (Schoof et al. 1999; Meharg et al. 2009). Other researches also showed that As_i (75%-90%) is high in different products of rice such as, baby rice, rice crackers, breakfast cereals, rice milk, and other products of rice (Sun et al. 2009).

3.4 Relation of Arsenic and soil physicochemical characteristics

Clayey and silty soils have finer texture, more surface area and higher As scavenging capability as compared to sandy soils, which is because of the Fe oxides presence. Hence, clayey soils plants show less toxic effects of As; As phytotoxicity is five times high in loamy and sandy soils (Quazi et al. 2011).

The highest OM value is present in soils containing dolomite, while those with greater pyrite and phyllosilicates levels showed very less OM content. The results shown that samples with higher OM content, displayed lower As content. Soil OM is responsible for the mobility of As also its complexes (soluble or insoluble) and chemical nature (William et al. 2011). Pikaray et al. (2005) testified that solubility of As decreased in soils with high value of OM, which affect its accessibility to plant, as OM has a high affinity for sorption of As because of the formation of different OM complex. However, on the other side, there is a positive correlation between As accumulation and soil OM in rice grain (Jia et al. 2013). OM increase in the soil can increase the As mobility with the help of increasing microbial activities and by decreasing redox potential of the soil (Turpeinen et al. 1999), which is a favorable condition for the reduction of Fe-oxyhydroxides which is linked to OM (Reza et al. 2010).

The highest adsorption was nearby pH 7 (Miyatake and Hayashi 2011). Tabassum et al. 2018 and Bibi et al. (2015b) presented strong positive correlation of As contents with pH, in Rawalpindi and Hasilpur areas. The leaching of As also its speciation depends upon the soil pH, therefore the availability of As as well as its solubility depends on soil pH (Chatterjee et al. 2013; Quazi et al. 2011). Some researches (Signes-Pastor et al. 2007) showed that the uptake and accumulation of As by rice plant is affected by both low and high pH. The reason may be that at low pH ($pH < 5$), Fe-oxyhydroxide compounds which are As-binding species, becoming highly soluble and increase the uptake of As by plants. Bhattacharya et al. 2010 also supported the negative relationship between soil pH and As concentration in rice. On the other hand, many authors supported the idea of a positive relationship between soil pH and As accumulation (Ahmed et al. 2011; Campbel et al. 1985). increasing soil pH (such as pH 8.5) rises the negative surface charges (hydroxyl ions), which facilitates As desorption from Fe-oxides that leads to mobilization of As in the root, which, in turn, increases accumulation of As in the plant (Ahmed et al. 2011). As the pH decreases As^{3+} solubility increases with the soil pH range (pH 3-9), whereas in the case of As^{5+} this pattern is reversed. In flooded paddy soils As^{3+} predominates. In this regard, for the current study, a decrease in soil pH can enhance the mobility of soil As, which gives the reason why we observed almost equal concentrations of As in rice grain irrespective of the levels of soil As (Sahoo and Kim 2013).

By the application of external P, the uptake of As is reduced and the toxicity symptoms of As^{5+} alleviates. Different researches (Pigna et al. 2010; Rahman and Hasegawa 2011) have described that with the increasing P value in nutrient solution, decreases As^{5+} uptake by the rice plant. In plant physiology and biochemistry, P plays a significant role (Shin et al. 2004). In As contaminated soil, there are some properties such as As concentration in soil solution, application of phosphatic fertilizers and other soil physicochemical properties control As uptake by rice plant (Geng et al. 2005; Farooq et al. 2016; Liu et al. 2004) described that if there is sufficient P in soil it will result in less Fe-plaques formation on the rice roots, while the lack of P in the soil solution enhances the plaque formation on the rice roots. Less amount of P in plant tissues can be useful in increasing oxygen transportation in rice roots (Kirk and Van Du 1997) which may encourage Fe plaque formation on the rice roots. Several studies supported the idea of application of phosphate to soil, lowers the As content in Fe-plaques leading to increase in solubility of As and bioavailability to the soil rhizosphere (Azam et al. 2016; Smith et al. 2002).

The Matsumoto et al. (2015) investigated that if the rice field is amended with Fe-oxide and metallic Fe, it will reduce As content in rice grain by 47% and 51%, respectively. This may be due to the fact that As binds with Fe-(hydr)/oxides in soil (Inskeep et al. 2002) which has a great effect on the mobility of As in soil solution (Marin et al. 1993). The strong affinity of Fe (an essential mineral of plants) towards As helps to decrease the As adsorption in rice (Yamane 1989; Nath et al. 2014). Some of the effects by the application of external Fe and its compounds in soil include: (i) Fe (Fe-oxide) deposits around rice roots reduces the uptake of As in rice roots, (ii) the co-precipitation of Fe and As enhances and (iii) it reduces the desorption of soluble As because of the adsorption of As^{5+} on the surface of Fe. Anaerobic condition for rice cultivation encourage the Fe-plaque formation around the roots of the rice plant (Armstrong 1964). Ferrihydrate (63%), siderite (5%) and goethite (32%) constitute Fe-plague (Hansel et al. 2002). The concentration of free Fe around the rice roots also rises its concentration in the rhizosphere that further lowers uptake of As in rice plants (Geng et al. 2005; Syu et al. 2014). Fe-plaques has high affinity towards As^{5+}, therefore it plays an important part in decreasing the As uptake in rice. For the sequestration of As, Fe-plague is probably the best solution which ultimatle reduces the transport of As from roots to shoot in rice plant (Liu et al. 2004). Leonardite had a higher efficiency to adsorb As than biochar’s because of the iron contents in leonardite which strongly bind to As anions (Dolphen and Thiravetyan 2019).

3.5 Comparison of As level in rice of mining and non-mining areas

One of the most important human activities that contaminate our environment with As is mining (Williams et al. 2009). Due to the presence of As in many minerals and other human activities such as mining, As-contaminated waste water irrigation, fertilizers and pesticides application containing As, As became one of the most common contaminants affecting human health via food chains (Zhu et al. 2014). As is present naturally in many ores such as Cu, Pb, Au and Zn ores. Therefore, in mine impacted areas, As is found in soils at higher levels, posing a risk to not only human health but also ecosystem health (Li et al. 2014). Current study reported high As_i, As_o and As_T in mining areas. In non-mining areas, the As_i concentration is higher in Peshawar (0.14 mg/kg) and while lower in Mardan (0.06 mg/ kg). As_o was higher in Charsadda (0.02 mg/kg) while lower in Mardan (0.002 mg/kg). While the concentration of As_T is higher in Peshawar (0.018 mg/kg) and lower in Mardan (0.07 mg/kg). By comparing these results with the mining areas result it was concluded that for As_i the highest value was detected in rice grown in DI Khan (0.24 mg/kg) and lowest in Shangla (0.05 mg/kg). For As_o the maximum concentration was detected in the rice of Lower Dir 0.03 mg/kg while the lowest concentration was found in Shangla (0.002 mg/kg). For As_T highest value is (0.28 mg/kg) in rice of DI Khan while lowest value is (0.06 mg/kg) in Shangla rice as shown in Fig 3. The overall results depicted that the highest values for the species of As as well as the As_T was in the rice of mining areas such as DI Khan. But there are some non-mining areas such as (Peshawar As_T= 0.18 mg/kg) which shows a little higher concentration than the mining areas (Buner As_T =0.09 mg/kg, Shangla As_T = 0.06 mg/kg and Upper Dir As_T = 0.08 mg/kg). The reason behind this may be due to higher level of pollution in Peshawar district. This gap need to be filled through further research that why non mining areas show higher concentration of As than the mining areas.

Both the natural and anthropogenic activities are the sources of As (Duan et al. 2013). Among the natural sources, volcanism and bed rocks weathering are important while among anthropogenic sources, metal mining and smelting, the use of As-pesticides, herbicides, feed additives, wood preservatives and irrigation with As-contaminated water are important sources that results in elevated levels of As in soil (Zhao et al. 2009). One of the main pathways of human exposure to As is the transport of As in soil-plant systems (Dave 2013). Most of the samples in mining sites shows a higher trend of As and its different species as compared to non-mining sites. The concentration of As in soil of mining area was higher (0.624 mg/kg) than the non-mining area (0.096 mg/kg) in Hunan Province, China (Zhu et al. 2008). As is a natural constituent some ores such as ores of Cu, Pb, Zn, and Au. This is the reason why As is mostly found at elevated levels, in mining areas soils posing a risk to health of both ecosystem and human (Li et al. 2014). None of the district of the study area exceeds the acceptable range (0.5 mg/kg) of As_T by (WHO 2011). Kwon et al., 2017 also stated that the values of As was high (0.247 mg/kg) in the rice of mining areas of Korea as compared to other lands.

3.6 As concentration in different rice types of Khyber Pakhtunkhwa

Arsenic concentration in different types of rice are presented in Fig 4, which shows that As_i is higher in basmati rice type (0.21 mg/kg) while low in khetai rice (0.03 mg/kg). As_o higher concentration was found in garma seela (0.3 mg/kg) while lower in china haripaka, china naray and khetai (0.00 mg/kg). Also the As_T concentration was high in basmati rice type (0.25 mg/kg) as compare to others, while lowest in Khetai rice (0.04 mg/kg). An overall assessment of As concentration was as follow; As_i basmati > garma seela > china polawal/ seela > china > aripaka (garma) > begamay/ naray > china naray/ china haripaka/ china begamay > aripaka > aripaka (yakha) khetai. As_o, garma seela > seela/ aripaka (garma) / china polawala > china / begamay/ basmati/ china begamay/ aripaka/ naray/ aripaka (yakha)/ china naray/ khetai/ china haripaka. As_T, Basmati > garma seela > seela > china polawala > china > aripaka (garma) > begamay > naray > china begamay > china haripaka > china naray > aripaka > aripaka (yakha) > khetai. Previous findings revealed that the average As values in American rice type (white Basmati) from Texas was (0.26 ± 0.08 mg/kg) (Zavala and Duxbury 2008).

3.7 Chronic Health Risk Assessment

3.7.1 Estimation of EDI

The local people were assumed to consume the local rice. In Pakistan, per capita consumption of rice is very low only 20.8 kg due to high cost of rice (Bashir et al. 2010). The mean estimated daily intake (EDI) and its standard deviation of As_i through rice consumption ranged from lowest 0.000273 mg/kg/day in Shangla to highest 0.00131mg/kg/day in DI Khan (Fig. 5). While, the estimated daily intake of As_o through rice consumption were ranged from 1.09×10^{-5} mg/kg/day in Mardan to 2.03×10^{-4} mg/kg/day in Lower Dir. Also, estimated daily intake for As_T showed that it was lower in Shangla (0.0003 mg/kg/day) higher in DI Khan (0.0015 mg/kg/day).

Previous findings indicate that EDI values for As_T were equivalent to those values calculated in Bangladesh rice (5.00×10^{-2}–5.00×10^{-1} mg/kg/day), Vietnam (1.1×10^{-3} –4.3×10^{-3} mg/kg/day) and Turkey (2.3×10^{-5}–5.21×10^{-3} mg/kg/day) (Caylak 2012; Karim 2000; Nguyen et al. 2009).

3.7.2 Cancer Risk Assessment

The cancer risk was calculated by the formula of ILTCR, which is attained by multiplying EDI of As_i with the CSF which is 1.5 for As_T. The ILTCR risk calculated was high for DI Khan district (1.9E-3 mg/kg/day). The lowest calculated cancer risk was for district Shangla (4.1E-4 mg/kg/day) as shown in Fig 6. Earlier risk assessments for As exposure via Indian rice consumption described risk results almost similar to this study using Indian intake values i.e. 7 adults in population of 10,000 (Meharg et al. 2009; Mondal and Polya 2008). In Bangladesh, studies (Meharg et al. 2009) also report same levels of cancer risk (with 19, 22 men and women 423 in10, 000 population) in adults.

Conclusion

The As speciation in rice plays an essential role in evaluating the human's toxicity. This study has focused on As speciation in rice, mechanism and the factors that can effect As uptake by rice. High rice consumption is the major exposure pathway of As in human beings. The rice in Pakistan is cultivated in paddy soils, which is one of the reason of As uptake by rice plants. The As^{3+} is the most toxic specie of As, which is highly carcinogenic in nature. Different factors such as redox Fe-Plague effect, pH, OM effect, soil texture effect, phosphate, As bond to Fe-Mn oxides, irrigation practices, seasonal variations and the genotype effect could affect the bioavailability and solubility of As in rice plants. These factors resulted in increasing or decreasing the As uptake by rice plant. The total level of soil As and rice As samples ranged from 13.72 mg/kg to 4.31 mg/kg and 0.28 mg/kg to 0.06 mg/kg respectively. The study analysis showed that there are mainly 5 As species (As(III), DMA, MMA, As(V) and BAs) in the rice samples, with As_i form being the most abundant and toxic species with concentrations of 0.23 mg/kg to 0.04 mg/kg. The hazardous effect of As on Khyber Pakhtunkhwa people cannot be neglected. The people of Khyber Pakhtunkhwa are at risk of exposure to adverse effects of As. Based on our study results, along with the risk assessment, we concluded that the values of ILTCR ranged from 4.1E-4 mg/kg/day to1.9E-3 mg/kg/d. While the said results are boosting further field research studies are needed to explore the sources of As contamination in rice paddies. Also factors that are responsible for the higher level of As in rice grown in non-mining areas.

Declarations

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Conflicts of interest/Competing interests; No conflict of interest.

Availability of data and material; all data and materials as well as software application or custom code support the published claims and comply with field standards.

Code availability; (software application or custom code)

Authors' contributions;

Tasneem Sarwar: Data collection, writing, methodology. Sardar Khan & Huang Qing: Supervision, editing, conceptualization. Javed Nawab & Said Muhammad: Reviewing and Editing. Shehla Amin: data collection. Janas Khan: software, visualization.

Ethics approval; NA

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Tables

Table 1. Physiochemical properties of soil in the selected districts of Khyber Pakhtunkhwa

Location	Sand %	Silt %	Clay %	Texture	pH	EC (mS/cm)	OM %	Fe(g/kg)	P(g/kg)
Batgram	65.6	33.8	0.59	Sandy loam	7.6±0.41	5.58±4.16	3.6±0.24	3.08±0.34	0.21±0.05
Banu	72.2	27.2	0.65	Loamy sand	8.1±0.64	1.69±2.53	4.2±0.97	3.17±0.13	0.22±0.06
Buner	72.0	27.4	0.64	Loamy sand	7.5±0.36	2.63±2.31	3.6±1.51	2.98±0.30	0.30±0.02
Shangla	67.0	32.6	0.58	Sandy loam	7.6±0.28	3.94±3.31	4.0±1.53	3.18±0.16	0.26±0.03
Swat	76.1	23.3	0.64	Loamy sand	7.9±0.14	0.85±0.07	4.3±0.25	2.67±0.14	0.23±0.06
Swabi	71.0	28.5	0.74	Loamy sand	7.6±0.29	0.77±0.04	4.1±0.72	3.26±0.19	0.30±0.06
Peshawar	63.0	36.4	0.69	Sandy loam	8.0±0.28	2.14±0.88	2.4±0.89	2.78±0.18	0.23±0.02
Hangu	55.2	43.7	0.69	Sandy loam	7.5±0.36	2.59±3.06	3.0±0.74	3.24±0.14	0.23±0.02
Mansehra	74.0	25.6	0.67	Loamy sand	7.6±0.35	7.53±0.24	4.6±0.60	3.19±0.22	0.22±0.02
Mardan	70.1	29.3	0.66	Loamy sand	7.7±0.33	0.78±0.19	4.6±1.29	3.23±0.18	0.24±0.09
Malakand	71.3	28.1	0.68	Loamy sand	7.6±0.32	1.70±0.16	3.7±0.95	2.45±0.94	0.24±0.10
Upper dir	55.0	44.3	0.65	Sandy loam	7.7±0.19	0.77±0.26	3.9±1.16	3.37±0.28	0.23±0.01
Lower dir	62.1	38.0	0.72	Sandy loam	7.6±0.26	1.08±0.58	2.0±0.45	3.16±0.53	0.23±0.02
Charsada	68.0	31.5	0.73	Sandy loam	8.0±0.19	1.22±0.41	3.7±1.34	2.06±0.87	0.15±0.08
Chitral	62.7	36.7	0.69	Sandy loam	7.6±0.31	2.57±0.61	3.7±1.70	2.66±1.03	0.27±0.05
DI Khan	74.8	24.5	0.76	Loamy sand	7.4±0.47	2.37±3.69	4.7±0.68	3.21±0.29	0.47±0.03

Figures

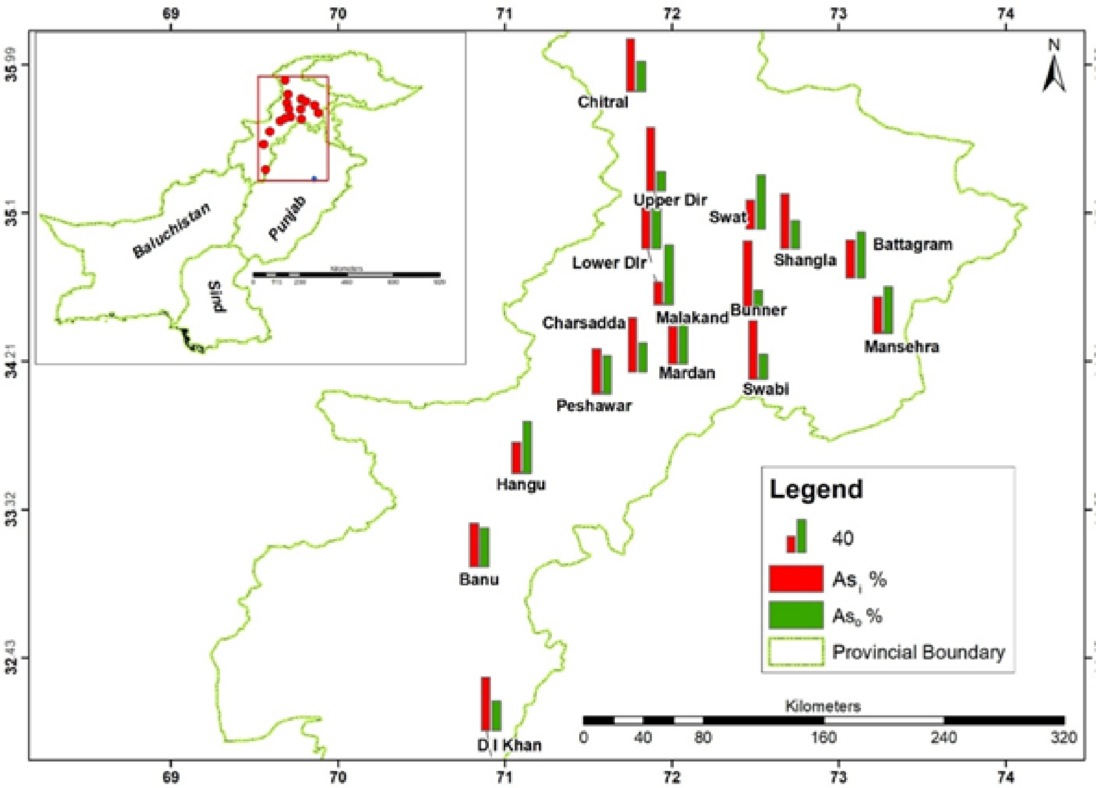

Figure 1

Inorganic and organic arsenic concentration in soil of selected Khyber Pakhtunkhwa districts

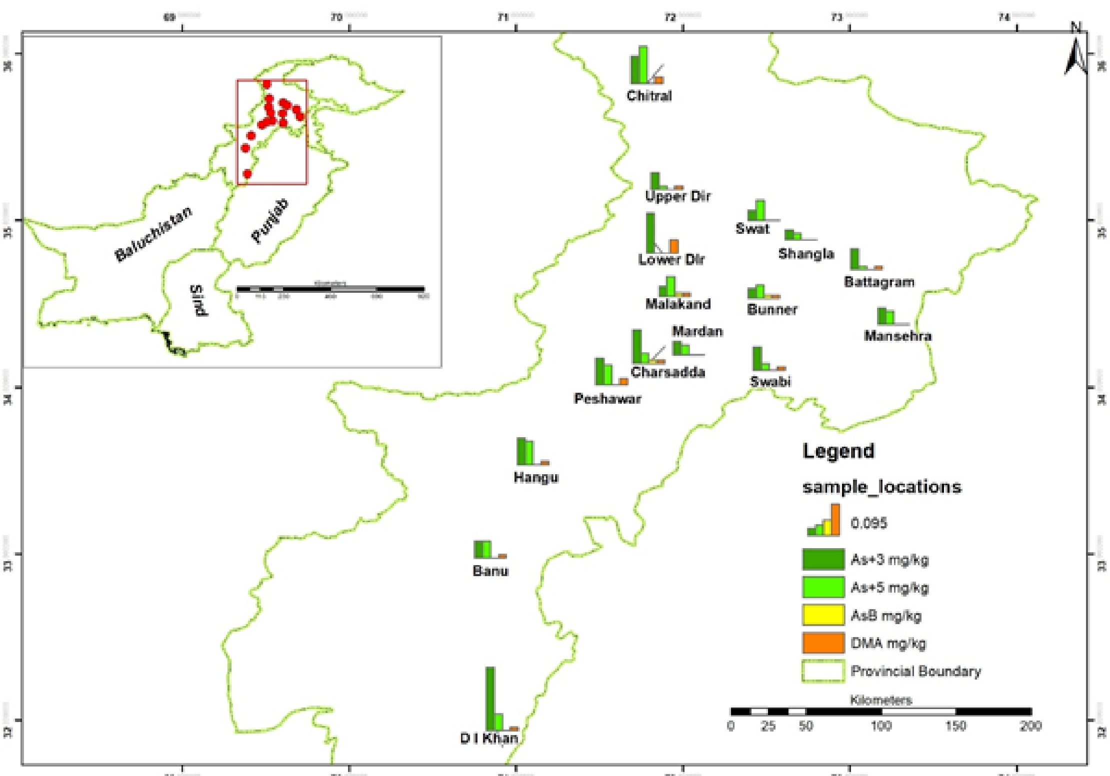

Figure 2

Arsenic speciation in rice of the selected districts of Khyber Pakhtunkhwa

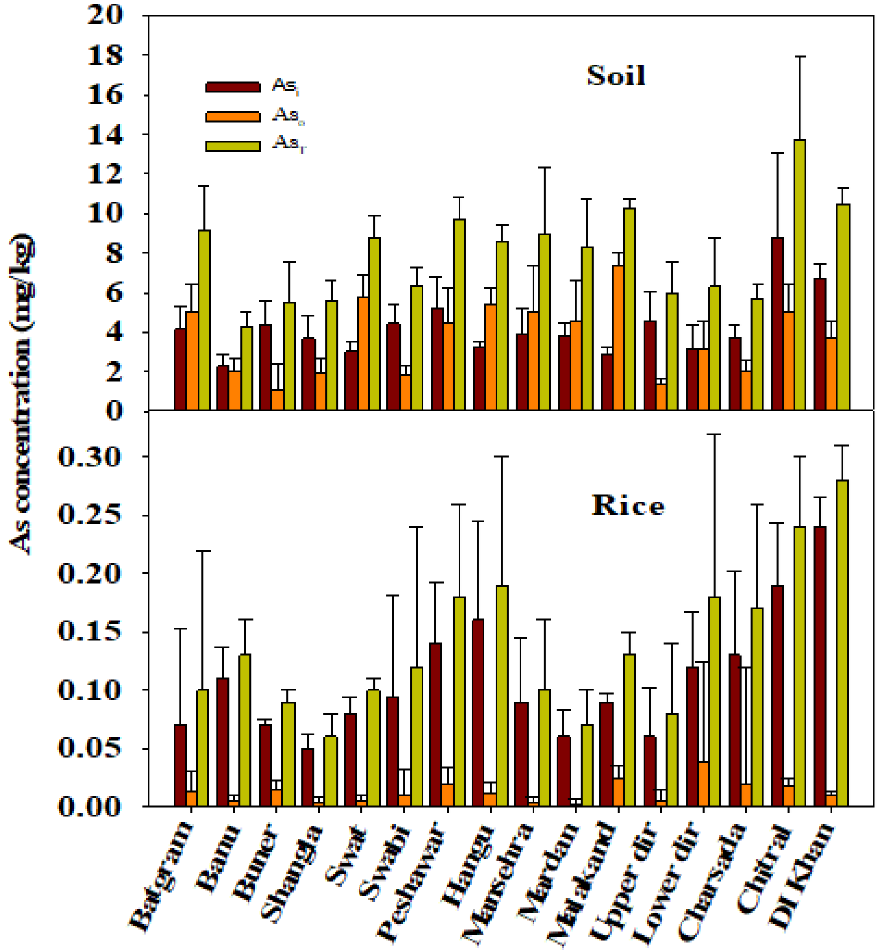

Figure 3

Comparison of As concentration in soil and rice of selected districts of Khyber Pakhtunkhwa

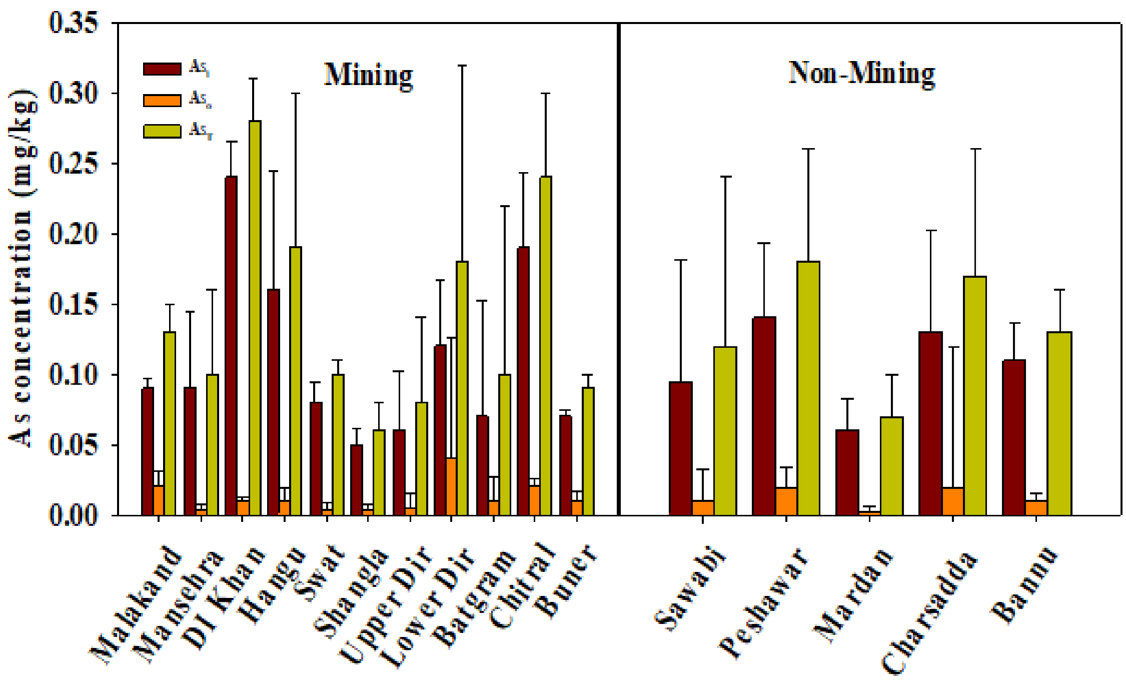

Figure 4

showing the comparison of As concentration in rice of mining and non-mining sites of selected districts of Khyber Pakhtunkhwa

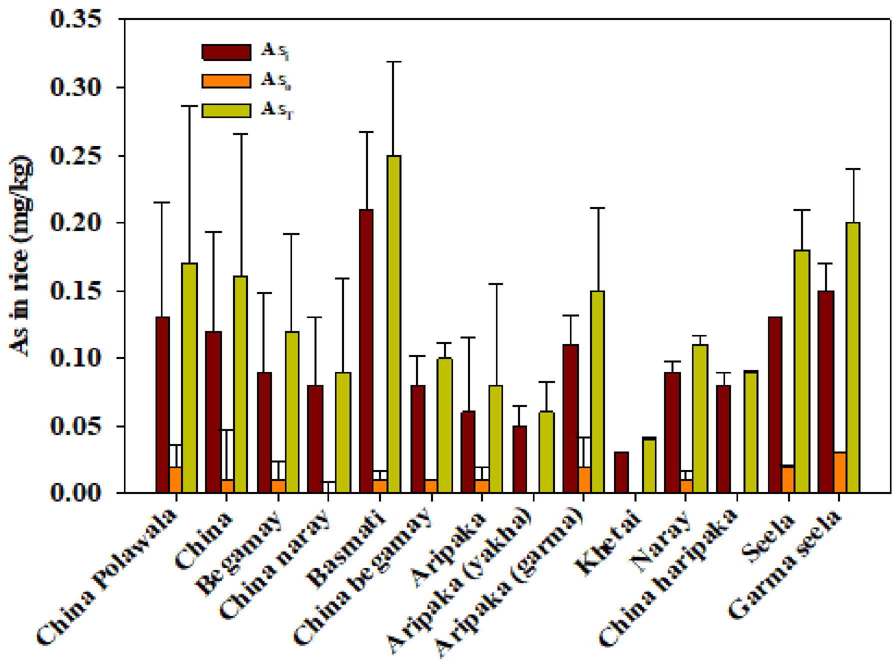

Figure 5

showing the comparison of As contamination in various types of rice in selected districts of Khyber Pakhtunkhwa

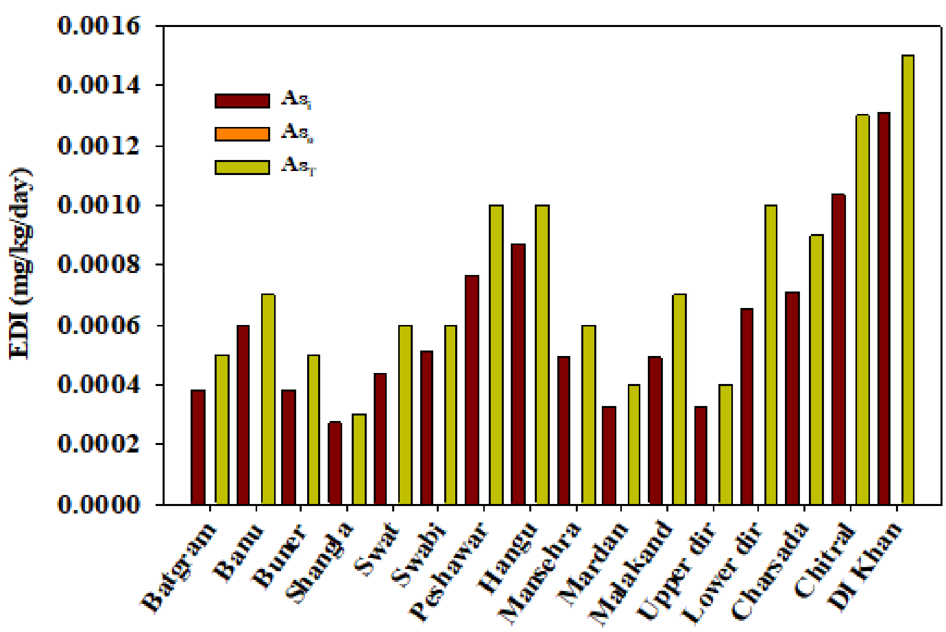

Figure 6

showing the values of EDI for the AsT, Aso and Asi through consumption of rice collected from selected districts of Khyber Pakhtunkhwa

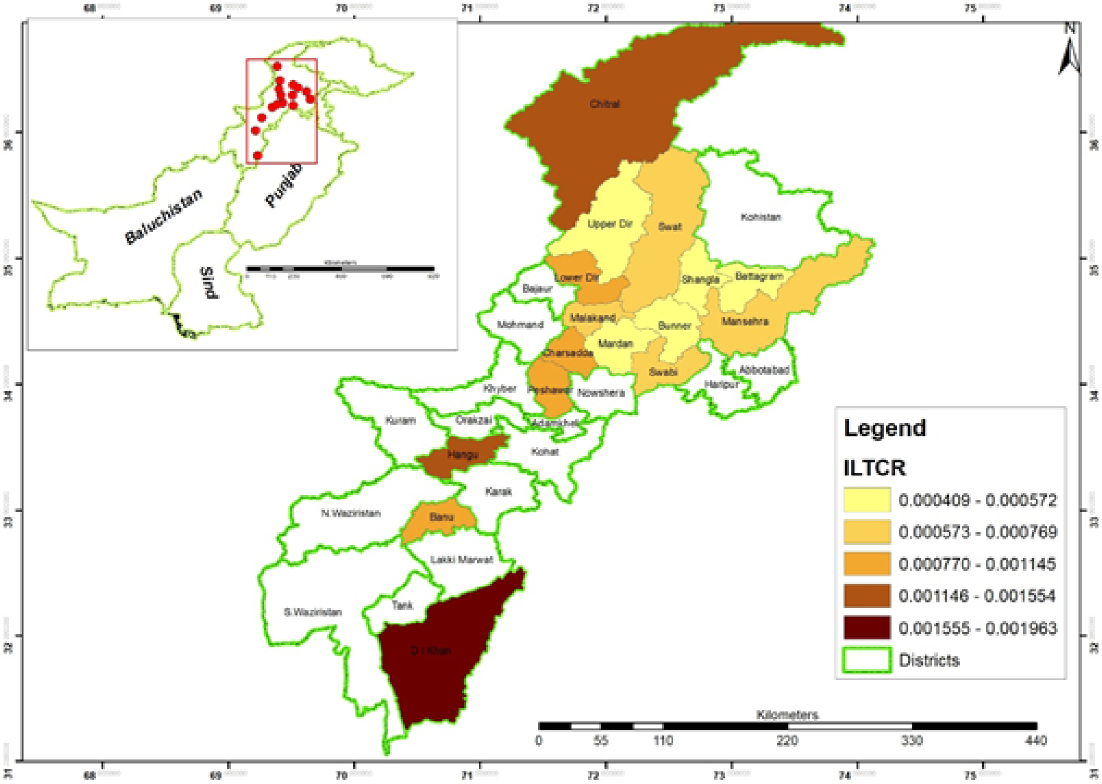

Figure 7

Showing the ILTCR for Asi through consumption of rice in selected districts of Khyber Pakhtunkhwa