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Human Arsenic exposure via dust across the different ecological zones of Pakistan

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ABSTRACT

The present study aims to assess the arsenic (As) levels into dust samples and its implications for human health, of four ecological zones of Pakistan, which included northern frozen mountains (FMZ), lower Himalyian wet mountains (WMZ), alluvial riverine plains (ARZ), and low lying agricultural areas (LLZ). Human nail samples ($N=180$) of general population were also collected from the similar areas and all the samples were analysed by using ICP-MS. In general the higher levels ($p<0.05$) in paired dust and human nail samples were observed from ARZ and LLZ than those of other mountainous areas (i.e., WMZ and FMZ), respectively. Current results suggested that elevated As concentrations were associated to both natural, (e.g. geogenic influences) and anthropogenic sources. Linear regression model values indicated that As levels into dust samples were associated with altitude ($r^2=0.23$), soil carbonate carbon density (SCC; $r^2=0.33$), and population density (PD; $r^2=0.25$). The relationship of paired dust and nail samples was also investigated and associations were found for As-nail and soil organic carbon density (SOC; $r^2=0.49$) and SCC ($r^2=0.19$) in each studied zone, evidencing the dust exposure as an important source of arsenic contamination in Pakistan. Risk estimation reflected higher hazard index (HI) values of non-carcinogenic risk (HI > 1) for children populations in all areas (except FMZ), and for adults in LLZ (0.74) and ARZ (0.55), suggesting that caution should be paid about the dust exposure. Similarly, carcinogenic risk assessment also highlighted potential threats to the residents of LLZ and ARZ, as in few cases (5–10%) the values exceeded the range of US-EPA threshold limits (10^{-6}–10^{-4}).

1. Introduction

Arsenic (As) has been widely reported to occur into earth's crust and is well known to have adverse health effects into human and wildlife (Mandal et al., 2003; Rodríguez-Lado et al., 2013; Subhani et al., 2015). During the last few decades, severe environmental degradation have also led to Arsenic mobilization into environment via surface run-off from surrounding agricultural fields, urban points, and several industrial activities i.e., coal combustion, brick kiln, stone crashing, steel mills, leather, paint and pesticides manufacturing factories (Hu et al., 2011; Subhani et al., 2015). Nevertheless, some other factors, including forest cover, geology, geographic position and climatic conditions of specific areas, may also play a fundamental role in the distinct large scale distribution scenario for dust-borne trace elements into the environment (Shah and Shaheen, 2007; Zheng et al., 2010). Pakistan possess flat-lying Indus Plain in the east, host three of the world's biggest and most spectacular mountain ranges, the Himalaya, the Karakoram and the Hindukush in the north, hill regions in the northwest, and the upland Baluchistan plateau in the west. The climate is mostly arid to semi-arid, although conditions are temperate in the north-west and arctic in the northern-mountains (Rafiq and Tahir, 1981). The different geological conditions create different hydro-geological regions in Pakistan, with young saturated Holocene sediments next to the Indus River and arid conditions towards the Thar desert in the southeast and

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Baluchistan in the western part of country. Taking into account all these factors, Pakistani environment is severely affected by geogenic As-contamination via natural processes i.e., alluvial material deposition through flooding into Indus delta, volcanic eruptions and also anthropogenic activities such as sewage irrigation, addition of animal manures, fertilizers and pesticides, etc. (Khan et al., 2010; Brahman et al., 2015; Bhowmik et al., 2015). Therefore, dust derived from these contaminated soils could contain high levels of different trace elements, including As (Subhani et al., 2015; Mohmand et al., 2015).

In developing countries such as Pakistan, most of the population inhibited into rural and sub urban areas, and are expected to expose to particulate matter/dust by both natural wind erosion and anthropogenic activities, such as use of agricultural chemicals, vehicle emissions, heating systems, building deterioration, construction and renovation works, corrosion of galvanized metal structures, etc. (Abdullah et al., 2015; Mohmand et al., 2015). Previous studies have extensively reported that As poses several potential risks to human health from either drinking water, food ingestion and/or air inhalation, and resulting into several health abnormalities e.g., hyperkeratosis, spotted melanosis, skin pigmentation and lung cancer, cardiovascular diseases, infertility (Shen et al., 2013; Brahman et al., 2015). Although different populations may be exposed to As through drinking water, but it is expected to be excreted rapidly via urination (Saha et al., 1999). However, when humans and other living organisms are exposed to contaminated dust via inhalation and/or ingestion, different toxic chemicals could be absorbed from the gastrointestinal tract and distributed into body through blood circulation, and affect normal body functions (Subhani et al., 2015). Human biomonitoring have been widely reported to quantify the concentrations of natural and synthetic compounds into body fluids (blood, urine and breast milk) and/or tissues (hair, nails, fat and bones). Moreover, this approach would be very useful to assess whether and to what extend chemicals have entered into human bodies and points toward the source (i.e., dietary and/or non-dietary) of these chemical (Brahman et al., 2015; Mohmand et al., 2015). However, this technique provides valuable information on environmental exposure and potential health risks at specific time period. In particular, keratin, the major structural protein in hair and nails, contains many cysteine residues, which are sites for As accumulation (Mandal et al., 2003; Subhani et al., 2015). Nails can be collected in a non-invasive manner, stored for an unlimited time, used for repeated analyses, easy to transport, and provide a longer term Arsenic exposure assessment (Vance et al., 1988; Saha et al., 1999; Subhani et al., 2015).

Pakistan, like other south Asian countries, has also been known as one of important hotspots in context of geogenic As contamination (Farooqi et al., 2007; Brahman et al., 2013). Nevertheless, taking into account the extensive land use activities and the climatic conditions of the region, Pakistan has characterized as one most vulnerable country in terms of dust and smoke production, which is generally twice of the developing world average and five times higher than those produced in the developed countries (Carmichael et al., 2009). To date, data on dust borne arsenic contamination and its implication for human health is scarce and need to be explored at wider spatial scale. In a recent study, Subhani et al. (2015) have reported outdoor As dust concentrations and their associations with biological samples (i.e. hair and nails of associated population), but the investigation was limited to only two cities of the Punjab province, Pakistan, and thus a detailed country wide study should be conducted. Moreover, biomonitoring of country-wide rural and sub-urban areas of Pakistan, where the agriculture sector mainly contributes towards the human dust exposure has never been investigated, which would be very useful to evaluate the possible human health implications. However, in the current study, the biomonitoring for environmental exposures of As has been investigated to assess levels and sources of As into dust and associated nail samples from four different ecological zones of the Pakistan and estimate the associated risks on human health.

2. Material and methods

2.1. Study area description

Pakistan is situated between the latitudes of 24° and 37° North and longitudes of 61°–75° East, stretching over 1600 km from North to South and 885 km from East to West, with a total area of 796,095 square kilometers. Within this area, there is a great altitudinal and ecological diversity ranging from high frozen mountains in the north, temperate wet mountains downwards on footstep of Himalaya, to vast alluvial Indus flood plains in the central to southern part of country, and inhibiting more than 100 million human populations. Our study encompasses different regions of Pakistan that are categorized into four major zones on the basis of their geographical characteristics and altitudes: Northern Frozen Mountainous (**FMZ**), Lower Himalyian Wet Mountainous (**WMZ**), Alluvial Riverine (**ARZ**) and Low lying zone (**LLZ**). The northern frozen mountain zone (**FMZ**), which included valleys of Hunza, Gilgit, Skardu and Swat, is characterized by the presence of world's mightiest mountain ranges of Karakorum, Himalaya and Hindukush, which remain covered with snow for most part of the year and situated in the northern part of Pakistan. Elevation of these valleys range from 1500 to >3000 m from Arabian sea level (CIESIN, 2005). Sources of As in these regions are mostly related to geogenic factors, such as soil and dust particles which are mainly derived from parent rocks and are generally enriched with toxic elements, in particular As (Kfayatullah et al., 2001; Khan et al., 2010; Shah et al., 2012). Although anthropogenic activities in these areas are minimal, while long range atmospheric dust fall from neighboring countries including China and India may be contributed to build up As level in these areas. The second zone **WMZ** comprises districts of Azad Kashmir and Khyber Pakhtun Khawa (KPK), including Abbotabad, Nowshera and Swabi. These areas are characterized by high rainfall and host lower Himalyian Mountains with some stretches of plains adjacent to the hills are inhibited by population settlements. These areas are covered with temperate forests, with elevation ranging from 750 to >1500 m from sea level (CIESIN, 2005). Nowadays, several anthropogenic activities have been observed in these areas including agricultural, mining and crushing activities etc., which contribute to a short distance atmospheric dust transport. The **ARZ** encompasses the districts of Punjab, including Gujranwala, Sargodha, Mianwali, Bhakkar, Layyah and Dera Ghazi Khan, which are parts of the upper Indus plains. These stretches of alluvial plains lie on the bank of Indus River, and river serves as a major source of water for agricultural and domestic purposes. Apart from the water supply, Indus River also brings the sediments and minerals from the mineral rich mountains that are deposited into these plains and become part of the soil composition (Farooqi et al., 2007). The region's livelihood depends mainly on agriculture, with massive use of chemicals and pesticides, and industrial activities; which together with dense population and poor drainage system may contribute to the elevated As burden in the region. The districts of low lying agricultural areas of Sindh province including Hyderabad, Khairpur and Sukkur, are categorized as **LLZ**. These areas are situated on the left bank of southern irrigated plains and/or the lower Indus Plains that stretch further downward to the Arabian Sea coast. These areas are characterized by alluvial material and mainly composed of permeable sand and silt loam close to the

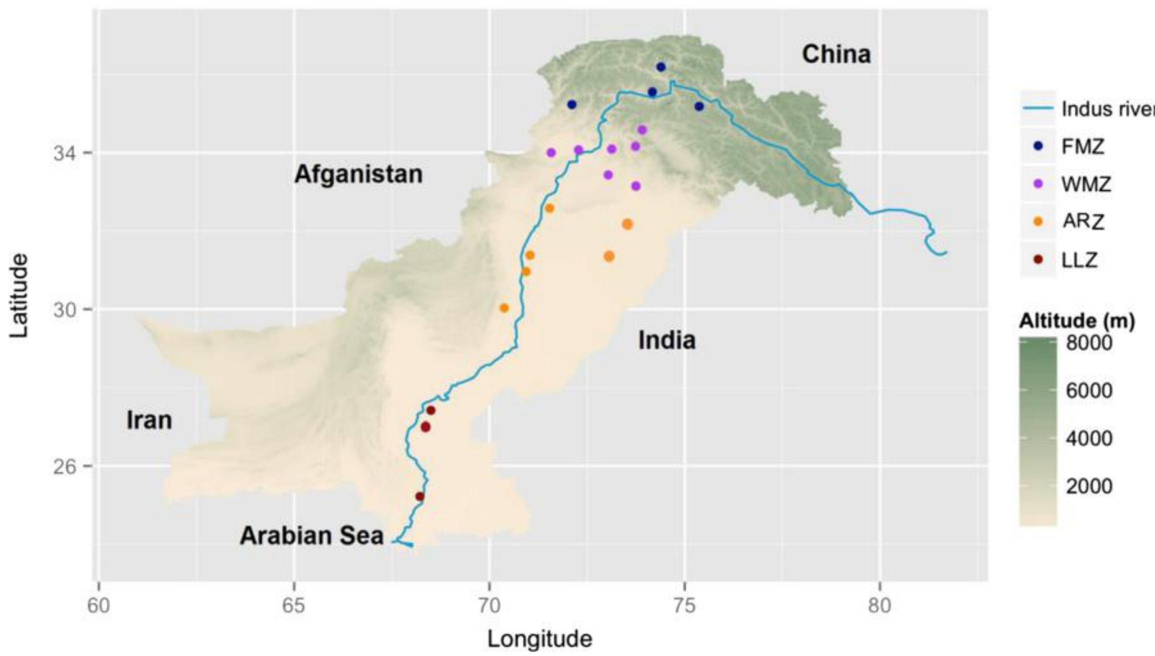

Fig. 1. Geographic location of Pakistan (a) within the Himalayan range and coastal-belt of Arabian Sea (top) and North–South altitudinal gradient in Pakistan with the sampling locations (b) in four different ecological zones, i.e. northern frozen mountainous (FMZ), lower Himalyian wet mountainous (WMZ), Alluvial riverine (ARZ) and low lying (LLZ). The coordinate reference system is WGS 1984.

river with increasing clay fraction away from the river (Rafiq and Tahir, 1981). Agricultural as well as industrial activities are mainly responsible for As contamination in this zone (Fatmi et al., 2009). Moreover, climatic condition i.e., semi arid characteristics with high temperature and sand storms and low vegetation cover, make the associated human population of LLZ and ARZ more vulnerable to dust exposure.

2.2. Sample collection and analytical aspect

Dust (n = 110) and human nails (n = 180) samples were collected from 22 locations in the selected districts, as shown in Fig. 1, during May–June 2013. Windstorms and/or dust storms are regular feature of the region especially during spring and summer months. At each site location, a room with four ways cross window was selected and a wood table with mirror on top were placed inside each room. The dust settled on the mirror surface from selected outdoor environment was periodically brushed off and collected in the sampling bags. The total glass area receiving the dust was also measured for the calculation of amount of dust fall per unit area per unit time and dust samples (< 50 μm) were used for chemical analysis. After each sampling, separate brushes were used in order to minimize cross contamination between the sites. Moreover, rate of dust fall and major activities of people and several other demographic information were also recorded at the time of sampling and all these values were used for the risk estimation. The toenail samples were collected from volunteer adult individuals (15–40 years) of both genders (male, N = .134; female, N = 46). Questionnaires were used to collect demographic information that could influence the As levels in the samples. Each subject was asked to answer the questions regarding personal background, awareness of illness, occupation, agricultural activities, smoking habits, and other information relevant to the possible contamination source. The study was approved by the Ethical Review Committee of COMSATS, Islamabad, Pakistan and a written consent was obtained from all the participants of this study. After collection, samples were wrapped in aluminum foils, and transferred to plastic air-tight bags, sealed, labeled and were transported to the laboratory. All the collected nail samples were stored at 4 °C until analysis and washed according to the protocol recommended by the International Atomic Energy Agency (IAEA, 1985). Briefly, the protocol includes the sequential washing with water, acetone + water and acetone. Then, the washed samples were dried at 50 °C in a drying oven. Prior to digestion, all the tubes were soaked overnight with 10% (v/v) HNO_3 and rinsed three times with ultra-pure water Milli Q system A (Millipore Corporation, Billerica, MA, USA). Three Aliquots (0.1–0.2 g) of each dried and cleaned dust and nail sample was weighed carefully and digested with 1 mL GR grade 65% (v/v) HNO_3 (CNW Corporation, Shanghai, China) overnight and the next day with 1 mL H_2O_2 GR grade 30% (v/v) (Sinopharm Chemical Reagent Co., Ltd, Beijing, China). For the dust sample, 1 mL of $HClO_4$ were also added to completely digest the samples. Finally, samples were mixed, sealed in Teflon microwave digestion tubes and digested in an accelerated microwave digestion system (Mars CEM, CEM Corporation, Matthews NC, USA) at 800 W, 120 °C for 10 min and then 800 W, 170 °C for 30 min. After cooling for 30 min, the vessels were opened carefully and each digested solution was transferred to a 50 mL volumetric flask. Samples were diluted to 50 mL using ultra-pure (Milli-Q) water and finally filtered through 0.22 μm nylon membrane. Reagent blanks and standard reference materials were also analyzed following the same procedure of samples.

Arsenic was analyzed by using Agilent 7500cx Inductively Coupled Plasma Mass Spectroscopy (Agilent Technologies, Santa Clara, CA, USA) coupled with a flow injection system. The operating parameters were set as RF power 1510 W, carrier gas 1.1 L/min, makeup gas 0.10 L/min, helium gas 3.5 mL/min, nebulizer pump 0.1 rps. The analytical mass was ^{75}As. The standard stock solution was obtained from the National Center of Analysis and Testing for Nonferrous Metals and Electronic Materials (NCATN).. In order to check the stability and sensitivity of the instrument, a mixture of internal standards (Sc, Ge, Rh, Lu) was also used and the mean and RSD of cps values of the targeted element was also calculated.

All samples were run in a randomized fashion to reduce the possible uncertainty from the artifacts related injection order and instrumental sensitivity change during the entire sequence. All glassware before use were washed with distilled water, soaked in nitric acid (30%) overnight, rinsed with deionized water (Behropur B25), and air-dried. A quality control (QC) sample was also prepared and injected after every 15th sample to check instrumental stability. The QC sample was prepared by mixing aliquots of each sample as a representative of the whole sample sets. The variation of element concentrations of QCs was $< 10\%$. Relative percentage difference for replicate analyses were $< 5\%$. Calibration curves, linear range (LR), relative coefficients (r^2) of calibration curves, limit of the detection (LOD) and the recoveries are given as Table S1.

2.3. Risk estimation

Chemical daily intake (CDI) was calculated by the following equations:

$$CDI_{ing} = C_{ucl} \times \frac{R_{ing} \times F_{exp} \times T_{exp}}{ABW \times T_{avg}} \times 10^{-6}$$

$$CDI_{dermal} = C_{ucl} \times \frac{SAF \times A_{skin} \times DAF \times F_{exp} \times T_{exp}}{ABW \times T_{avg}} \times 10^{-6}$$

$$CDI_{dermal} = C_{ucl} \times \frac{R_{inh} \times F_{exp} \times T_{exp}}{PEF \times ABW \times T_{avg}}$$

Where the chemical daily intake (CDI) of dust particles via ingestion, inhalation and dermal contact are CDI_{ing}, CDI_{inh} and CDI_{dermal}, $C_{ucl}=$ upper confidence limit concentration of As in dust particles (mg kg^{-1}), R_{ing}=ingestion rate (mg d $^{-1}$), R_{inh}=inhalation rate (m^3 d^{-1}), F_{exp}=exposure frequency (d y^1), T_{exp}=exposure time (y), SAF=skin adherence factor (mg cm^{-2} h^{-1}), A_{skin}=skin exposure area (cm^2), DAF=dermal absorption factor (unit less), PEF=Particle emission factor (m^3 kg^{-1}), ABW=average body weight (kg), T_{avg}=average time (d). Supporting information along with references is provided in Table S2.

Hazard quotient (HQ) is computed for non-carcinogenic risk by calculating dose and exposure pathway that is subsequently dividing with the reference doses (RfD) as follows.

Hazard quotient (HQ)=(CDI × BAF)/(RfD_0)

Hazard Index (HI) is the sum of calculated hazard quotients (HQ) and a HI value greater than 1 shows that there is a chance that non-carcinogenic effects may occur whereas a value of HI lower than 1 shows no significant risk of non-carcinogenic effects. Therefore, greater the HI value higher the probability of non-carcinogenic effects (US EPA, 2001). In the current study, HI and carcinogenic risk methods were employed to assess human health risk of element exposure to dust samples in Pakistan.

The cancer risk is calculated by multiplying doses with slope factors (US EPA, 2010; Ferreira-Baptista and DeMiguel, 2005) by the below given equation:

Carcinogenic risk (CR)=$CDI_{ing/\ Inh\ /dermal} \times BAF \times SLF$

Acceptable levels of CR based on US EPA (2001) is between 1×10^{-6} (one cancer per million people) and 1×10^{-4} (one cancer for 10,000 people).

2.4. Statistical analysis

The descriptive statistics and correlation matrix was computed by using StatSoft Statistica (Version 5.0) software and visualization of data was performed by Microsoft Office Excel 2013. One-way ANOVA, followed by Tukey's HSD post hoc test was applied for multiple comparisons of mean As concentrations among the studied zones. Spatial distribution of arsenic throughout the study area is presented by using Arc-GIS software (version 9.2). Moreover, risk estimation values of non-carcinogenic (HI $\geq$ 1) potential health risks used for risk mapping (Figs. 2 and 3).

To check the association of As concentration with geogenic variables, we compiled raster data of four soil properties variables, i.e. soil organic carbon density (SOC, kg C/m^2 for 0–100 cm depth range), soil carbonates carbon density (SCC, kg C/m^2 for 0–100 cm depth range), soil pH (30–100 cm depth range) and total available water capacity (WC, mm water per 1 m soil depth), as surrogates. The rasters (0.5 degrees (~55.5 km) resolution) were collected from the global soil properties dataset (Batjes, 2000). To evaluate the association of As exposure with the anthropogenic activities, we considered population density (PD) as a surrogate (higher density indicates higher anthropogenic activities and vice-versa (Zheng et al., 2014). The population density data for Pakistan was the extracted from the Gridded Population of the World Version 3: Population Density Grids (CIESIN and CIAT, 2005). The elevation (above mean sea level) data were evaluated using the digital elevation model (DEM) from the Shuttle Radar Topography Mission (SRTM) (Rodriguez et al., 2005). The raster data were cropped to the spatial extent of Pakistan and transformed to the WGS 1984 coordinate reference system. We extracted the value of each altitude, geogenic and anthropogenic variable from the rasters in each sampling location. Altitudinal gradients of the As concentration in the outdoor dust and human nail samples were identified by fitting simple linear regression models with As concentration as response and altitude as predictor variables. The slope of the regression models indicated the magnitude and direction of trends, where the strength of altitudinal gradient was indicated by the model r^2. To identify the geogenic and anthropogenic association for altitudinal gradient, we also fitted simple linear regression models with As concentration as response and each of the soil properties variables and PD as predictors, and identified the model slope and r^2.

3. Results and discussion

3.1. Arsenic contamination into dust

Arsenic concentrations (ppm) into outdoor surface dust samples from four different investigated zones (FMZ, WMZ, ARZ and LLZ) are presented as Table 1(a), Figs. 2 and S1. These results showed that the highest mean concentration (ppm) was measured in the dust sample collected from ARZ (10.64), followed by LLZ (9.98) and WMZ (6.64) and FMZ (2.33), respectively. However, exceptions of fewer cases from WMZ (i.e. Islamabad, Abbotabad and Swabi) were also observed, which ensemble with ARZ and LLZ data. In general, these results exhibited the altitudinal trends of As occurrence, pinpointing different As contamination sources into the associated dust samples of each zone. Regression analysis (Fig. 4) showed the following ($p < 0.05$) associated pairs i.e., As-altitude (r^2=0.239), As-SCC (r^2=0.333), and As-PD (r^2=0.259). In fact, looking at the As distribution throughout Pakistan (Fig. 2), elevated As concentrations are associated to both natural (e.g. geogenic influences) and anthropogenic sources (e.g. noxious industrial discharge and toxic agricultural runoff). For example, As concentrations measured in FMZ and WMZ could be subjected to geological influences (Muhammad et al., 2010; Shah et al., 2012). These data could be justified by the phenomenon of hydrology of this region, where surface water from the Himalayas eroded the colluviums and piedmont sediments, which are rich in “micas”, formed principally by biotite and conglomerate mineral containing As, and may release As into surrounding environment via short

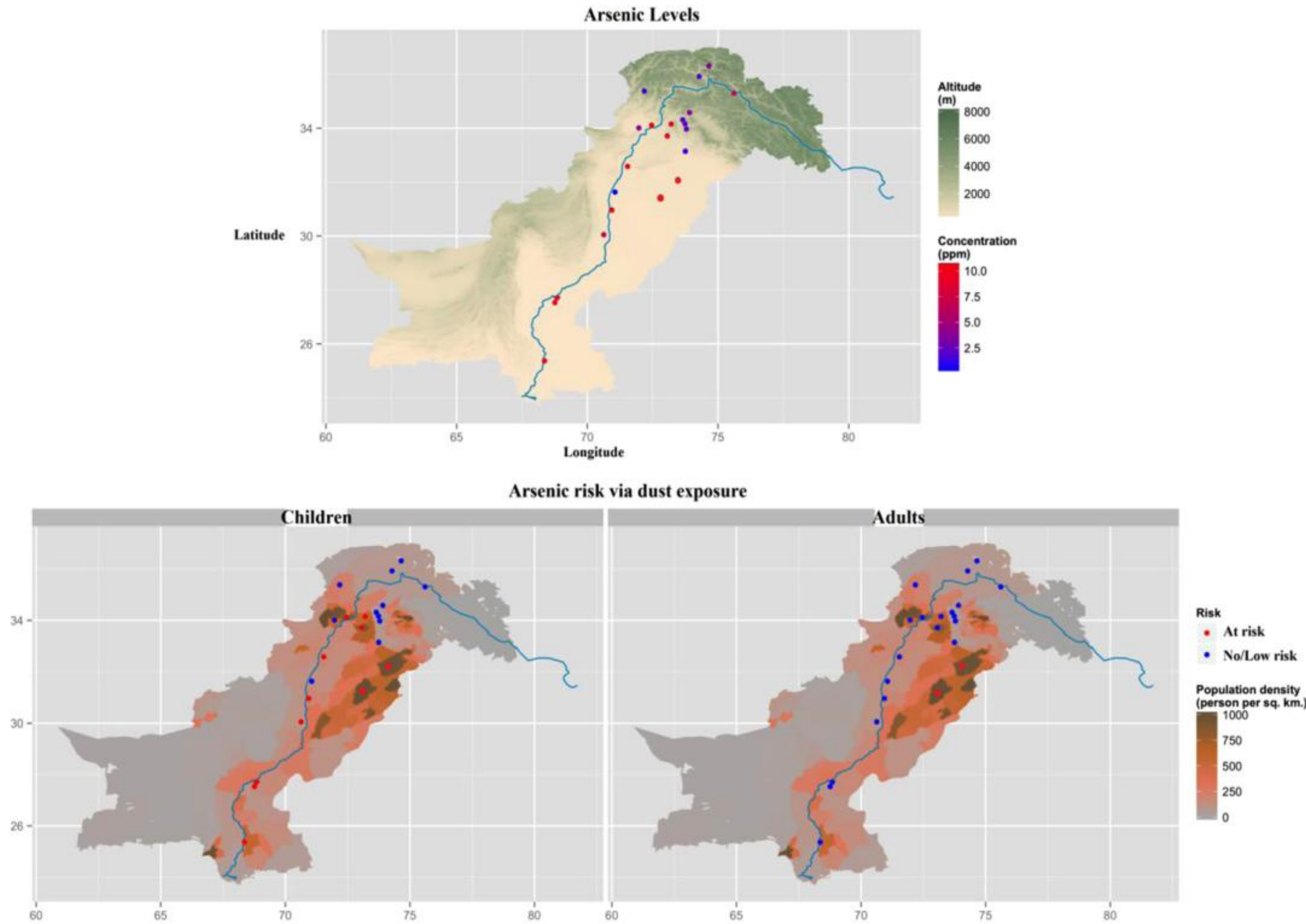

Fig. 2. Spatial variation of As concentration in the outdoor dust particles and sampling locations where adults and children are at are susceptible to health effects from As dust exposure (estimated HI value > 1), The corresponding population density in the background. The panel titles indicate "(Adults / Children) at risk, from (arsenic)".

distance atmospheric dust fall process (Shah and Shaheen, 2007). Considering the longitudinal sections of FMZ (Fig. 2), Sarkdu district, situated at 4500 m above the sea level, showed relatively higher concentrations (~6 ppm) than those of other FMZ-sites (i.e., Gilgit and Hunza). The process of altitudinal fractionation due to long range atmospheric dust transport from neighboring countries, including China and India, could explain the higher As concentrations in these remote areas. Nevertheless, quite extensive deposition of loess material has also been reported into WMZ (i.e., Pothwar and Lower Himalayan valleys) which probably deposited during the last glacial period, when the winds were forceful enough to carry silt particle up to these areas (Rafiq and Tahir, 1981). It should be taken into account that the active processes of picking of silt size particles by winds from the southern parts of the country and their deposition into the Himalayan submountainous region as well as the presence of recent material rich in weatherable minerals and other agricultural contaminants, play a pivotal role in generation of arsenic contaminated dust. The investigated areas are also characterized by high rainfall rates and huge forest cover, thus canopy forest could intercept atmospheric dust and other particulate matter containing trace elements and release these contaminants into the surface soils through the canopy related processes (i.e., through fall and stream-flow) and build up arsenic levels into forest soil (Huang and Matzner, 2007). Additionally, arsenic might also undergo chemical reactions with organic matter which is present in large amounts into top surface soils, owing to large inputs of litter through annual litter cycling in a temperate forest. These reactions are also considered fundamental in retaining and build up arsenic levels into forest soils (Huang and Matzner, 2007). Higher arsenic levels (i.e., 10 ppm) in few samples from WMZ (noticeably Islamabad and Abbotabad) can be explained by taking into account the severe environmental degradation in these areas and related to extensive anthropogenic activities e.g., stone crushing, mining, construction, though producing huge amounts of As contaminated dust (Kfayatullah et al., 2001; Shah and Shaheen, 2007).

ARZ and LLZ sites exhibited altitudinal trends and higher concentrations towards lower areas of southern Punjab and Sindh, except Bhakkar district (0.44 ppm) where As concentration in dust was lower from other spots in the zone (Fig. 2). It has been widely known that groundwater in many parts of Pakistan has been found to be highly contaminated with As, probably due to the presence of Holocene sediments brought by recent and sub-recent alluvial deposits and the consequent As release due to As-desorption in oxic aquifers (Farooqi et al., 2007; Brahman et al., 2013). These findings are also well in agreement with other previously studies in the same region, which showed higher levels of different pollutants, including As, in a wide range of environmental matrices (e.g., water, soil, sediment, vegetables etc) from different urban areas of Punjab and Sindh provinces, Pakistan (Brahman et al., 2014; Waheed et al., 2014; Abdullah et al., 2015; Subhani et al., 2015). The authors suggested that, in addition to geogenic

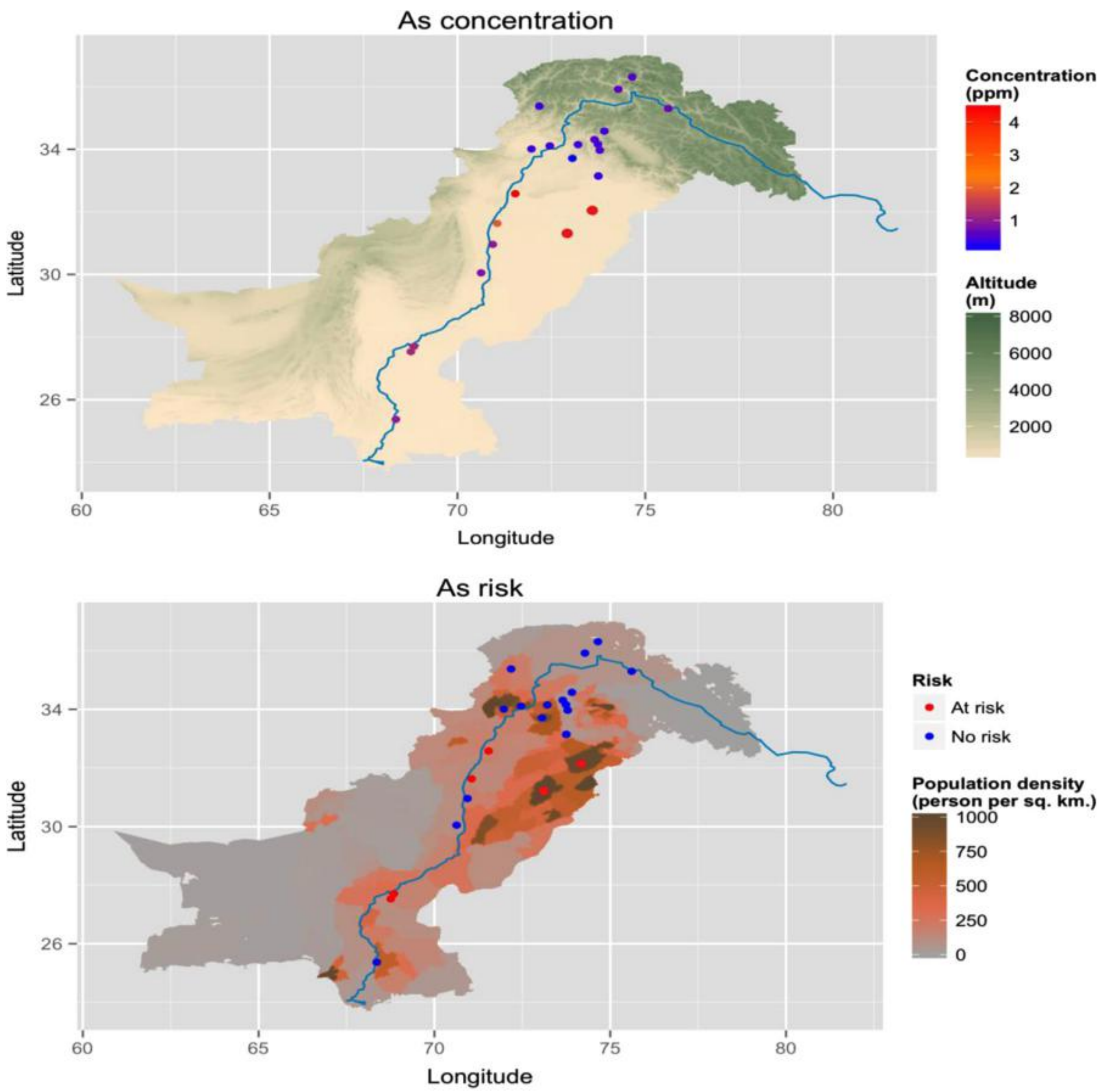

Fig. 3. Spatial variation of the As concentration (mean) in the nail sample and sampling locations where the associated populations are at risk (the As-nail values are crossing USEPA (2001) allowable limit of 1 ppm), with the corresponding population density in the background. The panel titles indicate "(population) at risk, from (arsenic)".

Table 1
: Basic statistics of As concentrations (ppm) in dust and nail samples from four studied zones of Pakistan.

	N (DF%)	Mean (S.D.)	Variance	Q25	Median	Q75
a. Dust						
FMZ	35 (100)	2.33 (2.16)	4.69	0.97	1.71	2.44
WMZ	26 (100)	6.64 (3.71)	13.78	7.47	9.16	9.65
ARZ	26 (100)	10.64 (2.04)	4.19	9.13	9.94	12.31
LLZ	23 (100)	9.98 (0.71)	0.5	9.49	9.93	10.3
All Zones	110 (100)	6.45 (4.31)	18.58	1.71	8.86	9.87
b. Nail						
FMZ	48 (96)	0.45 (0.31)	0.1	0.22	0.36	0.58
WMZ	50 (97)	0.33 (0.25)	0.06	0.12	0.28	0.49
ARZ	54 (100)	0.76 (0.59)	0.35	0.36	0.62	1.11
LLZ	28 (100)	0.97 (0.26)	0.07	0.77	0.94	1.13
All Zones	180 (100)	0.55 (0.42)	0.18	0.23	0.44	0.77

N = number of samples, DF (%), detection frequency.

contamination, rapid urbanization, growing industrial sector and widespread agriculture activities contributed a lot towards the high levels of environmental pollutants, especially arsenic. All the districts included in ARZ and LLZ zones are also characterized by harsh climatic conditions (i.e. high temperature, wind storms, low rainfall and less vegetation cover) and historical agricultural background. In this study, samples were collected through wide scale spatial entity and results revealed that one of main reasons for higher As levels into dust samples from ARZ and LLZ may be attributed to the extensive use of fertilizers and pesticides for crops. Both the use of calcium arsenate, arsenic acid, lead arsenate and sodium arsenate as pesticides and irrigation of agricultural land with industrial wastewater leads to soil contamination with different toxic elements (including As), which ultimately resulted into dust borne elements (i.e. arsenic) exposure of associated population via ingestion, inhalation and dermal contact (Farooqi et al., 2007; Jan et al., 2010; Subhani et al., 2015). Cement manufacturing, coal mining and disposal of untreated municipal and

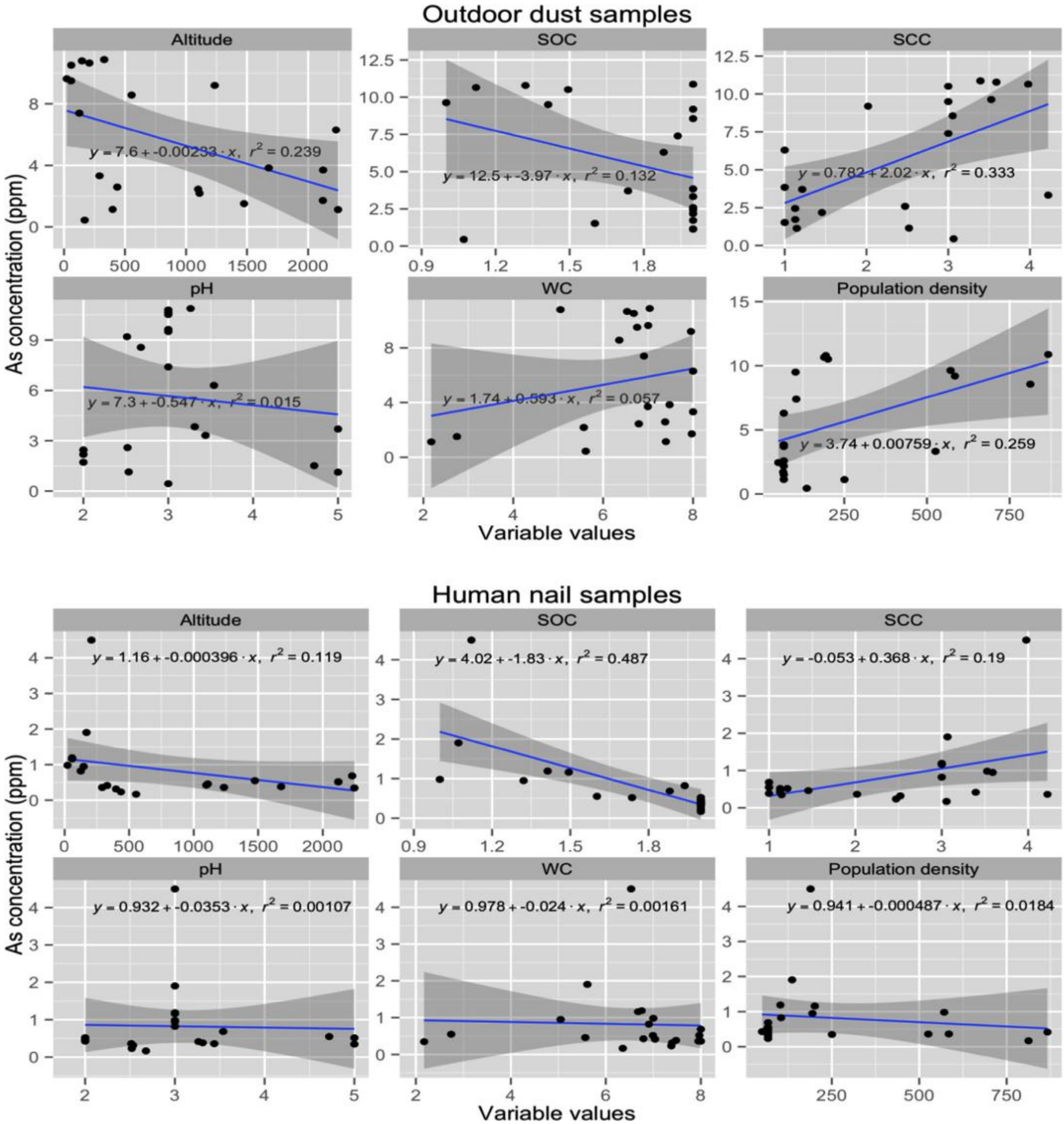

Fig. 4. Trends of the As concentrations in the outdoor dust particles and human nail samples in Pakistan along the altitudinal, geogenic and anthropogenic gradients.

hospital wastes into streams are also responsible for high As contamination in the east and southeast part of the country (Bhowmik et al., 2015).

We also compared our results with those from other areas around the world and found that the mean As concentration (ppm) in dust samples from our study (mean value: 10) was higher than those found in Angola (mean value; 5) (Baptistaa and Miguel, 2005), Newcastle, UK (mean value: 6.4) (Okorie et al., 2012) and Egypt (mean value: 5) (Khairy et al., 2011). In contrary to this, the current As levels were similar and/or lower than those determined by Amato et al. (2011) in Barcelona (Spain) (mean value: 12) and Zurich, Switzerland (19), and by Hu et al. (2011) from Guangzhou (17.02) and Nanjing, China (13.4), respectively.

3.2. *Nail as a biomarker of Arsenic toxicity*

Arsenic mean concentrations (ppm) in nail samples from all the investigated zones are reported in Table 1 (b) and Fig. 3 together with some statistic data (Fig. S1). Our study showed that the highest As level (ppm) was found in **LLZ** (mean: 0.97), followed by **ARZ** (0.76), **FMZ** (0.45) and **WMZ** (0.33) in descending order, respectively. In order to assess the association of paired dust-nail sample, we used simple linear regression models, by fitting soil properties variables and PD as predictors, and identified the model slope and r^2. By Looking into Fig. 4, it can be seen that significant ($p < 0.05$) relationship among As and SOC ($r^2 = 0.49$) and SCC ($r^2 = 0.19$), respectively. Higher r^2-values of As-SOC pair, indicated that fine weathered particulate material had more affinity to bind contaminants, and generating more fine dust with high As loads. In accordance to dust levels, As concentrations in nail samples from ARZ and LLZ were higher than those measured in FMZ and WMZ. Similar trends were also observed for As (Subhani et al., 2015; Brahman et al., 2015) and other elements (Mohmand et al., 2015; Abdullah et al., 2015) from few areas of Pakistan. It was also found that age and weight of individuals did not showed any marked relationship ($p > 0.05$), with the exceptions for few samples from FMZ and WMZ, which showed bioaccumulation of different pollutants due to colder temperature and people diet preferences.

Comparing our results with literature, the As nail values found in this study were consistent with those (0.69 ppm) measured by Anwar (2004) in Pakistan, and to those measured in USA (Vance, et al., 1988), Japan (Tabata et al., 2005), United Kingdom (Brima et al., 2006) and USA (Cottingham et al., 2013). In contrary, As levels in Cambodian (Gault et al., 2008), Bangladeshi and West-Indian (Das et al., 1995; Samanta et al., 2004; Rakib et al., 2013) populations were much higher. The health implications of As accumulation into human tissues above WHO-allowable concentration (1 ppm) may cause hypo and hyper pigmentation, cardiovascular disorders, diabetes, kidney malfunctions, hypertension and skin lesions, infertility (Shen et al., 2013; Subhani et al., 2015). Occurrences of such diseases have already been reported for Pakistan, e.g., arsenic in 70% of the human hair and nails samples in Punjab (i.e., Lahore and Sargodha) exceeded the WHO-threshold values (Subhani et al., 2015) and 1.3% of the rural population older than 15-years suffered from skin lesions (Fatmi et al., 2009). Similarly, other studies has also reported the bioaccumulation of trace elements in human hair, and nail (Mohmand et al., 2015; Brahman et al., 2015) and avian feathers (Abdullah et al., 2015) from Pakistan. In this study, As levels were higher in LLZ and ARZ, and approximately 40% of collected nail samples surpassed the permissible value of 1 ppm proposed by USEPA (2001). Our supporting detailed demographic data has also reflected that these individual cases are susceptible to human health risks due to arsenic toxicity. Moreover, Fig. 3 has also highlighted that arsenic risk due to higher nail concentrations (ppm) with the corresponding population density in the background from different areas of country. However, detailed studies should be demonstrated in future to confirm the associations of epidemiological evidence of arsenic toxicity in affected populations in Pakistan.

3.3. Human health risk and exposure via dust

The information for HI values greater than unity can be used to assess the potential human health risks via dust exposure. Nevertheless, HI values (even less than unity) can also be useful to estimate the contribution of dust as a source of contamination, which ultimately along with other sources (i.e. drinking water and diet) adding cumulative risk of arsenic into associated exposed population (USEPA, 2001). In our study (Table S4), HI values (Fig. 2) for ARZ, LLZ and few sites of WMZ were found higher than unity for children (0.8–2.25) and highlighted that children populations were mainly at risk in ARZ, LLZ and WMZ. Similarly, HI values (Fig. 2) for non carcinogenic risks for adults were ranged between 0.55 and 0.74 from all LLZ and ARZ sites and highlighted more health risks due to dust exposure than those of the residents from FMZ and WMZ. In ARZ and LLZ, less tree canopy interception due to low vegetation and more anthropogenic activities may aggravate the situation and resulted into high As-risk to the associated humans. By the visual inspection of Fig. 2, different sampling locations can be seen where the adults and children are susceptible to potential health effects from As dust exposure (estimated HI values > 1), together with the corresponding population density in the background. This information is also very useful to focus the priority areas by the environmental authorities and general public to manage this issue. Moreover, carcinogenic risk values were also calculated and for few cases (5–10%) from LLZ and ARZ, these values fallout from the range of US EPA threshold limits, which suggest low to moderate hazard concerns. Similarly regarding the route of exposure via dust; our calculated risk estimation values (Table S3) revealed that dust ingestion is one of the major routes of arsenic exposure followed by dermal contact and inhalation at all the studied sites for both non carcinogenic effects and carcinogenic risk.

Similarly, we also evaluated nail-arsenic levels by using the WHO threshold limit of 1 ppm and found exceedances from highly contaminated areas of ARZ, LLZ and fewer areas of WMZ, which also authenticated that associated human populations in ARZ, and LLZ are facing a threatening situation. Nevertheless, dust ingestion has also proved to occur as the main exposure route for arsenic, but additional contamination routes including water, air, and contaminated food, should be studied in detail in future. Moreover, in the human health risk assessment, other elements and exposure pathways, which might significantly contribute to human As exposure, were neglected. In fact, arsenic tends to be tightly bound to the keratin of hair and nails, but given that the toxicant can be present in air, soil, food and even into the personal care products; these additional arsenic exposure routes should be investigated in detail in the future. Despite these limitations, this study demonstrates that dust contamination contribute a significant role towards the evaluating Arsenic exposure to Pakistani population. Public awareness is also essential, and we recommend an immediate control on the industries that discharge different toxic elements including arsenic into the environment as well as a monitoring of pesticides and chemical fertilizers, that contain trace of elements-arsenic, into surrounding soil.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.ecoenv.2015.12.044.

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