Environmental Pollution 213 (2016) 213–222

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Spatial distribution of dust–bound trace elements in Pakistan and their implications for human exposure☆

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ARTICLE INFO

Article history:
Received 24 August 2015
Received in revised form
7 February 2016
Accepted 7 February 2016
Available online xxx

Keywords:
Dust
Trace elements
Spatial distribution
Risk estimation
Pakistan

ABSTRACT

This study aims to assess the spatial patterns of selected dust-borne trace elements alongside the river Indus Pakistan, their relation with anthropogenic and natural sources, and the potential risk posed to human health. The studied elements were found in descending concentrations: Mn, Zn, Pb, Cu, Ni, Cr, Co, and Cd. The Index of Geo-accumulation indicated that pollution of trace metals were higher in lower Indus plains than on mountain areas. In general, the toxic elements Cr, Mn, Co and Ni exhibited altitudinal trends ($P < 0.05$). The few exceptions to this trend were the higher values for all studied elements from the northern wet mountainous zone (low lying Himalaya). Spatial PCA/FA highlighted that the sources of different trace elements were zone specific, thus pointing to both geological influences and anthropogenic activities. The Hazard Index for Co and for Mn in children exceeded the value of 1 only in the riverine delta zone and in the southern low lying zone, whereas the Hazard Index for Pb was above the bench mark for both children and adults (with few exceptions) in all regions, thus indicating potential non-carcinogenic health risks. These results will contribute towards the environmental management of trace metal(s) with potential risk for human health throughout Pakistan.

1. Introduction

In recent years, anthropogenic activities in Pakistan, including fossil fuel combustion, coal burning, stone crushing, agriculture, widespread application of metal containing pesticides, and the poultry and animal industry, have generated huge quantities of metal-contaminated dust (Mohmand et al., 2015). The activities have increased the level of trace elements into the environment, in addition to the natural earthen provision (Mohmand et al., 2015; Shah and Shaheen, 2007). Like other regions of Southern and Southeastern Asia, the floodplains of Pakistan are also composed of soil and sediments eroded from high mountainous regions that may contain variable proportions of trace elements (Prabhakar et al., 2014; Rafiq and Tahir, 1981). Several local factors, including forest cover, geology, geographic position, and climatic conditions can also affect the large scale distribution of dust-borne trace elements into the environment (Crosbie et al., 2014; Carmichael et al., 2009; Wei et al., 2008). Due to climate changes and to rapid urbanization during the recent decades, it has become more challenging to predict the complex roles of both long-atmospheric dust transport and its short-range interception by forest canopy. Both these mechanisms bear immense significance for the biogeochemical cycles of the different toxic elements in the weathered soils of the arid and semi arid areas like low and mid elevation regions of Pakistan (Prabhakar et al., 2014; Carmichael et al., 2009). The final result is a greater unsteady spatial distribution variability of these toxic metallic impurities, in contrast to their expected

☆ This paper has been recommended for acceptance by Eddy Y. Zeng.

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http://dx.doi.org/10.1016/j.envpol.2016.02.017
0269-7491/

theoretical equilibrium (Ferreira-Baptista and De Miguel, 2005; Carmichael et al., 2009).

As a consequence, different human population settings are expected to become exposed to metal-contaminated dust at distinct levels (Alamdar et al., 2016). Dust easily enters the human body, directly and indirectly via different routes, inhalation, ingestion and dermal contact, due to its fine particle size and mobile nature (Mohmand et al., 2015). Exposure to toxic elements impacts on human health, causing several negative effects, among which disruption of the central nervous system, malfunctioning of internal organs, and infertility etc. (Zafar et al., 2015; Mohmand et al., 2015). Infants and young children are particularly affected by trace metal exposure, due to their rapid brain growth and differentiation. Moreover, children are also susceptible to ingest higher quantities of dust than adults, because of their intense touching activity, hand to mouth habit and licking of various contaminated objects (Mohmand et al., 2015).

Pakistan landscape is diversified, with the northern frozen areas of high elevation, the wet mountain areas in the lower Himalayan region, the adjoining floodplain areas along the Indus river, and the southern low lying coastal areas. The Indus floodplain and southern low lying areas hosts a large human population, intensive agriculture and other economic activities. Recently, the impacts of rapid urbanization and of severe environmental degradation in Pakistan were reported, and alarming situations were highlighted regarding trace elements contamination of drinking water resources (Bhowmik et al., 2015), of soil and wildlife (Abdullah et al., 2015; Khan et al., 2010; Shah and Shaheen, 2007), and of the human population (Zafar et al., 2015; Mohmand et al., 2015). However, no study has yet reported on the influence of short range transport of dust and other particulate originated by the different anthropogenic activities, on the biogeochemistry of trace elements, and their implications for human health. Our study, for the very first time aims to assess the distribution of potentially harmful trace elements in dust, their sources and to evaluate human exposure in the different ecological zones of Pakistan. We also estimate the potential risk posed by each trace metal to the health of the local populations, and most importantly of the children.

2. Materials and methods

2.1. Study area

This study was carried out in different districts along the River Indus, that bisects Pakistan from the northern highlands to the southern coast. The landscapes range from cold alpine highlands in the north, to temperate sub-humid mountains areas, to subtropical arid and semi-arid plains of Sindh and Punjab provinces. In order to account for such wide geographic, climatic and altitudinal variation, the country was categorized into four major zones (Fig. 1): frozen mountainous zone (FMZ), wet mountainous zone (WMZ), riverine delta zone (RDZ) and low lying zone (LLZ).

The FMZ includes the northern districts of Hunza, Gilgit, Skardu and Swat, with altitudes from 2000 to 4000 m a.s.l. (Arabian Sea level) and with the highest mountain ranges (Himalayas, Karakoram, Hindukush and Pamirs). These regions remain snow-covered for most of the year and host a scarce and scattered population. Land is used mainly for agriculture of orchids, leafy vegetables and other edible crops (Khan et al., 2010).

The WMZ lays in the Lower Himalayan region, a large area in the Hazara division, Khyber Pakhtoon, Khawa, that stretches to Azad Kashmir. This mountainous landscape ranges in elevation from 1200 to 1700 m, and its unique environment of moist temperate forest stores huge amounts of atmospheric carbon. The major activities taking place within 100 km from the forests are heavy automotive traffic, and agriculture that spreads large amounts of metal containing pesticides on the loose surface agricultural soil. Moreover, substantial mining of rock phosphates takes place in and around the forests. Also present are more than 3000 kiln for brick production, that burn large quantities of poor quality coal (Sheikh et al., 2000). The population density in this region is increasing rapidly and unsteady distribution of dust borne trace elements is largely expected. However, it has been reported that in these areas exposure to dust-borne elements to be largely affected by interception in the canopy of the thick forests that might play an important role in reducing dust fall (Alamdar et al., 2016).

The third zone (RDZ) includes six districts of Punjab i.e., Gujranwala, Sargodha, Mianwali, Bhakkar, Layyah and Dera Ghazi Khan, at altitudes from 150 to 250 m. The overall climate of the zone is dry, and windstorms are common in summer due to the barren plains and sandy soil and played important role to shift (from southern areas to northward) the contaminated dust into WMZ areas (Fig. 1). Its many irrigation canals are the backbone of agriculture and food production. A sediment study by Clift and Blusztajn (2005) revealed that Indus River carries a wide variety of minerals and sediments from the Karakoram Mountains of the north, ultimately causing changes in the geological conditions of the lower regions. The fourth zone, LLZ, includes three districts of Sindh, Sukkur, Khairpur and Hyderabad, with vast alluvial stretches of the lower Indus Plain at elevations from 0 to 70 m. Both the latter two regions are densely populated and characterized by high rates of dust fall that presumably exposes the resident of these regions to greater dust-borne contamination. Activities conductive to contamination in these two populated areas include heavy motorized traffic, spread of large amounts of metal containing pesticides over loose surface agricultural soil, substantial mining of rock phosphates, brick kilns burning large quantities of poor quality coal, and stone crushing (Abdullah et al., 2015; Mohmand et al., 2015; Alamdar et al., 2016).

2.2. Sample collection and laboratory analysis

A total of 110 composite dust samples, collected from 20 locations during May and June 2013. Windstorms and/or dust storms are a regular feature of entire country especially during spring and summer months. A room with four ways cross window was selected at each site and a wooded table with mirror on top had placed inside each room. The dust that had settled on the mirror surface was periodically brushed off and collected in the sampling bags. The total glass area receiving the dust was also measured for the computation of amount of dust fall per unit area and per unit of time. In order to avoid external contamination of the samples, dust was collected by hand in a plastic pan, using a clean, metal free plastic brush, and were directly deposited into an airtight bag. Separate brushes were used during sampling in order to minimize cross contamination between sites. Samples were wrapped in aluminum foils, transferred to plastic air-tight bags, sealed, and taken to the laboratory and all the samples were kept at 4 °C. Rate of dust fall, major activities of people, and demographic data were also recorded at the time of sampling. These values were used for the risk estimation.

Before digestion, blank HNO_3 (with 2 mL GR grade 65% (v/v) digestion (170 °C for 30 min)) was also carried to ensure the cleanliness of Teflon microwave digestion tubes. Moreover, microwave digestion tubes were soaked in 10% (v/v) HNO_3 overnight and rinsed three times with 1% HNO_3 and with ultra-pure water obtained from a Milli-Q system (Millipore Corporation, Billerica, MA, USA). Each dust sample was weighed and put into Teflon microwave digestion tubes with 1 mL GR grade 65% (v/v) HNO_3 and $HClO_4$ (CNW Corporation, Shanghai, China) overnight and on the

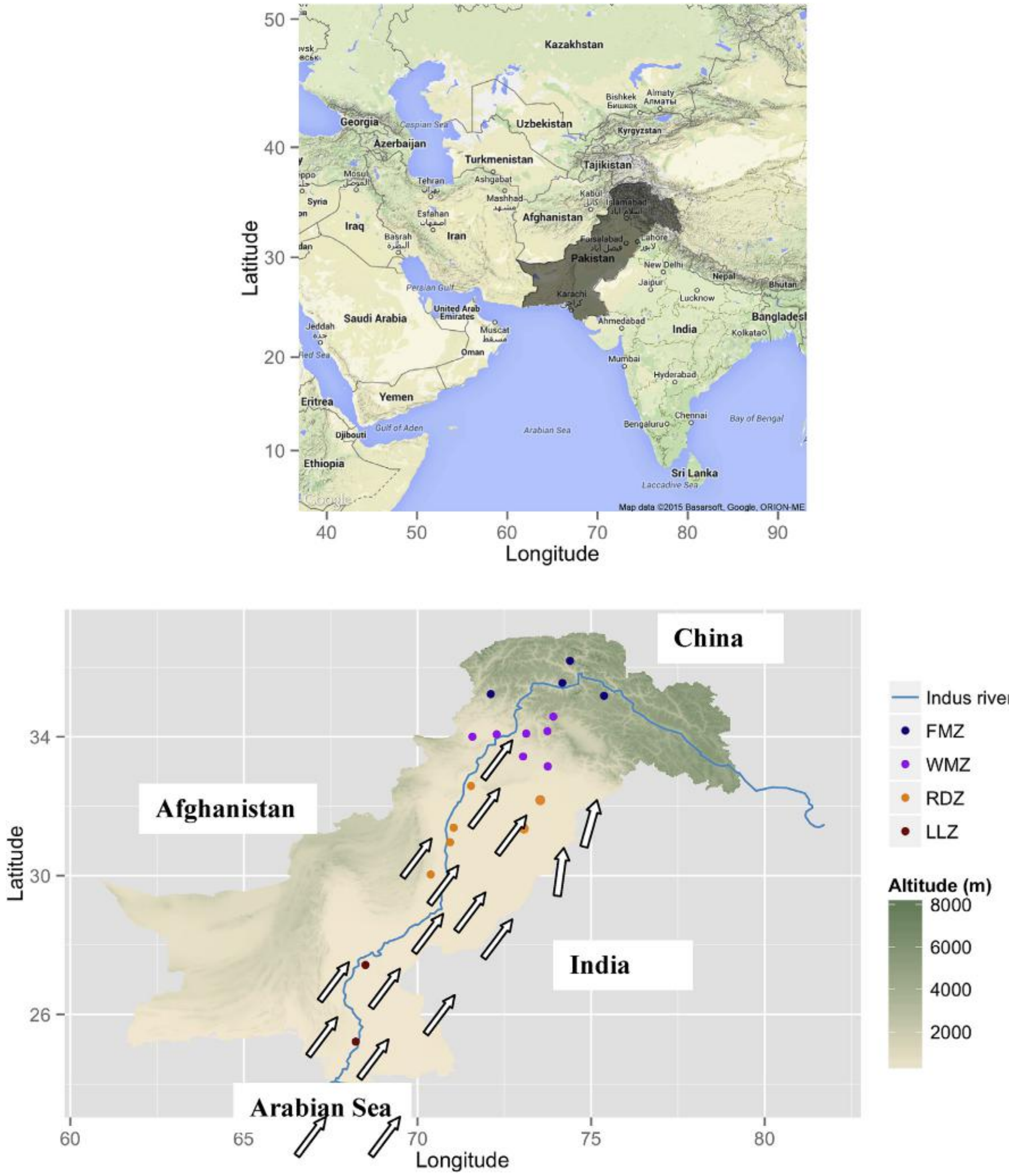

Fig. 1. Sampling locations in the four different ecological zones along the altitudinal gradient in Pakistan (FMZ frozen mountainous zone, WMZ wet mountainous zone, RDZ riverine delta zone, and LLZ low lying zone). (The arrows showing the wind direction in summer season, 2013).

subsequent day with 1 mL H_2O_2 GR grade 30% (v/v) (Sinopharm Chemical Reagent Co., Ltd, Beijing, China). The samples were then shaked thoroughly for uniform mixing, 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 at 800 W, 170 °C for 30 min. The volume of the digested samples was raised to 50 mL using ultra-pure water and finally filtered through 0.22 μm nylon membrane. The procedural blanks were also digested and prepared according to the same procedure.

2.3. Analytical aspects

The eight trace elements selected for this study (Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn) were analyzed on an Agilent 7500cx Inductively Coupled Plasma Mass Spectrometer (ICP-MS, Agilent Technologies, Santa Clara, CA, USA). The analytical masses were 53Cr, 111Cd, 208 Pb, 59Co, 55Mn, 60Ni, 63Cu and 66Zn. Calibration solutions were prepared using multi-element stock solutions of 100 ppm. The operating conditions were: RF power @ 1510W, carrier gas @ 1.1 L/min, makeup gas @ 0.10 L/min, helium gas flow @ 3.5 mL/min, and nebulizer pump @ 0.1 rps. The standard stock solutions mixed with elements (100 μg/mL, GSB 04-1767-2004) were obtained from the National Center of Analysis and Testing for Nonferrous Metals and Electronic Materials (NCATN).

A quality control (QC) sample was prepared and injected after every 15th sample (in order to check the instrumental stability). The QC sample was prepared by mixing aliquots of each sample and was therefore representative of the whole sample set. There was <15% variation in the metal concentrations of the QC. Spiked samples were also prepared in the same manner as dust samples. Some samples were spiked with Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn before digestion at the two final levels, 10 and 20 ng mL^{-1}. The recovery was also measured using these spiked samples and were ranged between 78 and 104% for all studied trace metals. The working solutions were prepared on a daily basis by appropriate dilution of a standard stock solution using a mixture of 65% (v/v) HNO_3, 30% (v/v) H_2O_2 and H_2O (v/v/v = 1:1:3). The relative difference for replicate analysis was <5%. All samples were run in a randomized fashion to reduce the uncertainties from artifacts-related injection order and instrumental sensitivity changes during the entire sequence. In order to check the instrumental sensitivity and stability, mixed internal standard (1 mg/L) was applied (Agilent, ICP-MS Internal Standard Mix: Sc, Ge, Rh, Tb). The intensity of Sc, Ge, Rh, and Tb was steady throughout the experiment (RSD < 5%) suggested the sensibility and stability of signal. The accuracy data for the studied trace elements are provided elsewhere (Mohmand et al., 2015; Peng et al., 2015).

2.4. Statistical analysis

The descriptive statistics were calculated from imputed values, whereas for the frequency and the minimum, we used the original values and the cases below detection limit. One-way ANOVA and Tukey's HSD post-hoc tests were used to compare the different sites. All significant differences cited in the results were at the 0.05 level, if not stated otherwise. Spatial PCA/FA was applied on zone-wise trace elements data, with Varimax rotation that maximizes the sum of variance of the factor coefficients. Correlation matrix using Pearson's moment correlation coefficient was also used to identify interrelationship between trace elements and to support the results obtained by PCA/FA. The package Statistica 5.5 was used for all these analyses.

The associations of each trace metal concentration with geogenic variables, altitude, and population density were identified by fitting linear regression models. We compiled raster data on four soil property variables (i.e. soil organic carbon density (SOC, Kg C/m^2 for 0–100 cm depth range), carbon density of soil carbonates (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)). The rasters (0.5° resolution, corresponding to ~55.5 km) were collected from the global soil properties dataset (Batjes, 2000). We considered the population density (PD) as a surrogate of anthropogenic activities, since higher density indicates more anthropogenic activities and vice-versa (Zheng et al., 2014). The elevations from mean sea level were obtained from the digital elevation model of the Shuttle Radar Topography Mission (Rodriguez et al., 2005) and the raster data for other geographic variables were cropped to the borders of Pakistan and transformed to the WGS 1984 coordinate reference system. Population densities for Pakistan were extracted from the Gridded Population of the World Version 3: Population Density Grids (CIESIN and CIAT, 2005).

2.5. Calculation of geo-accumulation index (I_{geo})

I_{geo} was calculated according to Aiman et al. (2016) as:

$$I_{geo} = \log_2 (C_n/1.5\ B_n)$$

where C_n is the concentration of the examined metal in the sediment, B_n is the geochemical background value of a given metal in the shale (Turekian and Wedepohl, 1961) and the factor 1.5 is used to account the possible variations in the background values. The degree of trace elements pollution in different zones was quantified using the same approach also by Zahra et al. (2014).

2.6. Human health risk estimation

Human exposure to trace elements via dust occurs through three main pathways, ingestion of dust particles directly from the environment, inhalation of dust through nose and mouth, and dermal contact. The daily chemical intake by the different routes (i.e., CDI_{ing}, CDI_{inh}, $CDI_{D.\ contact}$) through which dust can enter into the human body, and their respective definitions, are given in detail as supplementary text 1 and Table S1–2.

In order to estimate the potential non-carcinogenic risk of the trace elements, Hazard Quotient (HQ) was calculated for each zone as:

$$Hazard\ Quotient\ (HQ) = \frac{CDI \times BAF}{RfD_o}$$

Whereas CDI is the total Chemical Daily Intake through the three pathways (ingestion, inhalation and dermal contact); BAF (bio-accumulation factor) stands for the ratio between the content of each trace element that is bio-available and its total contents in the outdoor dust; RfD_o is the oral Reference Dose. BAF and RfD_o values for each studied trace metal is provided in Tables S–2.

Finally, the Hazard Index (HI) was calculated as the sum of the HQ. An HI value > 1 indicates a risk of adverse health effects (non-carcinogenic), whereas a value of HI < 1 denotes no significant risk. We mapped the risk from trace elements via dust exposure with population density in the background, in order to highlight the priority areas in need of management.

3. Results and discussion

The concentration of each trace metal in dust samples from the four zones of Pakistan is summarized in Table 1, Figs. S-1 and S-2. The detailed trends of occurrence of each metal are discussed below in Section 3.1. We also compare our results with those of the other studies conducted on trace metal contamination of dust throughout the world (listed in Tables S–3). The spatial trends, the sources of each element throughout the study area, and the associated risk for human health are also discussed.

3.1. Trace element concentrations in dust and its worldwide comparison

Our results showed that the level of five trace elements, Co, Cr, Cu, Mn and Ni, differed significantly ($p < 0.05$) among and within all zones (Table 1, Fig. 2). The mean levels (ppm) of Co (1.38), Cr (8.65), Mn (77.81) and Ni (3.99) were lowest in dust samples from FMZ, while higher values were observed, in WMZ (4.89, 19.7, 208 and 14.4 ppm respectively), RDZ (6.21, 24.8, 329 and 20.4 ppm respectively) and LLZ (8.03, 34.2, 431 and 26.1 ppm respectively). The Cu levels (ppm) recorded were highest in LLZ (27.43), followed by WMZ (13.53), RDZ (12.82) and FMZ (5.15). The levels of Co, Cr, Mn and Ni are similar to the highest values reported in the worldwide literature, with a few cases of values (for FMZ and WMZ) lower than those reported elsewhere (Tables S–3). The mean levels of Cd were highest in WMZ (0.42 ppm), followed by RDZ (0.41 ppm), LLZ (0.37 ppm) and FMZ (0.36 ppm), but they did not differ significantly among regions. In general, our Cd levels are

Table 1
Basic Statistics of trace elements concentrations (ppm) in outdoor dust from different studied zones of Pakistan.

Zone (no. Of samples)	Parameter	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
FMZ (n = 25)	Mean ± S.D.	0.36 ± 0.17	1.38 ± 0.35	8.65 ± 2.91	5.15 ± 4.29	77.8 ± 17.6	3.99 ± 1.72	47.9 ± 33.1	26.7 ± 15.8
	Median	0.41	1.37	8.47	3.78	80	3.96	27.8	19.9
	Min-Max	0.13–0.60	0.64–2.23	2.78–13.9	1.34–16.3	26.7–97.5	1.55–7.05	6.32–140	9.7–54.6
WMZ (n = 30)	Mean ± S.D.	0.42 ± 0.32	4.89 ± 5.09	19.78 ± 17.4	13.5 ± 14.7	208 ± 165	14.4 ± 13.09	63.9 ± 80.6	116 ± 174
	Median	0.36	1.66	8.24	3.43	107	5.76	24.8	13.5
	Min-Max	0.09–1.21	0.47–19.81	2.19–58.3	0.90–36.1	27.7–462	1.16–40.2	5.3–261	3.96–691
RDZ (n = 26)	Mean ± S.D.	0.41 ± 0.28	6.21 ± 4.32	24.8 ± 14.8	12.82 ± 9.21	329 ± 209	20.41 ± 12.59	90.7 ± 102	245 ± 356
	Median	0.29	8.27	32.79	15.06	457	27.41	41	72.6
	Min-Max	0.15–0.97	0.40–11.84	2.13–38.67	0.76–29.94	29.5–518	1.49–33.20	8.4–331	2.82–967
LLZ (n = 24)	Mean ± S.D.	0.37 ± 0.14	8.03 ± 0.53	34.2 ± 10.8	27.4 ± 13.3	431 ± 24.3	26.1 ± 2.02	87.2 ± 13.3	168 ± 12.2
	Median	0.30	8.14	33.4	19.29	424	25.7	72	108
	Min-Max	0.25–0.57	7.44–8.69	30.5–39.3	16.35–43.01	402–468	23.9–29.2	65–296	93–525
	p	0.93	0.002	0.0015	0.0039	0.00003	0.00012	0.069	0.063

n = number of sample, S.D. = Standard Deviation, Min = minimum, Max = maximum.

multifold lower than those reported globally, while few WMZ sample showed Cd values analogous to moderately contaminated samples reported worldwide (Tables S–3). The levels of Pb and Zn in dust were observed to increase gradually ($p > 0.05$) from FMZ (47.9, 26.7 ppm respectively), WMZ (63.9, 116 ppm respectively), to RDZ where the values were highest (90.7, 245 ppm respectively), while these values were measured as (87.5, 168 ppm respectively) in LLZ. It noteworthy that few samples from FMZ and WMZ also showed high Pb-concentrations, analogous to the values for the other highly polluted zones, RDZ and LLZ. Nevertheless, few samples from RDZ and LLZ showed higher Pb, and Zn levels, comparable to those reported in different other worldwide studies. Some Chinese, European and few other cities from different countries contained very high levels of these elements into dust than those in our studied areas (Tables S–3).

3.2. *Index of geo-accumulation (I_{geo})*

The I_{geo} values calculated in this study, are interpreted using the I_{geo} classes as given in Table 2. Our results highlighted that RDZ and LLZ regions were moderately and/or highly polluted by the studied trace elements, whereas WMZ and FMZ exhibited low to moderate pollution. These results point to variable sources of these contaminants. Generally, I_{geo} for both FMZ and WMZ were 0–1 and indicated the relatively low pollution level for all studied elements expects Pb. The I_{geo} values for Pb showed very high pollution throughout RDZ (3-4) and LLZ (3-4), and moderately to high pollution in FMZ (2) and WMZ (2), thus highlighting both natural and anthropogenic influences in these areas. Previously, studies from similar region suggested that Pb contamination is largely associated with manufacturing of electronic appliances, disposal of waste from nearby industries and agricultural chemicals runoff (Mohmand et al., 2015; Aiman et al., 2016). Similarly, coal burning activities and severe enrichment of trace metals from local parent rock material has also been observed to cause the metals toxicity in surrounding environment (Bhowmik et al., 2015). I_{geo} values for the other studied metals at both RDZ and LLZ sites were; Co (3) >Cr (2-3) <Mn ~ Ni (2) <Cd (1-2), pointing to moderate and/or high pollution levels due to extensive agricultural and to other anthropogenic influences. In general, our results are comparable with those I_{geo} values reported for environmental samples from Pakistan (Zahra et al., 2014; Aiman et al., 2016).

3.3. *Spatial patterns of trace elements and source identification*

In general, our results showed that the levels of the trace elements were higher in the regions with lower elevation (RDZ and LLZ) than in the mountainous ones (WMZ and FMZ). A higher spatial variability was exhibited (Fig. 3) by Mn (r^2 = 0.29), Cr (r^2 = 0.25), Co (r^2 = 0.22) and Ni (r^2 = 0.30), than by Cd (r^2 = 0.07), Pb (r^2 = 0.07), Zn (r^2 = 0.11) and Cu (r^2 = 0.17). The levels of the four elements Co, Cr, Mn and Ni into dust samples were significantly variable ($p < 0.05$) among the study regions, thus revealing that the sources of contamination were zone-specific. It has been widely reported that the biogeochemical cycles of trace elements at larger spatial scale are expected to show disturbances through processes of both long- and short-range atmospheric dust transportation due to the urbanization, industrialization and to agricultural activities (Carmichael et al., 2009; Sutherland and Tolosa, 2000). In our study, the high Pb concentration in a few samples from high altitudinal sites in the FMZ region can be attributed to the extreme enrichment of this metal during extensive coal burning. In addition, the altitudinal fractionation due to long range atmospheric dust transport from neighboring China and India could explain the higher Pb concentrations in these remote areas (Carmichael et al., 2009; Nasir et al., 2014; Alamdar et al., 2016). Unsteady spatial distributional trends were also observed in WMZ, with higher values for Cd, Pb, Cu, Zn, which could be related to both natural sources and to the large scale mining and rapid urbanization occurring in this region. These results are also in agreement with the peculiar climatic conditions across the WMZ region, also linked with the occurrence of trace elements into dust and soil (Shah and Shaheen, 2007). Moreover, interception and trapping of atmospheric impurities by tree canopy (Alamdar et al., 2016) and extensive deposition of loess material into lower Himaylaen areas (WMZ) were also been reported (Rafiq and Tahir, 1981). These processes increase the level of trace elements into the temperate forest environments of the high mountains, as reported from other similar regions (Huang and Matzner, 2007; Suchara and Sucharova, 2002). The extensive deposition of loess material, reported in WMZ (for the Pothwar and Lower Himalayan valleys) from southern lower lying areas, might have been formed when the winds were forceful enough during the summer monsoon months, to carry silt particles up to these regions (Ashraf et al., 1967; Alamdar et al., 2016). However, the recent material is quite rich in weatherable minerals; therefore the agricultural contaminants seem to play a pivotal role in the generation of metal contaminated dust (Rafiq and Tahir, 1981; Alamdar et al., 2016). Moreover, the concentrations of these elements except Pb were significantly correlated ($p < 0.05$) to SCC, while Cd (r = 69) and Pb (r = 41) were significantly correlated with population density (Tables S–4). The higher correlation values ($p < 0.05$) of population density with Cd and Pb reveal the role of the recent extensive anthropogenic activities in these areas, which include large industrial units, heavy traffic, construction and other development

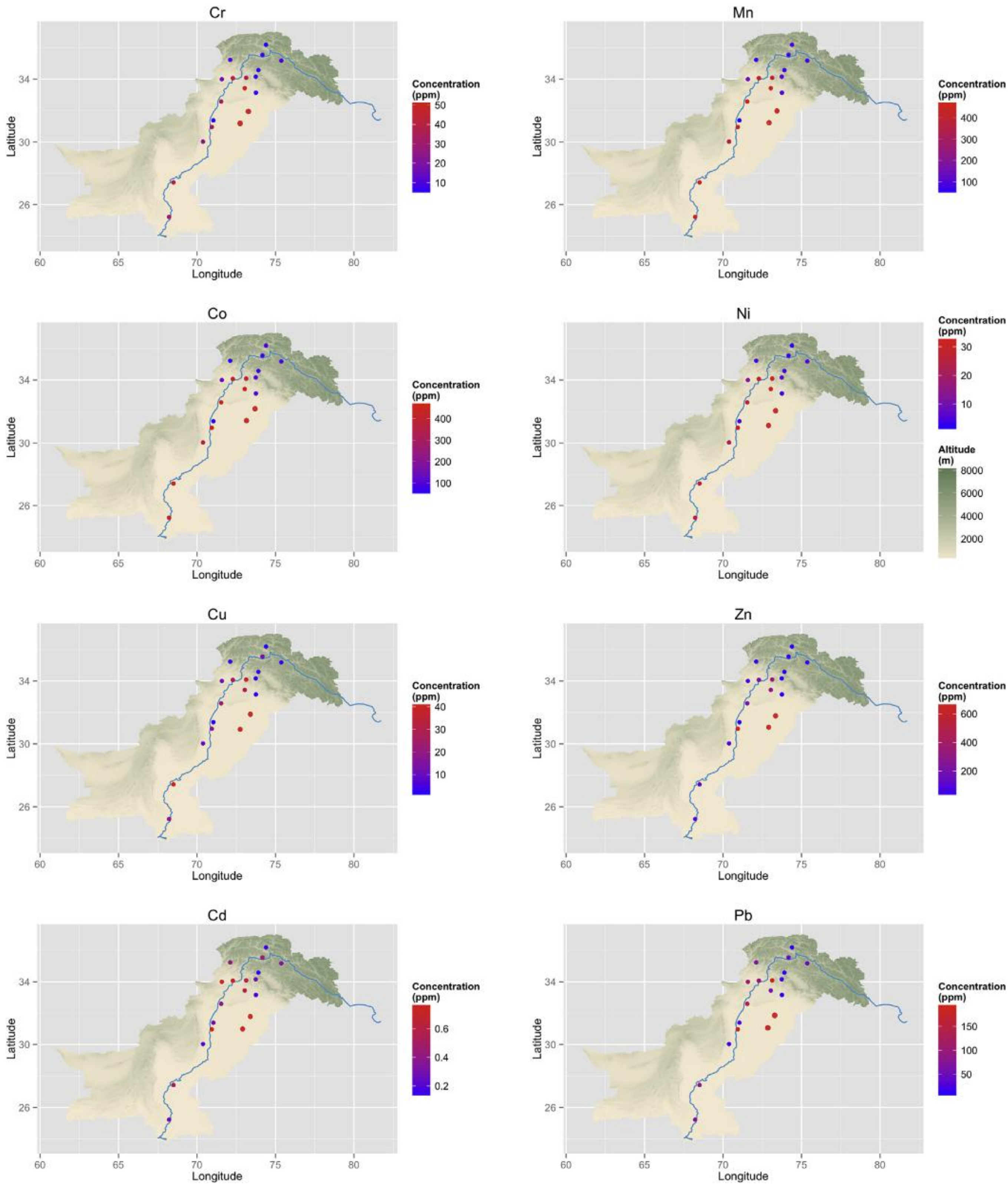

Fig. 2. Spatial variation of the trace elements concentration in the dust particles along the altitudinal gradient in Pakistan.

activities (Shah and Shaheen, 2007; Alamdar et al., 2016).

The results of PCA/FA (Table 3) as well pointed to zone-specific sources of trace elements. The correlation matrix of the study elements in each region supports the trends of PCA/FA (Tables S–5). The first two varimax rotation factors (VF-1 and VF-2) of the PCA/FA explained the maximum variation. Table 3 highlights the strong positive loading by VF-1 for Co, Cr, Mn and Ni and by VF-2 for Pb, Zn, Cd, in FMZ, respectively. Similarly, the extracted factors (VF-1

Table 2
Geo accumulation index (I_{geo}) values of studied elements from each studied zone and their classes based on I_{geo} scores.

I-geo values									
		Cr	Mn	Co	Ni	Cu	Zn	Cd	Pb
FMZ	Median	0.08	0.00	0.00	0.00	0.00	0.00	0.45	0.87
	Min-Max (Mean)	0–0.3 (0.22)	0.00	0.00	0.00	0.00	0.00	0–0.98 (0.4)	0–2.4 (1.44)
WMZ	Median	0.02	0.00	0.06	0.04	0.00	0.02	0.12	0.38
	Min-Max (Mean)	0–2.87 (0.81)	0–1.6 (0.5)	0–6.58 (1.01)	0–2.5 (0.73)	0–1.85 (0.6)	0–3.2 (0.6)	0–2.01 (0.59)	0–3.92 (1.26)
RDZ	Median	2.06	1.62	2.13	1.98	0.61	0.10	0.22	1.65
	Min-Max (Mean)	0.6–2.9 (1.5)	0–1.9 (1.1)	0.4–3.4 (1.5)	0.4–2.9 (1.4)	0.6–1.9 (0.6)	0–7.01 (1.62)	0.02–2.5 (0.47)	0.4–5 (2.2)
LLZ	Median	2.06	1.50	2.02	1.88	0.95	0.53	0.41	2.28
	Min-Max (Mean)	1.4–2.3 (2.09)	0.9–1.6 (1.5)	0.6–2.02 (2.1)	1.2–2.6 (1.9)	0.7–2.4 (1.3)	0.5–4.3 (0.61)	0–1.8 (0.62)	1.7–3.5 (2.57)
I-geo class									
FMZ		<1	0	0	0	0		<1	2
WMZ		<1	<1	<1	<1	<1	<1	<1	2
RDZ		2	2	3	2	1	1	1	3–4
LLZ		3	2	3	2	1	1	1	3–4

I-geo classes: 0 (unpolluted), 1 (unpolluted to moderately polluted), 2 (moderately polluted), 3, (moderately to high polluted), 4 (high polluted), 5 (high to very highly polluted), 6 (very highly polluted).

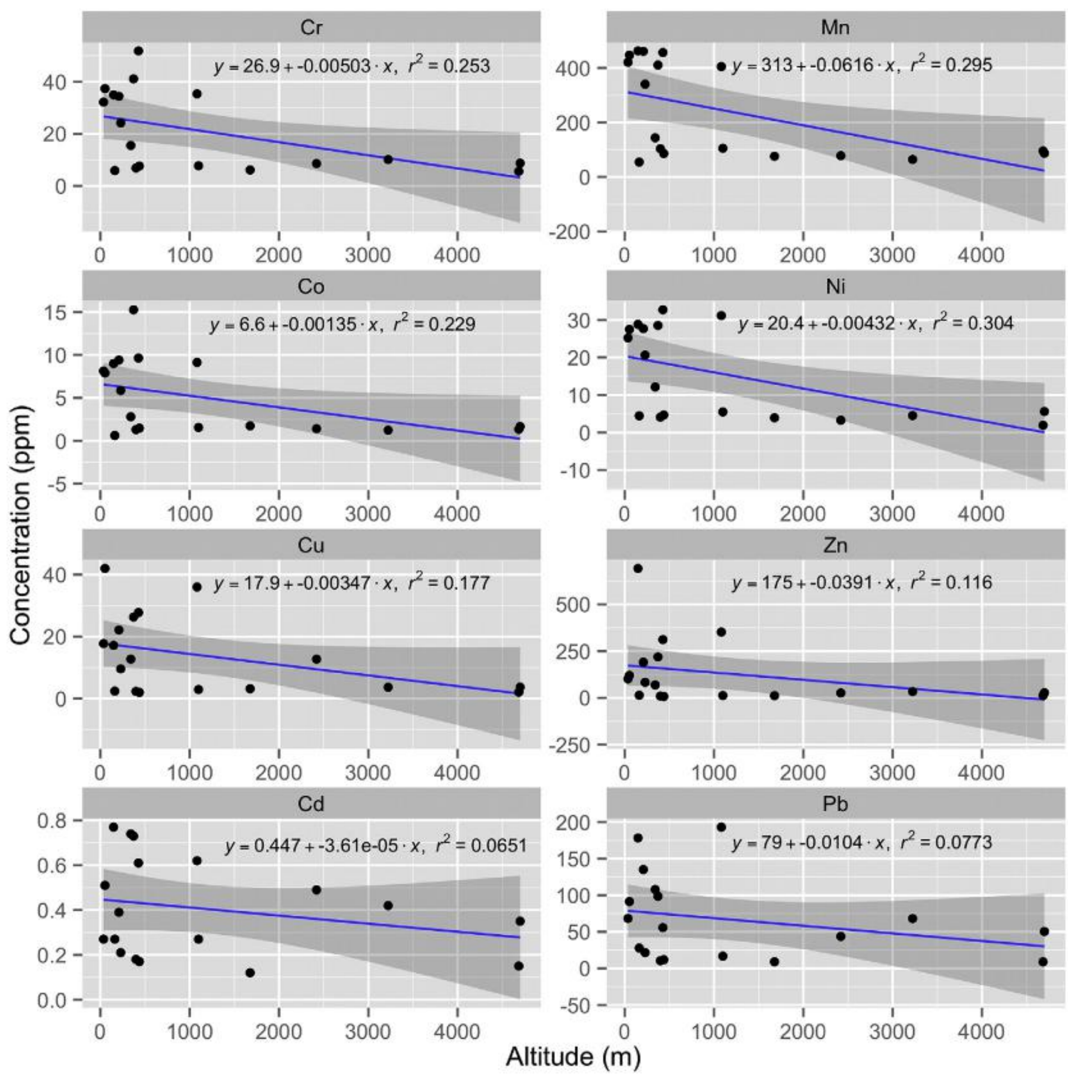

Fig. 3. Altitudinal trend of the trace elements concentrations in the dust particles in Pakistan. The trends for Cr, Mn, Co and Ni are statistically significant at $p < 0.05$.

and VF-2) showed strong positive loading for Co, Cr, Mn, Ni, Zn, Cd and Pb in WMZ. The possible sources of Co, Cr, Mn and Ni in the dust from FMZ and WMZ may be related to geological factors e.g., to the mafic and ultra-mafic rocks being enriched with trace elements, and to the release of these impurities into the atmosphere as fine dust particles (Khan et al., 2010; Muhammad et al., 2011; Shah and Shaheen, 2007). However in few cases from WMZ, anthropogenic influences such as mining and rapid urbanization have also been

Table 3
Loadings of studied trace elements from each studied zone on significant varimax rotated principal components (Marked loadings are significant > 0.70).

	FMZ		WMZ		RDZ		LLZ	
Studied metals	VF-1	VF-2	VF-1	VF-2	VF-1	VF-2	VF-1	VF-2
Cr	**0.94**	0.28	**0.90**	0.28	**0.96**	0.25	**0.89**	0.45
Mn	**0.94**	0.22	**0.94**	0.23	**0.96**	0.20	0.64	**0.77**
Co	0.34	0.20	0.13	**0.95**	**0.95**	0.30	−0.19	**0.98**
Ni	**0.94**	0.29	**0.96**	0.21	**0.95**	0.24	0.64	**0.74**
Cu	**0.84**	0.31	**0.94**	0.27	**0.89**	0.30	**0.99**	−0.04
Zn	0.30	**0.79**	**0.88**	−0.07	0.23	**0.92**	**0.91**	0.33
Cd	0.28	**0.88**	**0.71**	0.58	0.24	**0.95**	**0.99**	0.09
Pb	0.38	**0.79**	**0.78**	0.19	0.42	**0.76**	**0.99**	0.10
Eigen values	5.07	1.09	5.92	0.99	5.93	1.47	5.22	1.20
% Total Variance	63.40	13.56	73.95	12.37	74.13	18.36	67.95	15.37

indicated by PCA/FA as source of trace elements pollution in the area. On the other hand, extracted factors (VF-1 and VF-2) for the both RDZ and LLZ also highlighted strong positive loading of different studied elements and point to the similar source in both zones. Higher trace elements levels from mid-altitude agricultural and urban areas in the RDZ (i.e., Mianwali, Layyah and DG Khan, Gujranwala, Sargodha) and LLZ regions (i.e., Hyderabad and Sukhar) could be attributed mainly to agricultural and industrial activities and surface run-off of industrial waste from the high elevation areas via the stream network (Abdullah et al., 2015). These regions are characterized by semi-arid/arid conditions and receive local contaminated alluvial material by frequent dust storms from the surrounding areas, and also from the neighboring countries of central Asia (Clift and Blusztajn, 2005; Carmichael et al., 2009). Moreover, these regions also host huge brick kilns, cement and sugar factories, and other industries, as well as extensive agricultural areas where metal containing pesticides have been used since many years with consequent environmental contamination (Abdullah et al., 2015; Eqani et al., 2012). The high levels of trace elements into these areas (LLZ and RDZ) were expected, and are in agreement with previous studies (Abdullah et al., 2015; Kazi et al., 2009). Therefore, the influence of the local trace metal sources at lower altitudes is clearly discernible, unlike to the evidence for the frozen and wet mountain sites (FMZ and WMZ).

3.4. Calculation of human health risk

The index CDI estimates the intake into the human body by summing up the three routes of inhalation, ingestion and dermal contact, and the corresponding Hazard Quotient values (Table S-7). The HQ values for each route of exposure via dust and the calculated non carcinogenic risk reveal that dust ingestion is one of the major routes of all trace elements exposure followed by dermal contact and by inhalation, at all the studied sites. Nevertheless, various studies reported that particle-bound trace metals from inhalation bring about the same impact as from ingestion after retention of these particles (Mohmand et al., 2015). On the other hand, children showed higher values for all routes, ingestion, inhalation and dermal contact, and were affected more adversely than adults (Fig. 4). It is well established that children are prone than adults to ingestion of dust through mouthing/licking of hands, habits, toys, and other household objects. Associations have already been established between trace metal exposure and the skin allergies or asthma in children, and with children's neurodevelopment disorder and in girls' puberty surges (Martin and Griswold, 2009).

In this study, the HI at different studied sites exhibited the following trend: RDZ > LLZ > WMZ > FMZ among both children and adults (Fig. 4). The Hazard Index (Tables S–6) points to serious non-carcinogenic health risks (HI values > 1) from Co and Mn for children in the RDZ and LLZ regions, and from Pb for both adults (with few exceptions from FMZ) and children in all regions. The map of the sites where adults and children are at risk due to dust exposure with population density in the background (Fig. 4), highlights the priority areas in need of management aimed to reduce metal contamination. In general, higher values of the Hazard Index (Tables S–6) for all studied trace elements in RDZ and LLZ are associated with the peculiar climatic conditions, and to the geological conditions of these regions, that are characterized throughout the year by huge sand storms and abundant dust fall, i.e. by wet and dry deposition. Anthropogenic activities as well, including brick kilns, cements factors, wide scale use of pesticides and fertilizers, extensive cropping, may contribute to the elevated HI values. On the contrary, the WMZ and FMZ regions offer less human exposure to contaminated dust and pose lower health risks, due to their forest land cover, copious rainfall, high altitude and steeper slope (Alamdar et al., 2016). In developing nations like Pakistan, people are widely exposed to metal toxicity via dust due to their extensive outdoor activities, spent more day time into agricultural fields and also slept in open yards during night hours due to electricity shortfalls. The other main reason might be the careless behavior of people regarding washing their hands before eating, and also the widespread consumption of street food contaminated with outdoor dust (Mohmand et al., 2015). Trace metals, especially Pb, Co, and Mn, in such alarming concentrations poses severe health effects to humans like neurological disorders, developmental problems and disorders kidneys failure, miscarriages in pregnant women and even death (Martin and Griswold, 2009; Mohmand et al., 2015). The results of this study would be useful to raise awareness about environmental pollution in Pakistan, and would help people to avoid dust exposure, an important source of trace metals.

The HI values observed in this study were coherent with those, we found for other countries. In Shanghai, China, the total organic carbon contents and levels of Pb in urban dust were found to be higher than those of suburban dust (Shi et al., 2008). Similar to our findings, the highest level of risk for human exposure to road dust was through ingestion followed by dermal contact (Shi et al., 2008) and children had greater health risks than adults. Among other metals that were assessed in the study conducted in China, Pb was of most concern regarding the potential occurrence of health impacts (Shi et al., 2011). In Istanbul, Turkey (Karakus, 2012), the calculated Hazard Quotient (HQ) for non-cancer effects showed that ingestion was the major route of exposure to indoor dust, followed by dermal contact and inhalation pathways, resulting in a higher health risk of trace metals. However, in contrary to our study; the Hazard Index (HI) values for all studied elements were found to be lower than the safe threshold of 1, due to exposure to trace metals from dust in Turkey.

4. Conclusions

Our study, focused on dust as source of trace metal exposure throughout the different altitudinal zones of Pakistan, revealed significant roles of both natural and anthropogenic sources in determining metal concentration in dust. The analysis of the altitudinal trends of trace elements revealed that both the geological features of the soil, and the impact of human population density and the related activities contributed to the environmental contamination by trace elements. Mn, Cr, Co and Ni showed higher spatial variability throughout the study area than Cd, Pb, Zn and Cu. The risk estimates showed that ingestion was the major pathway of trace metal exposure through dust for both children and adults at all the studied regions of Pakistan, followed by dermal contact and

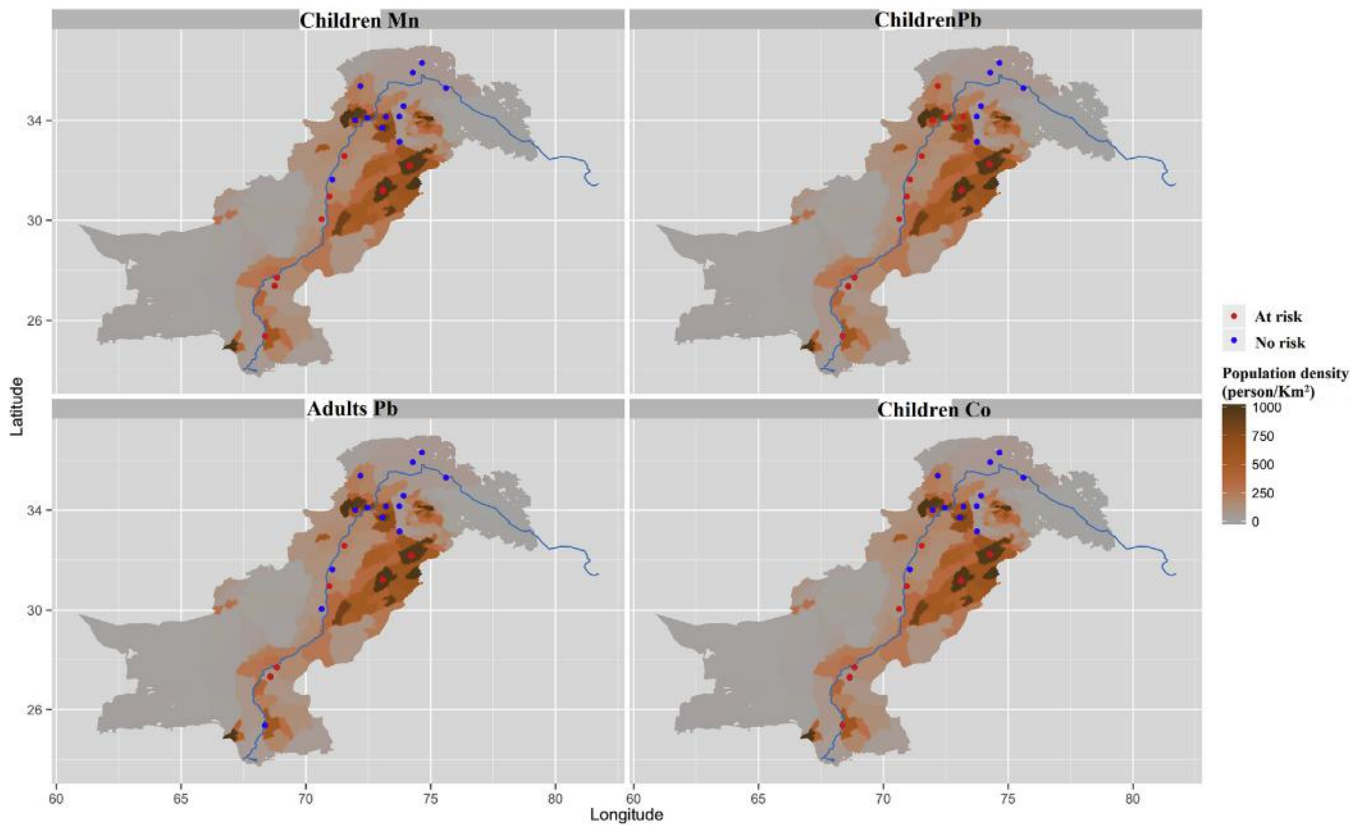

Fig. 4. Sampling locations where adults and children are at risk (HI > 1) from exposure to three trace elements (Co, Mn and Pb) via dust, with population density in the background.

by inhalation. Dust can be considered an important source of biological exposure, especially to Co and to Mn for children in RDZ and LLZ regions, and to Pb for both children and adults (with few exceptions) in all regions. However, other exposure sources like air, water, food, should be investigated in these regions. The findings of our study provide an ample baseline of information on trace metal exposure, and could aid the authorities in human health risk assessment and monitoring.

Acknowledgments

The authors wish to thank the NSFC, China (The Research Fellowship for International Young Scientists: NSFC# 21450110419) and President's International Fellowship for Postdoctoral Researchers. GRANT No# 2016PB009) for financial support.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2016.02.017.

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