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# Urban park soil contamination by potentially harmful elements and human health risk in Peshawar City, Khyber Pakhtunkhwa, Pakistan



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#### ABSTRACT

Urban soils may be highly contaminated with potentially harmful elements because of intensive anthropogenic activities. This study aimed to investigate the concentrations, sources, pollution levels and human health risk of potentially harmful elements in the soil of urban parks present in Peshawar, Khyber Pakhtunkhwa, Pakistan. For this purpose, the soil samples (n = 85) were collected from different parks (n = 8) and playgrounds (n = 3) and analyzed for total and bioavailable (EDTA extracted) potentially harmful elements (Cd, Cr, Cu, Pb, Ni and Zn) using an atomic absorption spectrophotometer. The basic soil properties such pH, electrical conductivity, organic matter, and soil particle size were also determined. The data revealed a significant (P = 0.01) variation in the concentrations of selected harmful elements among the different parks. The mean concentrations of Cd exceeded its maximum permissible limit (MPL) in all sites set by China (1995), India (2000), UK (1989) and EU (2000), while Ni concentrations exceeded its MPL in 5 sites. However, observed Zn, Cu, Cr and Pb concentrations were within their respective MPLs. Pollution indices (PI) of potentially harmful elements indicated low, moderate or high level of contamination in park soils linked with vehicular emissions, waste disposal and wastewater irrigation. The health risk was calculated using health quotient (for children) and total risk (for adults). Both noncarcinogenic and carcinogenic vulnerability were also calculated. The health risk data indicated that the main exposure pathway of potentially harmful elements to both children and adults was ingestion followed by dermal contacts. Hazard index (HI) values were lower than safe level (=1) but few parks showed the health risk existence. Children showed higher possible health risk than adults in the studied parks/playgrounds. The results of this study are important for the development of proper management strategies to decrease soil contamination with potentially harmful elements in the urban parks.

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### 1. Introduction

Soil is one of the foremost constituents of the environment, therefore a great interest has been paid to its contamination with potentially harmful elements in the urban environment (Waqas et al., 2015; Zacháry et al., 2015). In urban areas the most imperative sink for pollutants is soil (Cheng et al., 2014; Marcussen et al., 2014). It also acts as source of both essential and non essential elements and transforms them in to air, water and other living organisms (Iqbal and Shah, 2011). Among the contaminants, potentially harmful elements are of foremost importance due to their toxicity and persistency in the environment (Guagliardi et al., 2012; Khan et al., 2015a).

\*\* Correspondence to: Ningbo Urban Environment Observation and Research Station, Chinese Academy of Sciences, Ningbo 315830, China. Globally, serious environmental problems are associated with high concentrations of toxic metals present in urban soil (Cheng et al., 2014; Luo et al., 2012; Thornton et al., 2008; Wong et al., 2006). These toxic metals have adverse effects on humans, flora, fauna and even microorganisms (Khan et al., 2015b; Rehman et al., 2016). In city areas, anthropogenic activities (vehicular emissions, industrial discharges, wastewater irrigation, coal and fuel combustion, waste dumping and developmental activities) are severely concentrated, due to high urban population (Iqbal and Shah, 2011; Rashed, 2010) that lead to increase the contamination of environment (Martin et al., 2015). Due to urbanization and industrialization potentially harmful elements are frequently released to the urban environment and finally reach to soil (Bavec et al., 2015; Chen et al., 2013). The presence of harmful elements in soil is reported as a sign of great threat to ecological resources and humans (Guagliardi et al., 2012).

Urban park soils are not used for cultivation but have direct effects on the health of humans primarily children (Chen et al., 2005). In city, the soils of parks and grounds have high contamination of toxic metals (e.g. Pb) and health risk. The data regarding harmful elements in park

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soil showed that the concentrations of Pb, Zn and Cu have frequently exceeded the limits set for institutional, entertaining and residential sites (Mass et al., 2010). The application of metals is higher in the developed landscape than undeveloped areas (Li et al., 2013).

The discharge of potentially harmful elements badly disturbs the values of the metropolitan surroundings and causes threats to human beings. Children and adults are exposed to soil contaminants through incidental soil ingestion, re-suspension and consequent contact (Mitchell et al., 2014). USEPA (2003) suggested a value of 100 mg for soil ingestion per day for children of 1–6 years of age. Later on, USEPA (2008) suggested of the intake value of 50 mg/d for soil, 100 mg/d for soil and dirt and 1 g/d for soil through pica behavior. The children are exposed to soil particle smaller than 2 mm because of potential gripping to the skin of their hands. Consequently it is paramount important to estimate potentially harmful element levels in urban areas, metal ingestion rates and their threats to health.

In fact, individual well-being is strongly correlated to the worth and guality of soil and mainly to its level of contamination. Potentially harmful elements can be unsafe and cause hazardous impacts after their accumulation in body of the humans and other living organism (Duruible et al., 2007; Guagliardi et al., 2012). They badly affect the physical growth and inhibit the mental development of children. Organisms exposed to these pollutants were reported to have a wide range of problems including acute effects, endocrine disruption, reproduction dysfunction and cancer (Zhao et al., 2014). Furthermore, the intake of potentially harmful elements can also cause impacts on several vital nutrients within the body of consumers, decline the immunological defenses, stop development, cause psychosocial destruction, cause disabilities related with undernourishment and even upper gastrointestinal cancer (Khan et al., 2011). Pb through ingestion and contact can be harmful to enzymatic systems, affects the brainpower of humans (Babula et al., 2008) and causes various anemia, neurological disorders and hyperactivity (Marsden, 2003). Toxic metals (Cd, Ni, Cr, Cu and Zn) cause stomach pains, ulcers, vomiting, nausea, diarrhea, damages to liver, kidney, central nervous system and immune system, cancer growth, reproductive failure, modification of genetic material, melanoma, skin problem, bone crack, cardiovascular and respiratory diseases, lung cancer, liver demolition, kidney disorder and reduce the body weight (Agarwal et al., 1993; Barrento et al., 2009; Elinder, 1986; Oliver, 1997).

Several authors have indicated the need for a better understanding of urban soil contamination (De Kimple and Morel, 2000). Differences among cities regarding population, livelihood, traffic load and industrial behavior cause great differences in the concentrations of potentially harmful elements. Not only for biologists and ecologists but also for environmentalists these harmful elements in soil have been an issue of great concern. Thus the present study was designed to investigate the contamination load of potentially harmful elements (Cd, Cr, Cu, Ni, Pb and Zn) in the soil of urban parks and playgrounds present in Peshawar City because the children and young generation are exposed to it through hand to mouth and dermal contacts. To our knowledge, this is the first study focuses on parks/playgrounds' soil contamination with potentially harmful elements and associated health risk. This paper may play a great role to protect the young generation and children from the adverse impacts of these harmful elements. The findings of this study can facilitate the decision makers to manage the soil contamination and minimize health risks of urban inhabitants through stopping wastewater irrigation and other contributing factors.

#### 2. Material and methods

#### 2.1. Area description

Peshawar is the capital city of Khyber Pakhtunkhwa Province and lies between  $33^{\circ}$  44' and  $34^{\circ}$  15' north latitudes,  $71^{\circ}$  22' and  $71^{\circ}$  42' east longitude (Fig. 1). The total area is 1257 km<sup>2</sup> with total population

of 2.019 million. Peshawar basin is an intermontane basin present at the southern margin of the Himalayas. The basin is mainly composed of the Quaternary deposits such as fanglomerates, fluvial and lacustrine sediments (Burbank and Raynolds, 1984). It is bounded by the Attock-Cherat Range on the south, Gandghar Range on the east and Khyber Range on the west. The ranges of Gandghar and Khyber contain rocks of metasediments and unmetamorphosed foreland basin sediments of Kohat-Potwar Plateau. The metasedimentary rocks are intruded by granites are present in the north and northwest of the Peshawar basin (Hussain et al., 1991). Above-mentioned city is highly developed and populous area as compared to other cities in the province. Several industrial units such as leather, outfits, soap, hosiery, footwear, ghee, miniature arm, flourmills, match factories and steel re-rolling units are present in the region. The temperature is ranged from 25 to 42 °C, while relative humidity is changed from 46 to 76%. The mean annual rainfall is 400 mm in the study area (DCR, 1998). The lawns, parks and gardens are mostly irrigated with wastewater due to shortage of canal water.

#### 2.2. Sampling sites and procedure

Soil samples (n = 85) were collected from major public parks (Baghe Naran Park, Chacha Younas Park, Jinnah Park, Khyber Park, Parda Bagh, Shahi Bagh, Sher Khan Shaheed Stadium and Tatara Park; 8 samples from each) of Peshawar and main playgrounds (Cricket, Hockey and Volleyball grounds; 7 samples from each) present in the campus of University of Peshawar, Pakistan. Soil samples were collected from the top soil (0–15 cm) in triplicates. The samples were collected with stainless shovel and were placed in airtight polythene bags and were properly labeled and brought to laboratory for further processing. The materials such as stones or debris were grounded into powder, separately labeled in polythene bags and used for further analyses.

#### 2.3. Soil chemical analyses

Soil samples of the urban parks were analyzed for basic properties such as pH, electrical conductivity (EC), organic matter, particle sizes and texture (Table 1). Soil particle sizes were determined using Fritsch Analysette 3 PRO Sieve Machine. The air dried samples were used and the soil retained by every mesh was weighed and particle size in fraction for sand, silt and clay was measured (Liu et al., 2007). Soil sample (<2 mm) was used to determine the pH and EC using respective electrodes. Briefly the soil was mixed with deionized water (1:5 weight:volume) and shaken for 30 min and then pH and EC were measured using respective electrodes. Organic matter was determined through loss on ignition (LOI) technique adopted from Storer (1984).

For total concentrations of potentially harmful elements, the soil samples were digested with strong acids using the method adopted by Khan et al. (2008). Briefly, 1.0 g soil was taken into acidified rinsed digestion tube and 10 ml aqua regia (HCl:  $HNO_3$ ) was added into it. Next morning, the tubes were put in the digestion block and temperature was raised to 80 °C for 1 h, then cooled and 5 ml of  $HClO_4$  was added and finally heated to 160 °C until the solution in the tubes become clear. After cooling, the suspensions were filtered into acid rinse volumetric flasks and diluted to 50 ml with deionized water. The concentrations of Cd, Cr, Cu, Ni, Pb and Zn, were determined using Atomic Absorption Spectrophotometer (AAS, Perkin Elmer 700).

For determination of available potentially harmful elements, the air dried sample (5.0 g) was taken into a 125 ml Erlenmeyer flask. 25 ml of 0.05 M EDTA was added and shaken at 120 rpm for 1 h and then filtered through filter paper (Merry et al., 1981). The filtrates were analyzed for available concentrations of potentially harmful elements such as Cd, Cu, Cr, Ni, Pb, and Zn using AAS, (Perkin Elmer 700). All the samples were analyzed in triplicates.



Fig. 1. Location map showing the study area and sampling sites.

For accuracy and precision, certified reference materials (GBW07401–GBW07408) of soil (n = 3) were included in each batch and the recovery of selected elements was satisfactory ranged from 91 to 101%. Moreover, the reagent blanks were also included in each batch to check the contamination during digestion and subsequent analysis processes.

### 2.4. Soil pollution assessment

Soil pollution assessment was done by the quantification of pollution index (PI). PI is calculated by:

## $PI = C_{metal} / B_{metals}$

where C and B represent the concentration of selected metal in the sample and respective background concentration.

## 2.5. Human exposure and health risk assessment model

Risk assessment is a multi-step procedure (USDOE, 2011; USEPA, 1989) comprises statistics compilation and evaluation, exposure assessment, toxicity estimation, and risk characterization. The chronic daily intake (CDI) of toxic metals is one of the major concerns because of their possible health complications resulting in children and adults (Olawoyin et al., 2012). CDI values were used to calculate both the cancer risk and health quotient (HQ).

2.5.1. Non-carcinogenic hazard (child)

$$CDI_{ing-nc} = C \times IngR \times EF \times ED \times 10^{-6} / BW \times AT_{nc}$$
(1)

$$CDI_{inh-nc} = C \times EF \times ET \times ED \times InR/PEF \times BW \times At_{nc}$$
(2)

#### Table 1

Basic properties of soils collected from parks and playgrounds (n = 85).

Parks/playgrounds	pH	EC (µS/cm)	Organic matter (%)	Soil partic	le size (%)		Soil types
				Sand	Silt	Clay	
Baghe Naran $(n = 8)$	8.21	151	0.5	45.6	33.4	21.0	Loamy sand
Chacha Younas ( $n = 8$ )	8.05	221	0.5	48.5	34.4	17.1	Loamy sand
Jinnah park $(n = 8)$	7.90	195	0.4	30.0	22.0	48.0	Sandy clay
Khyber park $(n = 8)$	8.05	276	0.3	47.5	36.4	16.1	Loamy sand
Parda Bagh $(n = 8)$	7.99	295	0.9	53.7	21.0	25.3	Sandy loam
Shahi Bagh $(n = 8)$	8.77	432	0.8	41.3	32.6	26.1	Sandy loam
Sher Khan Shaheed Stadium $(n = 8)$	8.23	249	0.6	42.9	31.6	25.5	Sandy loam
Tatara park $(n = 8)$	8.22	380	0.6	40.7	32.2	27.1	Sandy loam
Hockey Ground $(n = 7)$	7.72	105	0.3	56.1	29.3	14.6	Loamy sand
Cricket Ground $(n = 7)$	8.25	74	0.7	57.1	21.4	21.4	Loamy sand
Volley Ball Ground $(n = 7)$	7.38	101	0.7	59.1	13.6	27.3	Loamy sand

$$CDI_{dermal-nc} = C \times SA \times AF \times ABS_d \times EF \times ED \times 10^{-6}/BW \times At_{nc}.$$
 (3)

2.5.2. Carcinogenic risk (adult)

$$CDI_{ing-ca} = C \times IngR_{adj} \times EF \times 10^{-6} / At_{ca}$$
(4)

 $CDI_{inh\text{-}ca} = C \times EF \times ET \times ED \times InR/PEF \times BW \times At_{ca} \tag{5}$ 

$$CDI_{dermal} = C \times ABS_d \times EF \times DFS_{adj} \times 10^{-6} / At_{ca}$$
(6)

The above-mentioned Eqs. (1)-(3) and (4)-(6) adapted from USEPA (1989, 1997 and 2001) and USDOE (2011), respectively. The values of these variables are given in Table 2.

The CDI for each factor and exposure trail were consequently separated by the equal reference quantity to calculate HQ. For carcinogenic the dose was multiply by the gradient issue to generate a rank of surplus life time cancer risk. HQ based on non-cancer risk can be considered by dividing daily dose to a specific reference dose (RFD). On human population through daily exposure RFD is an evaluation of utmost permissible risk. The HQs can be added and generate a hazard index (HI) to estimate the risk of mix metal contamination and refer to the sum of more than one HQ for multiple exposure pathways and are calculated for shorter, chronic and subchronic exposures. Hence it is possible to calculate the collective non-carcinogenic hazard expressed as the HI and carcinogenic risk expressed as the total cancer risk.

$$HQ = CDI_{nc}/R_{f}D$$
(7)

$$HI = \sum HQ = HQ_{ing} + HQ_{inh} + HQ_{dermal}$$
  
=  $CDI_{ing-nc}/R_f D_{ing} + CDI_{inh-nc}/R_f C_{inh} + CDI_{dermal-nc}/R_f D_{Dermal}$  (8)

Total Risk= $\sum Risk=Risk_{ing}+Risk_{inh}+Risk_{dermal}$ 

$$= CDI_{ing-ca} \times CSF_{ing} + CDI_{inh}-ca \times IUR + CDI_{dermal-ca} \times CSF_{ing}/ABS_{Gl}.$$
(9)

Eqs. (7) and (8) are adopted from USDOE (2011), while Eq. (9) is adopted from USEPA (2011). The values of these variables used in the above-mentioned equations are given in Table 2.

#### 2.6. Statistical analysis

Mean values, standard deviations of potentially harmful elements, the figures and tables were calculated through MS Excel (Microsoft 2007). Special package of statistic version 8.1 was used for ANOVA and SPSS (statistical package for social science) for Pearson's Correlation. Volleyball playground (located in the campus of University of Peshawar, Pakistan) was selected as a reference site due to less traffic (vehicular emission) and low/no wastewater irrigation or sewage problems.

### 3. Results and discussion

#### 3.1. Soil basic properties

Table 1 summarizes the soil basic properties such as pH, EC, organic matter, texture and type. The soil pH was neutral to alkaline and ranged from 7.38–8.77 units. The EC was significantly (p =0.01) varied in the soils of selected parks and playgrounds and changed from 74 to 432 µS/cm. Soil organic matter contents were greatly varied and ranged from 0.3 to 0.9%. The soils of the studied parks/playgrounds were loamy sand, sandy clay and sandy loam in nature. These soil properties play significantly role in the bioavailability of potentially harmful elements which is further discussed in Section 3.2.

#### 3.2. Total and bioavailable potentially harmful elements

Table 3 summarizes the potentially harmful element concentrations in the soils of selected parks and playgrounds and a distinct variation was observed in their concentrations. The concentrations of Cd, Cr, Cu, Ni, Pb and Zn ranged from 4.93–7.60, 13.9–45.0, 8.50– 57.4, 30.1–225, 0.9–37.2 and 26.5–158 mg/kg, respectively. Potentially harmful element concentrations in the soil of parks and playgrounds were compared with international standards of United Kingdom (UK, 1989), European Union (EU, 2000), State Environmental Protection Agency (SEPA, 1995) and Indian Standards (Awashthi, 2000) as mentioned in Table 3. Zn concentrations in all collected samples were within maximum permissible limits (MPLs). Ni concentration was higher than its MPL set by UK (1989) and India (Awashthi, 2000) in 54% parks. The concentrations of Pb, Cu and Cr were observed within their respective MPLs in all parks/

Table 2

Values of different variables used for the estimation of human exposure to urban park soils (USDOE 2011; USEPA, 2011).

Variables	Details	Values
ABS <sub>d</sub>	Dermal absorption factor	0.001
ABS <sub>GI</sub>	Gastrointestinal absorption factor	0.025 for Cd, 0.04 for Ni, 1 for Pb
$AF (mg cm^{-2})$	Soil to skin adherence factor	0.07 for child, 0.7 for adult
$AT_{ca}(d)$	Averaging time for carcinogenic effects	$LT \times 365$
$At_{nc}(d)$	Averaging time for non-carcinogenic effects	$ED \times 365$
BW (kg)	Average body weight	16.2 for child, 61.8 for adult
$C (mg kg^{-1})$	Concentration of metal in soil	Quantified in this study
$DFS_{adj}(mg yr kg^{-1}d^{-1})$	Soil dermal contact factor-age-adjusted	362
ED (yr)	Exposure duration	30 for resident and recreation, 6 for child resident
$EF(dyr^{-1})$	Exposure frequency	75
$ET (hd^{-1})$	Exposure time	1
IngR (mg d <sup><math>-1</math></sup> ) and InR (m <sup>3</sup> d <sup><math>-1</math></sup> )	Soil ingestion rate and inhalation rate for receptor	Soil ingestion 200 for children, 100 for adult, while inhalation 7.6 for children 20 for adults
$IngR_{adj}(mg yr kg^{-1} d^{-1})$	Soil ingestion rate	113
LT (yr)	Life time	65
PEF $(m^3 kg^{-1})$	Soil to air particulate emission factor	1.36E + 9
RfDing (mg kg <sup><math>-1</math></sup> d <sup><math>-1</math></sup> )	Chronic oral reference dose	1.0E – 3 for Cd, 2.0E – 2 for Ni
RfCinh (mg m <sup><math>-3</math></sup> )	Chronic inhalation reference concentration	1.0E – 5 for Cd, 9.0E – 5 for Ni
SA ( $cm^2 event^{-1}$ )	Skin surface area available for exposure	
	resident, 2800 for child and 5700 for adult	
CSFing $(mg kg^{-1} d^{-1})^{-1}$	Chronic oral slope factor	$8.5  imes 10^{-3}$
IUR ( $\mu g m^{-3}$ )	Chronic inhalation unit risk	1.8E – 3 for Cd, 1.2E – 5 for Pb, 2.6E – 4 for Ni

The concentrations (mg/kg) of to	tal and bioavaila	able fractions of pc	tentially harmful e	elements in soil sa	mples ( $n = 85$ ) a	nd their maximur	n permissible limi	IS.				
Parks/ground	Cd		Cr		Cu		Ni		Pb		Zn	
	Total	Bioavailable	Total	Bioavailable	Total	Bioavailable	Total	Bioavailable	Total	Bioavailable	Total	Bioavailable
Baghe Naran park	$6.01\pm0.36$	$0.17\pm0.04$	$27.5\pm20.04$	$0.2\pm0.23$	$8.5\pm2.8$	$0.5\pm0.1$	$41.8\pm9.5$	$1.3\pm0.15$	$17.2\pm5.4$	$1.35\pm0.83$	$59.6 \pm 22.5$	$1.67 \pm 2.82$
Chacha Younas Park	$5.6\pm1.96$	$0.2\pm0.04$	$40.3 \pm 4.2$	$0.3\pm0.28$	$17.9 \pm 3.13$	$6\pm4.59$	$52.5\pm2.82$	$1.5\pm0.66$	$25.8\pm3.06$	$3.7\pm1.24$	$103.2 \pm 22.9$	$0.006\pm0.005$
Jinnah Park	$6.25\pm0.60$	$0.19\pm0.051$	$38.4\pm6.3$	$1.8\pm0.99$	$21.2 \pm 7.7$	$1.7 \pm 1.7$	$52.7 \pm 2.23$	$1.39\pm0.32$	$25.6\pm2.6$	$0.32\pm0.12$	$79.6\pm14.3$	$0.011\pm0.005$
Khyber Park	$4.93 \pm 2.12$	$0.18\pm0.062$	$33.5 \pm 11.15$	$2.02 \pm 1.39$	$10.03\pm6.42$	$1.498 \pm 1.5$	$49.2\pm8.15$	$1.28\pm0.66$	$12.7\pm14.2$	$5.7\pm6.24$	$69.9\pm17.5$	$0.39\pm0.652$
Parda Bagh	$5.8\pm1.63$	$0.226\pm0.09$	$35.6 \pm 12.9$	$1.86 \pm 1.07$	$57.4\pm36.09$	$28 \pm 17.5$	$49.2\pm10.9$	$1.53\pm0.54$	$37.2 \pm 29.07$	$9.7\pm14.7$	$158.4\pm87.4$	$16.07 \pm 22.1$
Shahi Bagh	$5.8\pm1.35$	$0.18\pm0.05$	$42.1\pm0.55$	$0.706\pm0.13$	$40.6\pm24.13$	$11 \pm 9.06$	$224.8\pm2.28$	$1.81\pm0.22$	$34.3 \pm 15.1$	$7.36 \pm 3.51$	$117.5\pm54.8$	$0.037\pm0.020$
Sher khan Shaheed Stadium	$5.48\pm0.68$	$0.133\pm0.08$	$23\pm1.47$	$3.33\pm0.05$	$9.9\pm1.30$	$1.22\pm2.0$	$40.6\pm3.25$	$1.09\pm0.44$	$0.9\pm1.6$	$0.36\pm0.37$	$51.2\pm6.15$	$2.83\pm0.87$
Tatara Park	$6.9\pm0.35$	$0.21\pm0.04$	$45\pm15.1$	$0.4\pm0.05$	$16.4\pm1.90$	$0.7\pm0.4$	$57.8\pm15.9$	$1.33\pm0.41$	$26.2\pm1.6$	$5.86 \pm 7.75$	$83.4\pm18.35$	$0.006\pm0.005$
Cricket Ground	$7.2 \pm 4.15$	$0.17\pm0.46$	$41.1 \pm 23.7$	$0.55\pm0.11$	$13.2\pm7.6$	$0.4\pm0.1$	$51.5\pm29.7$	$0.17\pm0.13$	$20.7 \pm 11.9$	$2.3\pm0.82$	$54.5\pm31.4$	$2.16\pm1.53$
Hockey Ground	$7.6 \pm 4.3$	$0.14\pm0.10$	$41.7 \pm 24$	$2.5\pm0.81$	$13.8 \pm 7.9$	$0.3\pm0.2$	$53 \pm 30.5$	$0.14\pm0.10$	$25.2 \pm 14.9$	$0.9\pm0.6$	$57.4 \pm 33.1$	$0.61\pm0.09$
Volley Ball Ground	$5.2 \pm 3$	$0.18\pm0.06$	$13.9\pm8.02$	$3.2\pm0.02$	$5.7 \pm 3.2$	$0.02\pm0.005$	$30.05\pm17.3$	$0.18\pm0.06$	$11.7\pm6.7$	$2.1\pm0.80$	$26.55\pm15.2$	$1\pm 0.153$
Maximum permissible limit's												
SEPA,1995	0.6		250		100		60		350		300	
India, 2000 <sup>a</sup>	3–6		NA		135-270		75-150		250-500		300-600	
EU, 2000	ŝ		150		140		75		300		300	
UK, 1989	ŝ		400		80		50		300		200	
<sup>a</sup> Indian limits are taken from <i>i</i>	Awashthi (2000)											

playgrounds, while Cd concentrations exceeded its MPL in all these parks/playgrounds set by UK (1989); EU (2000) and SEPA (1995). In general, the concentrations of Cu, Cd, Cr, Ni, Pb and Zn were greatly varied in the soil of the studied parks and playgrounds (Table 3). Similarly, Luo et al. (2012) reported a great variation in the concentrations of potentially harmful elements in the soil samples collected from the urban parks, Xiamen, China. In the playgrounds of the study area, the concentrations of Cr, Cu and Zn were lower but Pb and Ni concentrations were higher than those reported by Guney et al. (2010) in the playground of Istanbul Turkey. Furthermore the concentrations of selected harmful elements (Cr, Cu, Pb and Zn) were lower in the soils of parks as compared to the results reported by Guney et al. (2010).

Bioavailable fractions of selected elements in the soil samples collected from different parks/playgrounds are also given in Table 3. Like total metal concentrations of potentially harmful elements, a great variation was also observed in bioavailable fractions of the selected elements. Bioavailable fractions of Cd. Cr. Cu. Ni. Pb and Zn. ranged from 0.14-0.23, 0.2-3.33, 0.02-28.0, 0.14-1.81, 0.32-9.70 and 0.01-2.83 mg/kg, respectively. Overall distributions of potentially harmful elements in the soils of different parks and playgrounds are given at Fig. 2. The bioavailable Cd (0.2% of the total contents) distribution was the same in all selected parks and playgrounds except one parks and playground. The highest value of bioavailable Ni (1.8%) was observed in one park (Shahi Bagh) as compared to other parks and playgrounds. The highest percentages of bioavailable Pb, Zn and Cu (9, 16 and 28%, respectively) were noticed at Parda Bagh, while the highest bioavailable Cr (3.3%) was observed at Sher Khan Shaheed Stadium. The distribution data of potentially harmful elements indicated that Parda Bagh was highly contaminated with selected harmful elements as compared to other selected parks in the study area. The previous studies have also reported great variations in distribution of potentially harmful elements in urban park soils (Guagliardi et al., 2012; Karim et al., 2015; Luo et al., 2012) which are consistent with the findings of our study.

The mobility and bioavailability of potentially harmful elements depend upon the chemical and physical properties of the soil ecosystem. Soil pH, cation exchange and organic carbon are strongly control the bioavailability of potentially harmful elements. At low pH, potentially harmful elements are more mobile and easier bioavailable as compared to high pH because of the precipitations occur between metals and different anions which are considered as a significant mechanism for controlling the availability of metals in soil (Li et al., 2003). Organic matter also minimizes the availability of potentially harmful elements through adsorption and stable complexes formation (Khan et al., 2015a; Nawab et al., 2016). After addition to the soil, potentially harmful elements immediately get adsorbed by the solid portion (Surita et al., 2007). The presence, probable toxicity and movement of harmful elements in the soil depend upon the dispersion of specific sites of adsorbent, the crystallinity of absorbent and the morphology of absorbent (Puls et al., 1992). Potentially harmful elements originated from anthropogenic sources are more mobile and potentially bioavailable in majority of soil conditions, therefore, can cause severe health risk in ecological resources and humans.

## 3.3. Sources of potentially harmful element contamination

In Peshawar City, several indentified and unidentified sources are responsible for soil contamination with potentially harmful elements in urban parks and playgrounds. Ni, Cu, Zn and Pb concentrations in soil are mainly related with anthropogenic sources including wastewater irrigation, waste disposal, vehicular exhaust, wastewater sludge and construction or other developmental activities (Artaxo et al., 1999; Gao et al., 2013; Gray et al., 2003; Martin, 2001). The normal activity and deterioration of vehicles on the roads can emit potentially harmful elements into the air, especially Pb and Cu (Martin et al., 1998; Ritter and Rinefierd, 1983). Cd originates from industrial units (power plants, coal combustion, metallurgical industry, auto-repair shops and chemical plants), while Cr emits from different manmade sources (disposal of plastics, paint, enamel, ceramics and batteries wastes) and finally these elements reach to soil through atmospheric deposition (Shi et al., 2008). Pb contamination is closely associated with overpopulation and urbanization in this city; however, the major sources of Pb discharge were included industries, waste incineration and the historical combustion of Pb added fuel (Karim et al., 2015; Koz et al., 2008).

Due to urbanization in Peshawar, the commercial activity has been increased rapidly which resulted in traffic enhancement and jamming problems. Soil contamination with potentially harmful elements was closely related with vehicular emission, lack of traffic management plan and substandard condition of vehicles. Low-quality vehicles also led to emission of smoke, soot particles and contaminated the environment with toxic elements. The urban parks and playgrounds were situated in the inner region of the city bounded by avenues of soaring density traffic so vehicular emission directly contaminated the soil (Khan et al., 2011).

In the study area, wastewater irrigation was another key factor of park soil contamination with potentially harmful elements. Long term irrigation of parks with wastewater led to accumulation of elevated level of toxic metals. Incompletely treated sewage water, sewage sludge, unsuitable septic scheme and leakages from sanitary also contributed to soil contamination with potentially harmful elements.

The park age and position also play significant role in soil contamination with potentially harmful elements. The soil in older parks (Shahi and Jinnah parks) was more heavily contaminated as compared to younger parks. Similarly, the parks visited by a large number of tourists, accompanied by heavy traffic, showed higher contamination. Previous studies also linked the degree of contamination with age and historical potentially harmful element contamination occurred in the metropolitan areas (Madrid et al., 2002). It is apparent that the history of the parks should be a supplementary factor correlated with the increase of the potentially harmful element concentrations in the soils.

#### 3.4. Pollution load indices

The pollution indices (PI) were calculated for soils of parks and playgrounds and significantly (P < 0.001) varied as mentioned in Table 4. The values of PI of Cd, Cr, Cu, Ni, Pb and Zn were ranged from 86.7-115, 65.7-101, 116-375, 0.26-2.65, 30.7-229 and 5.52-17.6, respectively. These results showed higher enrichment/contamination of potentially harmful elements as compared to Karim et al. (2015), the reason could be the low baseline values with them. The PI values were classified as low ( $PI \le 1.0$ ) to moderate ( $PI \le 3.0$ ) levels of contamination for Ni, while high (PI > 3.0) level of contamination for the rest of selected harmful elements. The values of PI from 0.5-1.5 indicate the enrichment of potentially harmful elements occurred mainly from weathering of rocks, crustal materials or other natural processes, while PI value higher than 1.5 suggests that the contamination occurred more probably from anthropogenic sources (Ghrefat et al., 2011; Karim et al., 2015). In this study, high contamination and PI in the soil of parks/playgrounds could be linked with high concentrations of metals such as Pb, Cr, Ni and Zn (334-555, 78-87, 27-68 and 277-453 mg/kg, respectively) in dusts of Peshawar City (Khan et al., 2003) and low background values of selected metals in the study area (Hag et al., 2005). The sites near the primary roads with high density of traffic were more highly polluted as compared to those located on secondary and tertiary roads. The highest PI value observed for potentially harmful elements can be caused severe health risk in the ecological resources and humans because of their high genotoxicity in the exposed organisms. Besides Cd, PI values for Cr, Ni and Pb were also higher as compared to Cu and Zn which could also be linked with heavy traffic and wastewater irrigation (Khan et al., 2011). In order to stop further enrichment of park soils with these harmful elements, the wastewater irrigation should be avoided immediately and plantation along roads must be performed to prevent the high deposition of dusts on soils in parks and playgrounds.



Fig. 2. Bioavailable concentrations (%) of potentially harmful elements (Cd, Cr, Cu, Pb, Ni and Zn), while BNP, CYP, JP, KP, PB, SB, SKSS, TP, CG, HG and VBG represent Baghe Naran Park, Chacha Younas Park, Jinnah Park, Khyber Park, Parda Bagh, Shahi Bagh, Sher Khan Shaheed Stadium, Tatara Park, Cricket Ground, Hockey Ground, Volleyball Ground.

#### Table 4

Statistical result of pollution index (PI) of potentially harmful elements in urban parks soils of Peshawar.

Sites (parks and playgrounds)	Cd	Cr	Cu	Ni	Pb	Zn
Baghe Naran Park	100.2	80.13	229.2	0.39	42.65	8.11
Chacha Younas Park	93.33	74.67	335.8	0.82	53.57	12.17
Jinnah Park	104.2	83.33	320.0	0.98	53.78	12.08
Khyber Park	82.17	65.73	279.3	0.46	50.20	5.99
Parda Bagh	96.67	77.33	296.7	2.65	50.20	17.55
Shahi Bagh	96.67	77.33	350.8	1.87	229.4	16.18
Sher Khan Stadium	91.33	73.07	191.7	0.46	41.43	0.42
Tatara Park	115.0	92.00	375.0	0.76	58.98	12.36
Cricket Ground	120.0	96.00	342.5	0.61	52.55	9.76
Hockey Ground	126.7	101.3	347.5	0.64	54.08	11.89
Volley Ball Ground	86.67	69.33	115.8	0.26	30.66	5.52
Back ground values	0.06a	0.12a	21.7b	0.98a	2.12a	62b

aHaq et al. (2005).

bSiddiqu and Khattak (2011).

#### 3.5. Human exposure and health risk

In case of urban parks, the human health risk associated with potentially harmful elements in contaminated soil is more important and occurs through oral intake, inhalation, or dermal contacts (Luo et al., 2012). In this study, the carcinogenic and noncarcinogenic risk CDI, HQ and total risk of potentially harmful elements were calculated. The model used in this research to compute the exposure of human to potentially harmful elements in soil is based on those developed by USEPA (2011). It showed that ingestion is the major cause of exposure followed by dermal contact and inhalation. According to USEPA (2011) the value 1.0E - 6 (one person per million) is considered as the carcinogenic target risk. Cancer risks lower than 1.0E - 6 are negligible, and cancer risks above 1.0E - 4 are considered non-acceptable by most of the international regulatory agencies (Guney et al., 2010).

The statistical results of chronic daily intake by children and adults are mentioned in Table 5. HI was calculated for Ni and Cd in all samples of studied sites. Due to unavailability of some data, HI was not calculated for Pb, Cr, Cu and Zn. The HI value for Cd was greater than 1 in 21% of parks/playgrounds, while HI for Ni exceeded the safe limit in 14% of parks. The results of this study were in agreement with those reported in previous studies like Luo et al. (2012) because they were also observed HI values greater than one for potentially harmful elements in urban park soils.

Due to unavailability of cancer slope factor (CSF) values of the selected harmful elements, except Pb, it was not possible to determine total health risk or cancer risk. Thus just cancer risk due to Pb in all parks/ playgrounds was calculated using the human health risk assessment model. The results showed that the total risk of cancer due to Pb in all sampling sites was greatly varied. In 14% of parks, Pb concentration showed carcinogenic health risk and their values ranged from 2.20E - 5 to 9.4E - 5, respectively. The value of HQ greater than 1 represents great concern. Thus HQ  $\leq$  1 indicates improbable unfavorable health effects, while HQ>1 suggests the adverse health effects. However, the HI values indicated that children face greater harmful risk due to potentially harmful elements in the park dust, therefore, particular attention should be paid to this aspect in the urban environment.

#### 3.6. One-way ANOVA and correlationships

One way ANOVA analysis was used for the statistical comparison of selected harmful element contamination in different sampling locations within the study area. ANOVA data showed that potentially harmful element contamination at different locations varied significantly. In 7% of parks, the concentrations of Cr, Cu, Ni, Pb and Zn showed significant variation (P = 0.001), while Cd was not significant (P = 0.13). In Chacha Younas park, Cr, Cu, Ni, Pb and Zn were significantly higher (P =0.001) than the reference site except for Cd (P = 0.411). In Jinnah park, Cr, Cu, Ni, Pb and Zn showed significant values (P = 0.001). In Khyber park Cr, Cu, Ni and Zn showed significant statistical value (P = 0.001) except Cd (P = 0.5) and Pb (P = 0.574). In Parda Bagh no significant value was shown for Cd (P = 0.185), while Cr, Cu, Ni and Pb showed significant values (P from 0.001 to 0.0001). Cd was not significantly (P = 0.185) different than reference site, while Cr, Cu, Ni showed significantly (P = 0.0001) higher contamination than the reference site. In Sher Khan Shaheed Stadium, again Cd showed no significant variation, while significant variation (P = 0.001) was found for Cr, Cu, Ni and Zn. In Tatara park, Cd, Cr, Cu, Ni, Pb and Zn showed significant variations (P < 0.001). In 14% of parks, Cd, Cr, Cu, Ni, Pb and Zn concentrations were found significantly (P = 0.001) higher than reference site and their variations were significant (P < 0.001). The above results suggested that different locations contributed differently to the mean metal concentration in the soil of selected parks. Mostly all the potentially harmful elements showed higher contamination values than the reference site.

Potentially harmful elements present in soil usually have complex interactions among each other. Various factors i.e., original contents of the harmful elements in parent materials, soil formation processes and anthropogenic factors, and properties of soil control their relative abundance (Li et al., 2008). To identify the association among potentially harmful elements in urban soils and their probable sources, Pearson's correlation was applied (Table 6). Correlation analysis has been mostly applied in environmental studies. The high correlation between soil potentially harmful elements may reflect that these elements had similar pollution level and sources. A very significantly strong correlation was found between Pb and Cu (r = 0.768), Zn and Cu (r = 0.936), Zn and Pb (r = 0.774) at 0.01 level. Pb and Cr also showed significant correlation (r = 0.721) at 0.05 level. Ni showed weak positive correlation with Cd, Cr and Cu. Overall; all the elements grouped together (Cu, Cr, Pb and Zn) indicated that the anthropogenic sources (vehicular emission, waste water irrigation, waste disposal and sewage application) were responsible and closely related for the soil contamination in the study area.

#### 4. Conclusion

On the basis of findings, it is concluded that the concentrations of selected potentially harmful elements (except Cd in 6 sites and Pb in

Table 5

Health risk exposure of non-carcinogenic hazard (children) and carcinogenic hazard (adults).

Potentially harmful elements	CDI (children)				CDI (adults)	
	Ingestion	Inhalation	Dermal	Ingestion	Inhalation	Dermal
Cd Cr Cu Ni Pb Zn	$\begin{array}{c} 3.3E - 7 - 3.9E - 3\\ 5.1E - 7 - 8.4E - 6\\ 5.0E - 8 - 7.1E - 5\\ 3.5E - 7 - 3.8E - 6\\ 5.3E - 7 - 1.4E - 5\\ 1.5E - 8 - 4.0E - 5 \end{array}$	2.9E - 15-2.3E - 3 1.8E - 12-4.3E - 6 1.7E - 12-3.7E - 11 8.8E - 13-9.6E - 12 2.0E - 12-1.4E - 11 1.7E - 14-3.7E - 4	$\begin{array}{c} 9.4E-10-4.5E-3\\ 1.2E-9-3.0E-3\\ 1.4E-10-0.9E-6\\ 9.9E-10-1.0E-8\\ 2.5E-9-2.5E-3\\ 4.2E-11-5.4E-6 \end{array}$	$\begin{array}{c} 4.6\mathrm{E}-8-8.03\mathrm{E}-3\\ 7.1\mathrm{E}-8-1.1\mathrm{E}-6\\ 4.3\mathrm{E}-9-0.02\mathrm{E}-2\\ 3.8\mathrm{E}-8-4.5\mathrm{E}-6\\ 1.1\mathrm{E}-7-3.4\mathrm{E}-6\\ 1.5\mathrm{E}-8-5.8\mathrm{E}-4 \end{array}$	3.7E - 10-6.5E - 10 9.6E - 11-1.1E - 9 1.4E - 12-8.1E - 8 4.0E - 10-4.4E - 9 6.6E - 12-2.8E - 8 2.3E - 13-6.9E - 4	$\begin{array}{c} 1.4E-10-2.0E-5\\ 2.2E-10-5.0E-3\\ 2.2E-11-1.8E-4\\ 1.6E-10-1.7E-3\\ 3.0E-10-0.01E-3\\ 4.2E-11-0.5E-4 \end{array}$

Pearson's correlation of selected potentially harmful elements in soil.

Potentially harmful elements	Cd	Cr	Cu	Ni	Pb	Zn
Cd	1.00	.097	.687	.777	.453	.405
Cr		1.00	.249	.351	.721*	.284
Cu			1.00	.449	.768**	.936**
Ni				1.00	.446	.370
Pb					1.00	.774**
Zn						1.00

\* Correlation is significant at the 0.05 level (2-tailed).

\*\* Correlation is significant at the 0.01 level (2-tailed).

one site) in the soils of parks and playgrounds of Peshawar City were significantly (P < 0.01) higher than the reference site. In all selected sites, Cd concentration was exceeded its MPL set by SEPA, India, EU and UK, while Ni concentration was only exceeded the limits of UK and India in some sites. All other selected harmful elements (Cr. Cu. Pb and Zn) were observed within their respective limits. Regarding bioavailable fractions, potentially harmful elements showed different percentages in the selected parks due their different basic properties. Pollution assessment of potentially harmful elements showed that the enrichment factor was moderate to high for Cd, Cr, Pb and Ni, while low for Cu and Zn. The potentially harmful element contamination sources were mainly heavy traffic, wastewater irrigation, sludge application and waste disposal. The young people were exposed to the selected harmful elements via dermal contact, inhalation and accidental ingestion of contaminated dust/soil. The HI values for Cd and Ni in some parks exceeded the safe limits suggesting that a particular attention should be paid to these harmful elements. HI values for children were higher than adults in the study area. This study suggests that the government should develop a proper management strategy to prevent urban parks' soil contamination with potentially harmful elements and human health risk.

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