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Distribution of Selected Heavy Metals in Urban, Suburban and Agricultural Soils in Pakistan

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ABSTRACT
Soils from different land use areas of Sheikhupura City, Pakistan were assessed for the concentrations of heavy metals- Cadmium (Cd), Chromium (Cr), Copper (Cu), Cobalt (Co), Nickel (Ni), Zinc (Zn), Lead (Pb), and Cyanide (CN-) along with the determination of inorganic substances and physical properties- Nitrogen (N), Potassium (K), Phosphorous (P) , Moisture Content (MC) and Electrical Conductivity (EC). 80 samples were collected using grab sampling from four land use areas identified as Agricultural, Industrial, Commercial and Residential. Each sample was tested in the lab for all the selected parameters. The metal concentrations were determined using Atomic Absorption Spectrophotometer. Nitrogen determination was based on Kjeldhal and acid based titration. The statistical analysis of correlation, mean, maximum, minimum and standard deviation were utilized to interpret all the data. The results determined a correlation significant at the 0.01 level among Cr, CN-, F, Pb, EC and pH. High levels of Cu, Cd, Pb, CN- were observed in Agricultural soil where as the concentration of Cd was exceeding the maximum permissible concentrations.
Keywords: Soil. Land use, Heavy Metals, Correlation, Sheikhupura

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INTRODUCTION

Soil acts as a sink for various types of pollutants. Heavy metals, organic and inorganic substances are released into the environment via anthropogenic sources especially by the utilization of fertilizers, pesticides, sewage sludge, leaded paints, and a variety of manufacturing and industrial procedures. Regardless of its origin, heavy metals are potentially hazardous because of their long resident times, persistence, toxicity, and bio-accumulative potential. With their toxicity not declining through degradation, heavy metal loadings increase in soils, especially in rapidly expanding urban and industrial areas with intense traffic flows. Heavy metals accumulate in the soil and degrade the quality of the soil affecting the fertility and the crop yield. They have adverse impacts on living organisms i.e. humans, plants and animals and the overall ecosystem. Heavy metals have great ecological significance with respect to their toxicity and accumulation, as they can be leached into water or can be up taken by plants and crops and can be released into the atmosphere affecting human health directly or indirectly [1].

Industrial areas are considered to be the major source of soil pollution in any given area. Studies have been conducted to back this theory up. Urban soils have a tendency to vary spatially according to the composition of the soil and depending upon the climatic and environmental condition. Decomposers face great stress during their activity due to increased concentration of heavy metals in the soil [2]. Several studies have revealed that heavy metals are potentially dangerous to human as well as wildlife, depending upon their concentrations in the environment. Industrial sector is a major contributor and is liable for the high levels of toxic metals that are derived from the disposal of untreated and contaminated liquid effluent to the land. Increment in the contamination of heavy metals in soil as well as increased urbanization and industrialization along with intensive agricultural practices have lead to an increase in the contamination of heavy metals in soils, and has now become a major concern [1]. Therefore the regulatory bodies of various countries along with the World Health Organization (WHO) and the United

States Environmental Protection Agency (USEPA) have established the values for heavy metal concentration based on the health guidelines [3].

MATERIALS AND METHODS

Study Area

The soils in the urban and suburban areas of Sheikhupura City, Pakistan were analyzed in 2016 for the existence of heavy metals, organic and inorganic substances. Figure 1 shows the geographical location and extent of the Sheikhupura District. The city is situated in the province of Punjab having and estimated population of 361,000. Sheikhupura is known for its vast industrial sector. The industrial sector is expanding including numerous industries. Among them reside agricultural, textile manufacturing, metal processing, paint, and petrochemicals facilities. Based on the findings in other developing industrial locations by various researchers [4],it can be hypothesized that the soils of Sheikhupura are being contaminated with all sorts of pollutants originating from a wide variety of sources. This research investigation especially focused on heavy metals was therefore carried out to gain an insight on the spatial distribution of the selected parameters on the soils of Sheikhupura City.

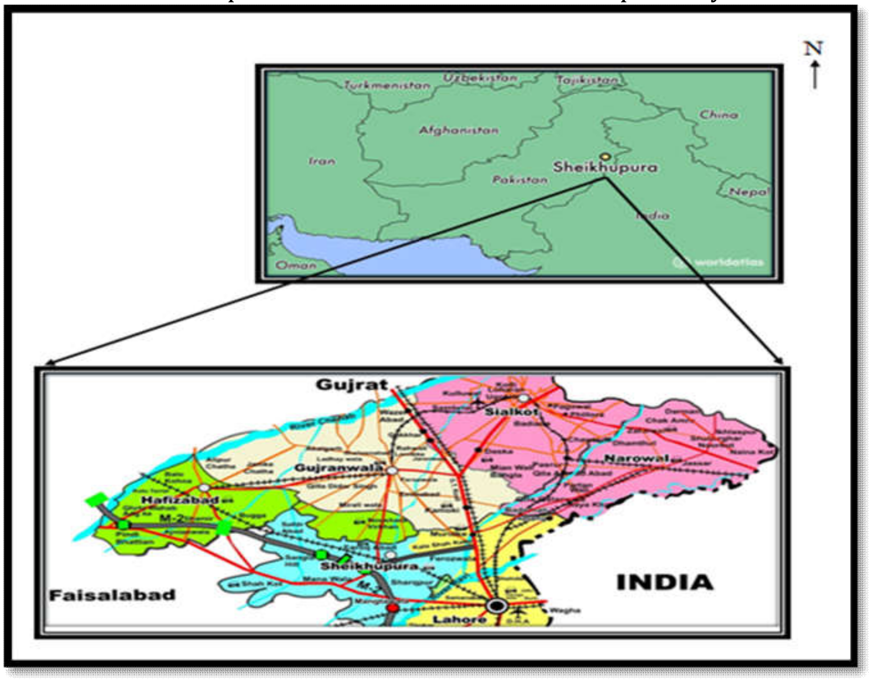

Figure 1: Map of Sheikhupura City

Sampling Technique

After conducting a field visit of the city, a map was used to identify the land use categories. To obtain a respectable sample size a total of 80 samples were collected from four different land uses. The number of samples gathered from each of the four land uses was 20 samples each from agricultural, Industrial, Commercial and Residential land use. A Global Positioning System (GPS) was used to record the geographical location of each sampling site. The samples were collected using a grab sampling technique. From each land use area 5 sampling sites were selected and from each location 3 samples were collected from varying depths and a composite sample of 3 subsamples was prepared.

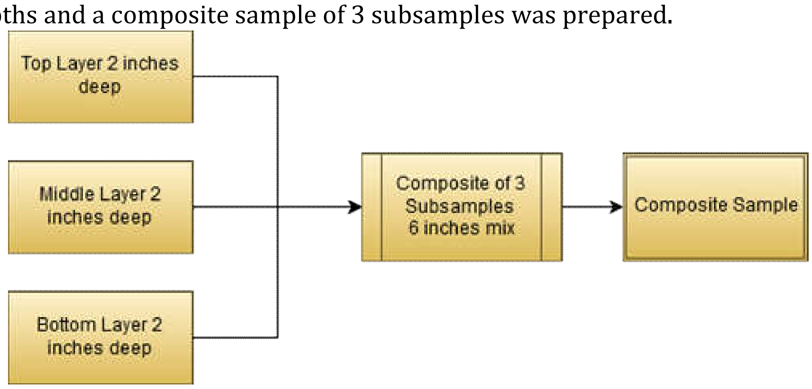

Figure 2: Soil sampling technique for the present study

The samples were collected in clean zip lock bags and then sealed. All samples were labeled with the area coordinates, land use and the date and time of collection. The samples were then brought to the lab; air dried and were then stored at a suitable storage place for further analysis.

Analysis Procedure

Each of the 80 samples were analyzed for the determination of Cadmium (Cd), Chromium (Cr), Copper (Cu), Cobalt (Co), Nickel (Ni), Zinc (Zn), Lead (Pb), and Cyanide (CN-). Along with the determination of physical properties and inorganic substances **-**Nitrogen (N), Potassium (K), Phosphorous (P), Moisture Content (MC) and Electrical Conductivity (EC) (Table 1). These metals were selected due to the agricultural and industrial practices simultaneously in the selected city such as oil refinery, shoe factory, steel mill, and textile mill. With the knowledge that heavy metals are persistent and non degradable, it is important to determine their concentration. Even low concentrations of heavy metals are toxic to plants, animals and humans [5]. Therefore it is pivotal to place great importance on these contaminants with respect to the environment, animal and human health.

Table 1: Standard Procedures followed to carry out the analysis of selected parameters

Physical and Chemical Parameters			
Parameters	**Standard Procedure**	**Model Number**	**Method Number**
Moisture Content (MC)	Oven Drying	**Memmert Oven** UNE 200	-
Electrical Conductivity (EC)	Conductivity Meter	Eutech Instrument Pc 510	HACH 8160
Potential Hydrogen (pH)	pH Meter	Eutech Instrument Pc 510	HACH 8156
Metallic Parameters			
Parameters	**Standard Procedure**	**Model Number**	**Method Number**
Copper (Cu)	Atomic Absorption Spectrophotometer	Buck Model 210 VGP	HACH 8143
Chromium (Cr)	Atomic Absorption Spectrophotometer	Buck Model 210 VGP	HACH 8023
Cobalt (Co)	Atomic Absorption Spectrophotometer	Buck Model 210 VGP	HACH 7200
Zinc (Zn)	Atomic Absorption Spectrophotometer	Buck Model 210 VGP	HACH 8009
Nickel (Ni)	Atomic Absorption Spectrophotometer	Buck Model 210 VGP	HACH 1001
Cadmium (Cd)	Atomic Absorption Spectrophotometer	Buck Model 210 VGP	HACH 8017
Lead (Pb)	Ion Exchange Electrode	Thermo Electron, Orion Dual Star	EPA 8317
Cyanide (CN-)	Ion Exchange Electrode	Thermo Electron, Orion Dual Star	EPA 8027
Inorganic Parameters			
Parameters	**Standard Procedure**	**Model Number**	**Method Number**
Total Nitrogen (N)	Kjedhal Method	-	EPA 10208
Potassium (K)	Flame Photometer	Sherwood 410	HACH 8049
Phosphorous (P)	UV Visible Photometer	Stand-alone UV-6000	EPA 8048
Fluoride (F)	Ion Exchange Electrode	Thermo Electron, Orion Dual Star	-

Statistical Interpretation

The results obtained by the analysis of the soil sample were recorded and then interpreted statistically using IBM SPSS version 20 through the calculation of mean, maximum,minimum,standard deviation and establishing the correlation of different factorsto determine the relation of the metal concentration with respect to different land use.

RESULTS AND DISCUSSION

The results presented in (Table 2) show the maximum, minimum, mean and standard deviation of all the samples tested the results obtained can be compared with the World average values and maximum allowable limits (MAL) for heavy metals in soils (Table 3).

Continuous urbanization and development has lead to increased levels of heavy metals in soils. Over the last few decades human activities have been continuously contributing towards the elevated levels of heavy metals in urban soils .The contents of the heavy metals found in the soil are greatly relying upon the origin and geochemical properties of the parent material and their existence in the soil is a result of the natural weathering of the parent rock [1].

In developing countries, soil pollution has now become a key environmental issue due to the change in land use .The accumulation of selected and tested metals were seen to be mostly nil with some exceptional metals like lead, potassium, cyanide, and cadmium. The soils ability to retain metals is primarily determined by pH and the ability of cation exchange capacity of metals and the level of organic carbon content [6]. However, previous studies have deduced that high pH values can be a reason of increased retention of metals leading to decreasing the solubility and may limit the capacity to absorb elements from the soil [7]. However, the mean value of of Industrial samples was seen to be 7.1670, Commercial soil samples had a mean pH of 5.9725, Residential mean pH 6.2215 where as the Agricultural mean pH was observed to be 6.8625. The maximum pH was observed in the industrial whereas the lowest pH was observed in the commercial site samples. The pH of the Agricultural samples held a greater emphasis as soil fertility and its quality is of great importance with respect to farming and agricultural practices. However the mean value of pH in the samples was 6.66 which was satisfying the optimum pH of soil within the range of 6-8 according to FAO (Table 2).

Table 2: Maximum, Minimum, Mean and Standard Deviation of all tested parameters

	N	Minimum	Maximum	Mean	Std. Deviation
pH	80	5.73	7.78	6.5576	.54928
Electrical Conductivity(µs/cm)	80	96.0	882.0	220.989	126.1115
Moisture Content (%)	80	.025	1.728	.69029	.443427
Fluoride (ppm)	80	9.41	13976.00	1744.3449	3156.78401
Cyanide (ppm)	80	21.33	586.30	143.7665	145.59101
Potassium (ppm)	20	.16	.58	.3825	.14560
Lead (ppm)	80	62.42	3486.00	891.0980	986.21788
Cadmium (ppm)	1	3.50	3.50	3.5000	.
Copper (ppm)	2	1.50	1.75	1.6250	.17678
Chromium (ppm)	17	1.40	1.90	1.4588	.16605

Table 3: World average values and maximum allowable limits (MAL) for heavy metals in soils (µg/g) in different countries

Metal Element	World Average Values	World Toxic Limit Values	Canada MAL	Britain MAL	Germany MAL
Cadmium (Cd)	0.06	3	8	3	2
Chromium (Cr)	100	50	75	50	200
Nickel (Ni)	40	100	100	50	100
Lead (Pb)	10	100	200	100	500

Metal Element	World Average Values	World Toxic Limit Values	Canada MAL	Britain MAL	Germany MAL
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The heavy metals which pose key threats to human life include lead, cadmium, mercury and arsenic. Their effects on humans have been extensively studied and reviewed over years by National and International certified organizations such as WHO, World Health Organization [8]. The results revealed noticeable difference in the concentration of cyanide, lead and potassium (Table 5) from among different sampling locations. The maximum value of Cadmium in the soils of Sheikhupura city exceeded the World Average Values as well as the World toxic limits. Moreover the mean concentrations of lead were around 80 times greater that the World Average limits. However, the concentrations of copper, chromium, nickel and zinc were lower than the maximum allowable limits for Canada, Britain and Germany (Table 3).

Cadmium was only detected in one sample attained from the agricultural sector which exceeded the World Average Values as well as the World toxic limits (Table 3).
Sources of Cadmium may be natural or anthropogenic including emissions from the industrial sector, fertilizers, sewage sludge which may cause soil contamination. Soil contamination may hence lead to increased uptake of Cadmium by vegetables and crops entering the food chain. Low pH levels enhance the ability of soil to uptake Cadmium [9].
Copper concentrations are commonly found near mines and industrial areas, landfills and waste disposals. Mainly copper is released into the air by the burning of fuels. The particles settle down as a result of rainfall and enter into the soil causing soil contamination of copper [1].Copper was detected in only two samples both from different sectors; commercial and from the agricultural. However, the remaining samples where all below detectable limits.
To determine whether there were similarities and differences in the contamination of the sources of heavy metals cyanide, potassium and lead a correlation was build upon the different land uses (Table 5) provides a correlation matrix for the heavy metals found in four different land uses the significant correlation among the heavy metals could be observed.

Table 4: Correlations between Heavy Metals detected in all samples

		Cyanide	Potassium	Lead	Copper	Chromium
Cyanide	Pearson Correlation	1				
	Sig. (2-tailed)					
	N	80				
Potassium	Pearson Correlation	-.010	1			
	Sig. (2-tailed)	.968				
	N	20	20			
Lead	Pearson Correlation	.759**	.204	1		
	Sig. (2-tailed)	.000	.388			
	N	80	20	80		
Copper	Pearson Correlation	1.000**	1.000**	1.000**	1	
	Sig. (2-tailed)	.	.	.		
	N	2	2	2	2	
Chromium	Pearson Correlation	-.312	.b	-.258	.b	1
	Sig. (2-tailed)	.222	.000	.317	.	
	N	17	5	17	0	17

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

The correlation of lead and other metals (Table 4) (Table 5) with respect to land use was significantly correlated at 0.01**. The concentrations of lead however were exceeding the permissible limits i.e. 120µg/g as per EPA standards. The concentrations of lead were significantly higher than the maximum allowable limits of Germany, Britain as well as of Canada (Table 3).
The exposure to lead occurs mostly in occupational premises like in smelters and mines or even in battery plants. The areas near the mine or smelter may have high levels of inorganic lead present in the air. Airborne contamination can be deposited anywhere soil, water or even enter the food chain.
Acute lead poisoning can be identified by the presence of the following symptoms headache, irritability, abdominal pain or complains related to the nervous system. Sleeplessness and restlessness can be the signs of lead Encephalopathy. Children with lead poisoning may suffer from behavioral disturbances, and face difficulty in learning or concentrating. Severe cases may even experience acute psychosis, confusion and reduced consciousness. Long term exposure may lead to diminished intellectual capability in children especially [7]. A research carried in 2004 reported that in comparison to European Countries the average air levels of lead in Islamabad are significantly higher. This may also be likely related to the city of Sheikhupura, Pakistan as it is an industrial hub and has similar traffic density. Evidently, lead, one of the toxic constituents of airborne particulate matter, contaminates soil from atmospheric depositional processes in not only Lahore City but also other areas of Pakistan [10].
Different Land use drew consideration towards the possibility of various impacts on soil. Thus, the spatial distribution becomes an important factor determining the distribution of metals [11]. Foley et al studied the universal importance of land use which signifies that although in short term, updated land use practices have provided amplified supplies of modern goods [12].

Table 5: Correlation of land use with detected Heavy Metals in all samples

			Cyanide	Potassium	Lead
	Cyanide	Pearson Correlation	1		
		Sig. (2-tailed)			
		N	20		
Agricultural	*Potassium*	Pearson Correlation	-.665	1	
		Sig. (2-tailed)	.221		
		N	5	5	
	Lead	Pearson Correlation	.951**	-.448	1
		Sig. (2-tailed)	.000	.449	
Industrial		N	20	5	20
	Cyanide	Pearson Correlation	1		
		Sig. (2-tailed)			
		N	20		
Commercial	*Potassium*	Pearson Correlation	-.445	1	
		Sig. (2-tailed)	.453		
		N	5	5	
	Lead	Pearson Correlation	.238	.553	1
		Sig. (2-tailed)	.311	.334	
		N	20	5	20
	Cyanide	Pearson Correlation	1		
		Sig. (2-tailed)			
		N	20		
	Potassium	Pearson Correlation	-.277	1	
		Sig. (2-tailed)	.652		
		N	5	5	
	Lead	Pearson Correlation	.359	-.628	1
		Sig. (2-tailed)	.120	.256	
		N	20	5	20
	Cyanide	Pearson Correlation	1		
Residential		Sig. (2-tailed)			
		N	20		
	Potassium	Pearson Correlation	-.871	1	
		Sig. (2-tailed)	.055		
		N	5	5	
	Lead	Pearson Correlation	.163	.154	1
		Sig. (2-tailed)	.491	.805	
		N	20	5	20

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

Nitrogen is a pivotal component in soil especially in agricultural soil. Nitrogen is naturally present in the soil system in one form or the other as it can easily transform forms. It is mostly available to crops in the form of ammonia or nitrate [5]. The samples analyzed revealed that the minimum concentration of nitrogen was seen to be 0.10ppm whereas the maximum concentration was 3.30ppm, with an average nitrogen concentration of 1.2550. The average concentration of Nitrogen in agricultural soil was 1.20 ppm. The concentration of N is said to be low if < 10ppm and medium if within the range of 10-20ppm and if within the range of 20-30ppm it is considered high above 30ppm it is considered as excessive and toxic. In this case it can be deduced that the concentration was significantly low. Nitrogen deficient crops can be recognized by numerous symptoms such as stunted growth the crops may appear smaller and maturation may be postponed, loss of green pigment from leaves also known as yellowing and other symptoms may be less prominent like protein loss may lead to less plump seed and flesh of fruits [13].

Potassium is also one of the three most essential macronutrients in soil and is considered the second most important after nitrogen. Potassium is important as it is essential for the proper growth and maintenance of plants and crops. Potassium undergoes numerous reactions with the other components in soil like calcium, magnesium and sodium, which affects the availability of Potassium for vegetation [14]. Concentrations greater than 800 ppm are considered as extremely high. The average value of K was 0.3825 ppm in the studied land uses.

Out of all metals chromium was the most occurring and was the only metal detected in all 4 land uses with an average value of 0.66 µg/g. Chromium does not leach into the soil rather is considered as a binding agent of soil as it is very persistent. Chromium is an element in electroplating, paints, cement and even in wood preservatives. Chromium VI is a known carcinogen however chromium III is a nutrient. Inhalation of chromium can cause irritability, respiratory problems, and asthma. Extended exposure can damage the nervous system and impair liver and kidney functioning [15].

CONCLUSION

The results indicated that heavy metals were infrequently found in the soils of Sheikhupura with exceptions of chromium (0.66 μg/g). It can be suggested that differences among different land uses were not significant. However, the concentrations of lead were exceeding thrice times than the permissible limits (120μg/g). Heavy metals are polluting the water, atmosphere and crops in not only Sheikhupura City but also other cities and villages across Pakistan. Increasing population, unlimited rural to urban migration pressures, and unanticipated industrialization activities could be considered as major contributors of elevated accumulation of pollutants in Sheikhupura City.

CONFLICT OF INTEREST: The authors declare that there is no conflict of interest.

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