Research Article

Heavy metals status of the urban and agricultural soils of Peshawar, Pakistan

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Abstract

Soil is a crucial component of urban and rural environments, and in both places land management is the key to soil quality. Unfortunately mining, manufacturing, and the use of synthetic products viz., pesticides, paints, batteries, industrial waste, and land application of industrial or domestic sludge can result in heavy metal contamination of urban and agricultural soils. Heavy metal pollution of soil is a significant environmental problem and has its negative impact on human health and agriculture. Therefore, the present study was mainly conducted to investigate the physico-chemical characteristics and concentrations of heavy metals viz; Zn^{2+} , Fe^{2+} , Cu^{2+} , Mn^{2+} , Cr^{2+} , Cd^{2+} , Ni^{2+} , and Pb^{2+} in the selected soil samples collected from three depths receiving municipal wastewater of Peshawar City. Results showed that textural class of the soil varied from silt loam to sandy loam with pH of soil samples ranging from 7.30 to 8.89 with an average value of 8.09 that was slightly alkaline. The EC of the soil samples ranges from 0.2 to 0.9 dS m^{-1} with an average value of 0.5 dS m^{-1} showing no salinity problem. The concentrations of Zn^{2+} , Fe^{2+} , Cu^{2+} , Mn^{2+} , Cr^{2+} , Cd^{2+} , Ni^{2+} , and Pb^{2+} ranges from 0.86-3.98, 11.92-31.73, 2.85-6.83, 14.92-19.19, 0.11-0.86, 0.04-0.58, 0.54-0.96, and 3.16-38.3 mg kg^{-1} with an average values of 2.14, 21.44, 5.11, 17.59, 0.35, 0.28, 0.73 and 17.18 mg kg^{-1} in surface soils (0-15cm), respectively. While it ranges from 0.64-3.37, 11.03-23.91, 2.48-6.83, 10.7-16.33, 0.05-0.23, 0.01-0.35, 0.06-0.64 and 1.44-40.36 mg kg^{-1} with an average values of 1.78, 18.42, 4.31, 14.03, 0.12, 0.15, 0.42 and 12.85 mg kg^{-1} in sub-surface soils (30-45cm), respectively. The concentrations of Cr^{2+} , Fe^{2+} and Ni^{2+} were within safe limits while Cu^{2+} and Mn^{2+} concentrations were above the permissible limits of WHO standards. The concentrations of Zn^{2+} , Cd^{2+} and Pb^{2+} in the soil samples collected from the bank of municipal wastewater drain of Peshawar city were above the permissible limits of WHO standards. None of the soil samples showed phytotoxically excessive concentrations of aforementioned heavy metals.

Keywords: Soil; physical; Chemical; Characteristics; Heavy metals; Waste water; City effluents.

Introduction

Pollution can be defined as the human alteration of physical or chemical characteristics of the environment to a level that is harmful to living creature. Soil pollution refers to an increased degree of harmful human-made chemicals in the natural soil environment. Soil pollution is becoming a serious problem due to rapid growth of population, urbanization and industrialization. The excessive soil pollution can cause major problem for ecosystem by affecting the lower pyramid levels of the food chain and disrupting its proper functioning. Of the nine major forms (air, light, littering, noise, radioactive, thermal, visual and water), soil pollution is one of the most important one. Soil contamination occurs when chemicals are released by spill or underground leakage. Soil is considered to be the safe heaven and ultimate sink for variety of wastes and pollutants. Among the most significant soil contaminants are hydrocarbons, MTBE, herbicides, pesticides, chlorinated hydrocarbons, paints, batteries, industrial waste, and land application of industrial or domestic sludge can result in heavy metal contamination. Heavy metals also occur naturally, but rarely at toxic levels [1].

Heavy metals are conventionally defined as elements with metallic properties and having an atomic number >20 . Metals are natural components in soil with a number of heavy metals being required by plants as micronutrients. Regarding the role of heavy metals in living systems, they are divided into two groups i.e. essential and non-essential. Essential heavy metals are those, which are needed by living organisms for their growth, development and physiological functions like Mn, Fe, Ni, Cu and Zn [2] while non-essential heavy metals are those, which are not needed by living organisms for any physiological functions like Cd, Pb, Hg and As [3-5]. Higher levels of heavy metals

disturb the normal physiology and biochemistry of living systems. The most dangerous heavy metals are Pb, Hg, As, Cd, Sn, Cr etc [6, 7]. Among these, Cd and Pb are the most dangerous metals for human health [8].

Heavy metal pollution of soil is a significant environmental problem and has its negative impact on human health and agriculture. The increasing use of wide variety of heavy metals in industries and agriculture has caused a serious concern of environmental pollution [9, 10]. Heavy metals like Zn^{2+} , Fe^{2+} , Cu^{2+} , Mn^{2+} , Cr^{2+} , Cd^{2+} , Ni^{2+} , and Pb^{2+} are the most hazardous pollutants because of their non-biodegradable nature. These metals find specific adsorption sites in the soil where they are retained relatively stronger either on inorganic or organic colloids. They find their way to food chain disrupting or impairing the natural biotic cycle [11-14]. Excess of heavy metal accumulation in soils is toxic to humans and other animals. Exposure to heavy metals is normally chronic (exposure over a longer period of time), due to food chain transfer [15].

The use of city effluents for irrigation purpose may also result in accumulation of macro (Na^+ , K^+ , Mg^{2+} , Ca^{2+}) and micro-essential elements (Fe^{2+} , Mn^{2+} , Zn^{2+}) as well as trace and toxic elements (Pb^{2+} , Ni^{2+} , Cd^{2+} , Cr^{2+} , and Co^{2+}) in phytotoxic concentrations [16, 17], which may adversely affect the human metabolism. Therefore, wastewater application on agricultural lands and their heavy metal accumulation by vegetables is a cause of serious concern due to the potential public health impacts. The sensitivity of plants and animals differs strongly for the deficiency and excess levels of particular metal. It is very difficult to establish a single critical value of deficiency or potential toxicity of particular metal for various species of plants and animals [18]. Soils in vegetable growing areas contain large amounts of Cd^{2+} , Pb^{2+} , Cr^{2+} , Cu^{2+} , Zn^{2+} , Mn^{2+}

and Fe^{2+} , and there are possibilities of elevated uptake of heavy metals by food crops in Cd-contaminated soils [19]. Long-term application of city effluent may increase the concentration of heavy metals to considerable levels in soil and ultimately in vegetation growing in these soils [20].

Like other developing countries raw wastewater is used in Pakistan for agricultural purposes. Peshawar is the capital city KPK Province of Pakistan. The soils of Peshawar valley are generally alkaline in nature and produce all types of crops and fruits [21]. However, due to poor management practices and pollution of soil particularly by heavy metals, the production is not of satisfactory level. The growing crops especially vegetables and fodders in the vicinity of Peshawar are irrigated with polluted water that affects the soil, plants and animals. To evaluate the potential effects on crops productivity and toxicity to animals and human beings, it is important to determine the concentrations of heavy metals in soil as well as soil physical and chemical properties, which affect the availability of heavy metals. As soil is a crucial component of rural and urban environments, and in both places land management is the key to soil quality [15]. Keeping in view the importance of heavy metals, the present study was therefore mainly designed to determine the pH, electrical conductivity, texture and concentrations of eight species of heavy metals in soil receiving municipal wastewater of Peshawar City.

Materials and Methods

Collections and preparation of soil samples

Soils located in the vicinity around Municipal area of Peshawar receiving wastewater and grown with vegetables & fodders were collected for their analysis of physico-chemical characteristics. Composite soil samples from five diverse locations each comprising of three depths i.e., 0-15, 15-30

and 30-45 cm depth were collected thus a total of fifteen (15) soil samples altogether were taken. Soil Auger was used for sampling. About 1kg of sample that was a composite of 10-15 core samples was mixed, labeled and brought to the laboratory of Soil and Environmental Sciences Laboratories of KP Agricultural University Peshawar. The soil samples were then air dried in shade, ground with a wooden mortar and sieved through 2 mm sieve. The samples were then tightly packed in polythene bags, labeled and stored for further analysis. Each sample was analyzed in triplicate for the desired parameter.

Analysis of soil samples

The soil samples were analyzed for pH, Electrical conductivity (EC), and texture and AB-DTPA extractable heavy metals. The rationale of using AB-DTPA method is that it extracts the soil easily available fraction of metals.

The pH and EC of the collected soil samples were determined in 1:1 soil and water suspension by using pH meter model HI 8418 (Hanna) and conductivity meter model pcm 3 (Jenway) respectively at 25 °C [22]. The texture was determined by Bouyoucos hydrometer method using Na_2CO_3 as dispersing or deflocculating agent, as described by [23].

AB-DTPA extractable heavy metals (Zn^{2+} , Fe^{2+} , Cu^{2+} , Mn^{2+} , Cr^{2+} , Cd^{2+} , Ni^{2+} , and Pb^{2+}) in soil samples were determined with the help of atomic absorption spectrophotometer model Perkin-Elmer 2380 USA, by using NH_4HCO_3 -DTPA extracting solution, as described by [24].

The AB-DTPA (0.5M) extracting solution was prepared by dissolving 1.97g of DTPA in pure water. Two mL of 1N NH_4OH was added to facilitate dissolution of DTPA and prevent effervescence when bicarbonate (HCO_3) is added. When most DTPA was dissolved, 79.06g NH_4HCO_3 was added and stirred gently until dissolved. The pH was

adjusted (by adding 0.5N HCl) to 7.6 and the solution was finally made to 2L volume. The extracting solution was stored in refrigerator. Twenty mL AB-DTPA extracting solution was added to exactly 10g air-dried soil sample and shaken for 30 minutes. After shaking, the suspension was filtered thorough Whatman filter paper No 42. The filtrate was then analyzed for extractable *viz.*, Zn^{2+} , Fe^{2+} , Cu^{2+} , Mn^{2+} , Cr^{2+} , Cd^{2+} , Ni^{2+} , and Pb^{2+} by using atomic absorption spectrophotometer.

Results and Discussion

Physicochemical characteristics of soil

The range and average values of pH, electrical conductivity (EC) and texture of soil samples collected from the vicinity of different sites of Peshawar city receiving municipal waste water are shown in Table 1 & 2. The pH value of surface soils (0-15cm) was ranging from 7.30 to 8.43 with an average value of 7.98. In sub soils (30-45cm), it ranges from 7.45 to 8.70 with an average value of 8.16. The pH values increased with depth in almost all the soils. The relatively low pH values in the surface soils could be associated with microbial activities and high organic matter content that upon decomposition produces acidic compounds. The overall pH of the soils ranges from 7.30 (sample No. A-1) to 8.89 (sample No. E-3), with an average value of 8.09, indicating that the soil of this area is alkaline and might cause nutritional imbalance for crops grown in this area. Similar observations are also recorded by Liang et al. [31] in China. However, contrary results have been reported by [25], which might be due to sandy textural soil.

The EC (electrical conductivity) values of surface soils (0-15cm) ranged from 0.4 to 0.6 dS m^{-1} with an average value of 0.5 dS m^{-1} . In sub-soils (30-45cm), it ranges from 0.2 μS to 0.9 μS with an average value of 0.5 μS . The overall EC (when averaged across depth and locations) of the soils ranged from 0.2 dS m^{-1} (sample No. C-2) to 0.9 dS m^{-1} (sample No.

A-3) with an average value of 0.5 dS m^{-1} showing that none of the soil is saline and the salinity might not present any problem to agricultural crops. It was further noted that the EC values slightly increased with an increase in depth (except soil sample No. 3) that may be due to leaching of salts from the surface soil. EC is a measure of the salt concentration in the soil solution. Soil electrical conductivity is one of the soil physical properties, which have a good relationship with the other soil characteristics [26]. Research revealed that EC has been shown to increase with increased manure/compost application rates [27, 28]. Shiralipour et al. [29] reviewed the effects of 6 municipal solid waste compost on soil properties and concluded that while municipal solid waste compost could induce salinity damage, the effects were likely to be much less than from sewage sludge applied at the same loading rate. Bevacqua & Mellano [30] reported municipal compost causing salinity problems that could threaten the production of sensitive crops. However, present results of EC values are contrary to the work presented by this study?

The texture of soils studied varied from silty-loam to sandy-loam. The variation in texture may be due to parent material and the kind of loess deposition that might have taken place at their respective sites. These findings are also in line with results obtained by [31] in Dunhua sewage irrigation areas of China.

Heavy metals status of soils samples

The ranges and average values of AB-DTPA extractable heavy metals Zn^{2+} , Fe^{2+} , Cu^{2+} , Mn^{2+} , Cr^{2+} , Cd^{2+} , Ni^{2+} , and Pb^{2+} in various soils samples collected from different sites of Peshawar City, receiving municipal wastewater are shown in the Table 3 & 4.

The concentrations of Zn^{2+} , Cu^{2+} , Fe^{2+} , Mn^{2+} , Ni^{2+} , Cr^{2+} , Cd^{2+} , and Pb^{2+} ranging from 0.86-3.98, 2.85-6.83, 11.92-31.73, 14.92-19.19, 0.54-0.96, 0.11-0.86, 0.04-0.58 and 3.16-38.30 mg kg^{-1} with an average values of 2.14,

5.11, 21.44, 17.59, 0.73, 0.35, 0.28 and 17.18 mg kg⁻¹, respectively in surface soils (0-15cm). In sub-soils (30-45cm), the concentrations of Zn²⁺, Cu²⁺, Fe²⁺, Mn²⁺, Ni²⁺, Cr²⁺, Cd²⁺, and Pb²⁺ ranges from 0.64-3.37, 2.48-6.83, 11.03-23.91, 10.7-16.33, 0.06-0.64, 0.05-0.23, 0.05-0.23, 0.01-0.35 and 4.36-1.44 mg kg⁻¹ with an average values of 1.78, 4.31, 18.42, 14.03, 0.42, 0.12, 0.15 and 12.85 mg kg⁻¹, respectively. Results also showed that the concentrations of metals decreased with an increase in soil depth, which might be due to their adsorption on organic matter or due to inputs from municipal wastewater.

By comparing the concentrations of metals of various soils with critical soil test value for crops in soil according to Halvin and Sultanpour [24] showed that all the essential microelements (Zn²⁺, Cu²⁺, Fe²⁺ and Mn²⁺) were above the critical value of plant requirement that may cause phytotoxicity. Whereas, according to WHO prescribed permissible limits, it was observed that the concentrations of Zn²⁺, Fe²⁺, Cr²⁺, Cd²⁺ and Pb²⁺ were within the WHO permissible limits except soil No. 1 and 2, which had Zn²⁺, Cd²⁺ and Pb²⁺ concentrations above the set limits. Achakzai et al. [32] demonstrated that the total concentrations of Cu²⁺, Fe²⁺, Mn²⁺, Zn²⁺ and Ni²⁺ in lettuce receiving city effluents are within the recommended international standards set by WHO/FAO, but could be reached to toxic level either by the consecutive use of effluents or by increased dietary pattern of the consumers community. As we know that crops grown in polluted soil are taking up excess amount of heavy metals, which ultimately seriously suffer the human health by consuming such crop plants or their parts especially roots [1]. Research studies also revealed that among all heavy metals, Cd and Pb are the most dangerous ones for human

health [8]. Cd is considered as the most serious pollutant of the modern age [33]. Cd concentrations above the threshold limit values have been found to be carcinogenic, mutagenic and teratogenic for a large number of animal species. Cd has also been implicated as an endocrine disruptor. Pb has been found to be responsible for quite a number of ailments in humans such as chronic neurological disorders especially in fetus and children. This eventually results in behavioral and attitude changes with progressive retardation [34]. Pb-poisoning in children causes neurological damage leading to reduced intelligence, loss of short-term memory, learning disabilities and coordination problems [35]. Contrary to the WHO standard, in the present study the concentration of Cr²⁺, Cd²⁺, Ni²⁺ and Pb²⁺ according to Kabata-Pendias and Pendias [36] were below safe limit indicating that it is not the soluble fraction of the metal rather the total concentration that should be taken in to account while considering the suitability of soil or wastewater for crops. The higher concentrations of heavy metals in soils might be due to irrigation with municipal wastewater containing the respective metals or may be due to aerial dust fall as the soil sampled were adjacent to the heavy traffic road. The crops and plants grown in these soils might accumulate higher concentrations of the respective heavy metals. However, the reported concentrations of the metals are not high enough to cause phytotoxicity but the prolong exposure of soil to wastewater irrigation may cause buildup of metals in soil that may be harmful for human and animals consuming the crops in future.

No correlation was found between the concentrations of heavy metals studied and physico-chemical properties of soils. It might be due to different thermodynamic conditions of soils or some geo-chemical properties and anthropogenic factors might be governing the solubility and mobility of metals in soils [37].

Table 1. The pH and EC of different soils, receiving municipal wastewater of Peshawar city

Soil	Sample No.	Depth (cm)	pH	EC (dS m ⁻¹)
1. Sardar Ahamd Colony	A-1	0-15	7.30	0.5
	A-2	15-30	7.45	0.8
	A-3	30-45	7.72	0.9
	Average	--	7.49	0.73
2. Ring Road Chowk	B-1	0-15	7.46	0.4
	B-2	15-30	7.92	0.3
	B-3	30-45	7.68	0.4
	Average	--	7.69	0.37
3. Sardar Colony	C-1	0-15	8.30	0.6
	C-2	15-30	8.47	0.2
	C-3	30-45	8.21	0.2
	Average	--	8.33	0.33
4. Ganda-wear End	D-1	0-15	8.12	0.5
	D-2	15-30	8.47	0.3
	D-3	30-45	8.13	0.6
	Average	--	8.34	0.47
5. Budni-Drain (near filter plant)	E-1	0-15	8.43	0.5
	E-2	15-30	8.70	0.6
	E-3	30-45	8.89	0.4
	Average	--	8.67	0.50

Table 2. Particle size distribution of different soils, receiving municipal wastewater of Peshawar City

Soil Series	Sample No	Depth (cm)	% Sand	% Silt	% Clay	Textural Class
1. Sardar Ahamd Colony	1	0-15	14	76	10	Silt-loam
	2	15-30	11	81	8	//
	3	30-45	9	80	11	//
2. Ring Road Chowk	4	0-15	8	78	14	//
	5	15-30	13	74	13	//
	6	30-45	13	73	14	//
3. Sardar Colony	7	0-15	68	26	6	Sand-loam
	8	15-30	64	27	9	//
	9	30-45	63	29	8	//
4. Ganda-Wear End	10	0-15	65	24	11	//
	11	15-30	66	19	10	//
	12	30-45	67	19	14	//
5. Budni-Drain (near filter plant)	13	0-15	19	68	13	Silt-loam
	14	15-30	17	72	9	//
	15	30-45	22	64	14	//

Table 3. Heavy metals concentrations (mg kg⁻¹) in different soils, receiving municipal wastewater of Peshawar city

Soil	Soil sample	Depth (cm)	Zn ²⁺	Cu ²⁺	Fe ²⁺	Mn ²⁺	Ni ²⁺	Cr ²⁺	Cd ²⁺	Pb ²⁺
1. Sardar Ahmad Jan Colony	A-1	0-15	3.98	6.26	31.73	14.92	0.54	0.32	0.58	38.30
	A-2	15-30	3.46	6.75	31.00	11.30	0.08	0.21	0.40	41.16
	A-3	30-45	3.37	6.83	23.91	10.70	0.06	0.05	0.35	40.36
	Mean	--	3.60	6.61	28.88	12.31	0.23	0.19	0.44	39.94
2. Ring Road Chowk	B-1	0-15	3.64	6.83	23.42	18.70	0.96	0.22	0.50	33.72
	B-2	15-30	3.51	5.13	23.28	16.33	0.85	0.18	0.38	38.00
	B-3	30-45	3.27	2.48	21.63	16.01	0.70	0.14	0.28	14.22
	Mean	--	3.47	4.81	22.77	17.01	0.84	0.18	0.39	28.65
3. Sardar Colony)	C-1	0-15	0.86	6.23	11.92	19.04	0.56	0.86	0.15	6.52
	C-2	15-30	0.76	5.65	11.93	15.81	0.45	0.34	0.09	6.70
	C-3	30-45	0.64	4.59	11.03	15.02	0.38	0.23	0.09	5.52
	Mean	--	0.75	5.49	11.63	16.62	0.46	0.48	0.11	6.25
4. Ganda-Wear End	D-1	0-15	1.02	3.38	19.81	16.13	0.64	0.22	0.04	3.16
	D-2	15-30	0.89	2.75	19.71	12.45	0.50	0.14	0.03	2.66
	D-3	30-45	0.67	3.54	19.03	12.09	0.30	0.12	0.01	2.70
	Mean	--	0.86	3.22	19.52	13.56	0.48	0.16	0.03	2.84
5. Budni-Drain (Near filter plant)	E-1	0-15	1.18	2.85	20.32	19.19	0.94	0.11	0.11	4.20
	E-2	15-30	0.97	3.85	20.05	17.58	0.82	0.05	0.02	4.86
	E-3	30-45	0.95	4.09	16.50	16.33	0.64	0.08	0.01	1.44
	Mean	--	1.03	3.59	18.96	17.70	0.80	0.08	0.05	3.50

Table 4. Ranges and average concentrations (mg kg⁻¹) of heavy metals in selected soils receiving municipal wastewater of Peshawar city

Soil	Zn ²⁺	Cu ²⁺	Fe ²⁺	Mn ²⁺	Ni ²⁺	Cr ²⁺	Cd ²⁺	Pb ²⁺
Top-soil	0.86 – 3.98	2.85 – 6.83	11.92 – 31.73	11.92 – 31.73	0.54 – 0.96	0.11 – 0.86	0.04 – 0.58	3.16 – 38.30
Average	2.14	5.11	21.44	17.59	0.73	0.35	0.28	17.18
Sub-soil	0.64 – 3.37	2.48 – 6.83	11.03 – 23.91	10.7 – 16.33	0.06 – 0.64	0.05 – 0.23	0.01 – 0.35	40.36 – 1.44
Average	1.78	4.31	18.42	14.03	0.42	0.12	0.15	12.85

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