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Assessment of various heavy metals level in groundwater and soil at tannery manufacturing areas of three mega cities (Sialkot, Lahore and Karachi) of Pakistan

Ghulam Murtaza[a,*], Muhammad Usman[b]

[a]*Faculty of Environmental Science and Engineering, Kunming University of Science and Technology, Kunming, PR China, email: murtazabotanist@gmail.com*
[b]*Department of Botany, GC University Lahore, Pakistan, email: usmanphytologist@gmail.com*

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ABSTRACT

Heavy metals pollution of water and soil caused by industrial activities has become a prominent environmental concern in Pakistan. Thus, it is important to examine the contaminants concentration in water and soil close to the industrial areas. In this study, we have evaluated the different heavy metals contamination in groundwater and soil at tannery areas of three large cities of Pakistan, Lahore, Karachi and Sialkot. Groundwater and soil samples collected from Lahore, Karachi and Sialkot tannery areas and examined for chromium, iron, nickel, cadmium, lead, copper, and manganese by atomic absorption spectrometer. The results presented that groundwater and soil in the Lahore, Karachi, and Sialkot are highly contaminated with several heavy metals. Particularly, the concentration of chromium varied from 0.41 to 1.107 mg L^{-1} in Lahore, 0.35 to 2.209 mg L^{-1} in Karachi and 0.31 to 2.29 mg L^{-1} in Sialkot and from 1,731 to 2,554 mg kg^{-1} in Lahore, from 1,676 to 3,018 mg kg^{-1} in Karachi and from 1,793 to 3,274 mg kg^{-1} in Sialkot in groundwater and soil, respectively. Correlation exploration has recognised that metals in soil and groundwater of study areas having common origin/source, believed to be leather processing industries of Lahore, Karachi and Sialkot.

Keywords: Heavy metals; Leather; Contamination; Groundwater; Soil

1. Introduction

Environmental pollution is one of the major challenges in the modern human society. Environmental contamination and pollution by heavy metals is a threat to the environment and is of serious concern [1]. Rapid industrialization and urbanization have caused contamination of the environment by heavy metals, and their rates of mobilization and transport in the environment have greatly accelerated since 1950s [2]. Furthermore, the groundwater contamination can be due to continuous leaching/seepage of several heavy metals. Groundwater contamination through metals may cause a more severe and long-term health risk to the environment and humans [3,4]. Soil contamination by heavy metals due to tanneries residue is a globally issue. Heavy metals are well-known environmental pollutants due to their toxicity, persistence in the environment, and bio-accumulative nature. Their natural sources include weathering of metal-bearing rocks, while anthropogenic activities include mining and several industrial and agricultural activities. Industrial and mining processing for extraction of mineral resources and their subsequent applications for agricultural, industrial and economic development has led to an increase in the mobilization of these elements in the environment and disturbance of their biogeochemical cycles [5,6,41,42]. Contamination of terrestrial and aquatic ecosystems with toxic heavy metals is

* Corresponding author.

an environmental problem of public health concern. Being persistent pollutants, heavy metals accumulate in the environment and consequently contaminate the food chains. Accumulation of potentially toxic heavy metals in biota causes a potential health threat to their consumers including humans [7,40,43]. Several substances such as chromium sulfate, calcium hydroxide, sulphuric acid and sodium chloride are largely applied during leather manufacturing. Therefore, wastewater of leather industry is enriched with sodium and chromium. Substantial releases of Cr abundant effluent from the leather manufacture plants have resulted in Cr-contaminated groundwater and soil at manufacture sites, which are serious risk to human health [7,8]. Leather manufacturing is a substantial manufacturing process in the Pakistan, where around 700 tanneries located in major three cities (Sialkot, Karachi, and Lahore). Residues release from leather tanneries contaminated water and soil causing serious health issues. The most extremely affected areas around the Lahore, Karachi, and Sialkot, which have maximum numbers of leather industries. Recently, increased environmental contaminations by leather industries are seriously affecting the human health. Many diseases including dysentery, lung infection, typhoid, and respiratory disorders are frequently detected in local peoples living around leather industries areas [5]. A large amount of small-scale leather industries situated in the Pakistan has no facility for wastewater remediation and discharge their wastes to land [9,10]. Huge areas of Lahore, Karachi and Sialkot industrial areas land have been infeasible for the agriculture due to pollution with various heavy metals. Groundwater pollution by different metals is one of the main dangers to human health is these three big cities [11]. It is extremely necessary to examine and remediation the concentration of metals from the leather industries effluent. The main objectives of this study was assessment of selected heavy metals including Pb, Cd, Ni, Mn, Co, Fe, and Cr present in tanneries effluents affected soil and the relevant groundwater by using atomic absorption spectrophotometer as well as the correlation between metals measured to identify possible origins of metal contaminants in groundwater and soil. This study will provide to the future planning, remediation, and environmental monitoring for tanneries waste affected groundwater and soil in Lahore, Karachi and Sialkot.

2. Methodology

2.1. Study areas

Lahore (31.52° N. 74.35° E), Sialkot (32.49° N. 74.52° E) and Karachi (24.86° N. 67.00° E) are industrial cities in Pakistan. The population of these mega cities are 29.04 million. Water from the Indus, Ravi and Chenab rivers and groundwater drawn from tube wells are used for the irrigation of the main crops rice, wheat, cotton, sugarcane and rice. For daily use and drinking most inhabitants use groundwater extracted by tube wells. These mega cities are well-known for its industrial activities and leather processing dominates. The other notable industries produce sugar, woodwork, textile, embroidery, and glazed pottery [14].

2.2. Samples collection of effluent, ground water and soil

Fifteen tannery effluent samples were collected from the drainage of randomly selected tanneries located in Lahore, Sialkot and Karachi. In total, 35 soil samples and as many groundwater samples were collected in the vicinity of the tanneries (Fig. 1). A monolith of 30 cm × 30 cm × 30 cm was dug for the collection of soil. Soil from each point was thoroughly mixed and about 1.5 kg of soil from each point was collected and placed in a polythene bag. The selection of soil sampling points was made randomly on the basis of visual investigation of the whole waste-water affected site.

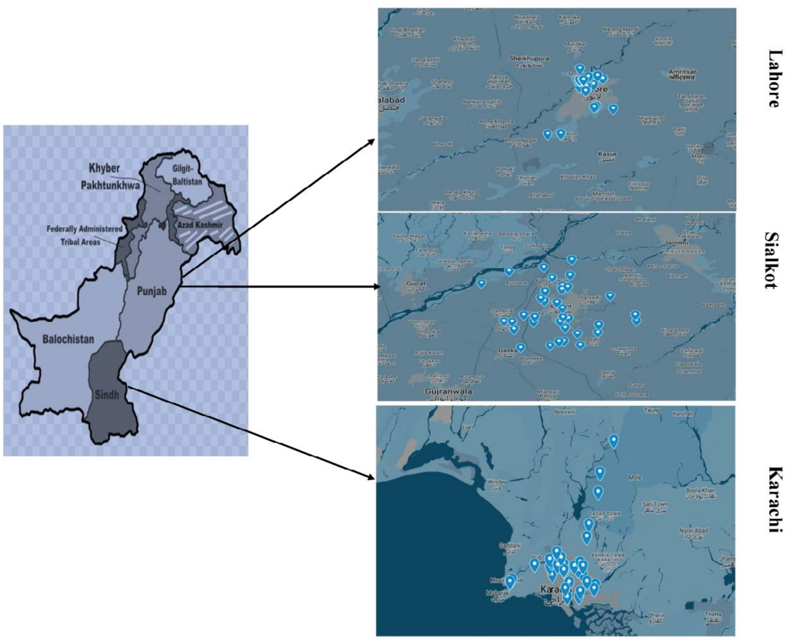

Fig. 1. Map of the study area (Lahore, Karachi and Sialkot, Pakistan).

Applying the standard sampling guidelines [14], the tannery effluent and groundwater samples were collected and placed in 1-litre plastic bottles. The groundwater samples were collected either from a hand pump or electric pump installed in the area around the polluted site. Containers/bottles containing samples were clearly labelled. The water samples were placed in an ice box and immediately transported to the laboratory for analysis. To ensure the trueness and precision, triplicate wastewater and groundwater samples were drawn from each sampling point. Twenty samples of groundwater and soil were collected from areas distant from the tanning units to establish background heavy metal levels.

2.3. Digestion of effluent and soil for determination of the metal contents

For the assessment of heavy metal content in soil, acid digestion of soil was recommended as most of the heavy metals are strongly bound with the mineral matrix [15,23]. It was reported that water soluble and exchangeable fractions in soil never exceed 3% of the total metal concentration [24]. Conferring to the approach considered for present research, soil was believed the most contaminated compartment of the environment around tanneries in Pakistan. In view of the loss of soil fertility and yield of crops, any investigation such as the present one, based on the determination of total amount of heavy metals in soil cannot be simply performed. It was, therefore, considered to examine and analyse the acid digestion extract of the soil samples for the total amount of selected heavy metals in soil [14]. This was a more accurate approach and presents a true picture of total amount of selected heavy metals in the soil. For the digestion of soil, 0.4 g air-dried soil sample was ground to make it into fine dust, placed in a quick fit vessel and 2 mL 70% nitric acid (HNO_3), 6 mL 35% hydrochloric acid (HCl), and 3 mL 40% hydrofluoric acid (HF) were added. The mixture was refluxed on a heating plate until a transparent solution was attained. After cooling, 15 mL saturated boric acid was added to bind excess HF and the volume was made up to 100 mL with double de-ionized water [24]. The digestion mixture was filtered through Whatman1 no. 42 filter paper and the filtrate was used for the determination of concentration of selected metals in the soil. The effluent samples were digested with mixture of HNO_3 and HCl as described earlier [23].

2.4. Exploration of groundwater and soil samples

Atomic absorption spectrometry (AAS) was used for the valuation of Mn, Co, Zn, Pb, Cd, Ni, Fe, and Cr in groundwater, soil, and effluent samples. The groundwater samples were directly analyzed without filtration and addition of any stabilizer for pH adjustment. Soil, groundwater, and effluent filtrate (from digested soil and effluent samples) were diluted, where necessary, with double de-ionized water.

2.5. Quality assurance and quality control

According to manufacturer's instructions, standard optimum analytical conditions were maintained and periodically checked on the Atomic absorption spectrometry system for each metal. Blank and sample solutions were prepared in the same way in all determinations. An inter-laboratory comparison of the completed data was performed at the University of Agriculture, Faisalabad. A regular check on the accuracy of the results and the precision of the instrument and other analytical methods was executed by using standard reference material. Normally, the sets of results matched within ±1.0 to ±1.5%.

2.6. Human health risk assessment

2.6.1. Exposure assessment

The human health risk assessment model derived by the USEPA was used to evaluate the toxic effects of metals present in drinking water on the health of people in three study locations [16]. The health risk assessment was done to estimate the probability of individuals being exposed to metals poisoning from drinking water. For this purpose, average daily dose (ADD) of metals due to the intake of metal-contaminated drinking water was calculated by the following equation [17],

$$\text{ADD} = \frac{\text{C} \times \text{IR} \times \text{ED} \times \text{EF}}{\text{BW} \times \text{AT}} \quad (1)$$

where C represents the concentration of metals in water (mg L^{-1}), IR is the water ingestion rate (L d^{-1}), ED abbreviates exposure duration (assumed 67 y to make a comparison with previous studies from Pakistan and other countries), EF indicates exposure frequency (365 d y^{-1}), BW is the body weight (72 kg) [18], and AT means average life time (24,455 d).

2.6.2. Chronic and carcinogenic risk assessment

Chronic and carcinogenic risk levels were also determined in individuals of the study area. The hazard quotient (HQ) was computed from ADD by the following equation (USEPA 2005):

$$\text{HQ} = \frac{\text{ADD}}{\text{RfD}} \quad (2)$$

where RfD represents oral reference dose (0.0003 mg kg^{-1} d^{-1}) for As calculated by US-EPA [16]. Cancer risk (CR) was calculated using the following equation:

$$\text{CR} = \frac{\text{ADD}}{\text{CSF}} \quad (3)$$

where CSF is the cancer slope factor for heavy metals which are 1.5 mg kg^{-1} d^{-1}, according to US-EPA model [16].

2.6.3. Statistical analysis

The basic statistical analysis of the data was conducted using STATISTICA software [26]. Some of basic statistics parameters (standard deviation, average absolute deviation, and skewness) were used to process the analytical data in terms of selected metals distribution in groundwater and soil. Correlation between studied metals in soil and groundwater was also determined.

3. Results and discussion

3.1. Characterization of effluents

Physiochemical characteristics of Lahore, Karachi, and Sialkot tanneries effluent exhibited that it contained high values of chemical oxygen demand (COD), biochemical oxygen demand (BOD), total dissolved solids (TDS), sulfate, chloride, lead, cadmium, iron, and chromium did not match with acceptable limits recommended by NEQS (National Environmental Quality Standards (Table 1)). Conversely, among the heavy metals, the chromium showed higher mean level 101.39, 79.86, and 117.42 mg L^{-1} for Karachi, Lahore, and Sialkot, respectively as compared to other metals. Likewise, in previous research, a higher mean level (128 mg L^{-1}) of chromium was noticed in the tannery effluent of the Kasur, Pakistan [19,20].

3.2. Concentrations of heavy metals in soils

The data signifying the distribution of the measured heavy metals in terms of level along with statistical estimation is exhibited in the Table 2. The content of chromium in the soil was found extremely higher 2,754; 3,018, and 3,274 mg kg^{-1} (mean values) in Lahore, Karachi, and Sialkot, respectively. The main reason of higher concentration of chromium in these cities is a result of the disposal of Cr-rich waste-water at these sites over a long period of time. The tanneries of these three cities are eminent for the chrome tanning, during which hides are treated with chromium in presence of the different salts to generate leather. During treating 40%–60% of added Cr is absorbed through collagen in hide and residual un-used Cr is discarded in the waste-water [21,22]. Lower levels of other selected metals were noticed in Co 27.25; Zn 19.53; Mn 9.81; Pb 16.17; Cd 17.8; Ni 33.49; and Fe 123.8 in Lahore, Co 25.66; Zn 20.83; Mn 10.06; Pb 13.72; Cd 25; Ni 41.64; and Fe 131.35 in Karachi, Co 27.61; Zn 22.64; Mn 10.09; Pb 12.28; Cd 14.65; Ni 32.35; and Fe 121.36 mg kg^{-1} in Sialkot study areas. Though, these concentrations are substantially higher than all previously noticed in the tannery effluent-polluted soil [23–26]. This likely is due to our use of acid digestion of soil, whereas other studies used water extraction. Acid digestion is more efficient in extracting inorganically and organically bound metal from soil than water extraction. Water extraction does not fully release components that are not water soluble, such as metal silicates, and thus underestimates the concentrations of these [21,27]. Based on the mean values metals in soil follow the declining level order such as chromium > Iron > nickel > cadmium > copper > lead > zinc > manganese. Other metals and chromium showed higher level than generally expected concentration in the soil, giving rise to concerns over suitability of soil for agricultural use in the scrutinize areas [28]. The distribution of metals in soil samples did not follow normal distribution since results have high degree of average absolute deviation, standard deviation as well as skewness. To obtained information, this is first description where an extensive analysis of tannery effluent dirtied soil of studied areas has been conducted using acid digestion of the soil. Higher concentrations of metals in the soil can seriously affect soil productivity and eventually be unsafe to humans by the food chain.

Table 1
Physiochemical attributes of Karachi, Lahore and Sialkot tanneries effluent

	Mean values			
Parameters	Karachi	Lahore	Sialkot	NEQS
pH	7.59	7.52	7.64	6–10
BOD (mg L^{-1})	571	543.5	586	80
COD (mg L^{-1})	1913	1450	2108	150
TDS (g L^{-1})	13.08	12.07	8.21	3.50
Na (g L^{-1})	11.01	10.51	14.02	Not given
Sulfate (g L^{-1})	6.37	7.22	4.41	0.60
Chloride (g L^{-1})	13.73	11.53	10.43	1.0
Chromium (mg L^{-1})	101.39	79.86	117.42	1.0
Iron (mg L^{-1})	5.76	6.60	4.79	2.0
Nickel (mg L^{-1})	0.84	0.55	0.91	1.0
Cadmium (mg L^{-1})	0.29	0.43	0.14	0.1
Lead (mg L^{-1})	2.07	3.05	2.03	0.5
Zinc (mg L^{-1})	3.59	2.52	4.17	5.0
Copper (mg L^{-1})	0.39	0.55	0.61	Not given in list
Manganese (mg L^{-1})	0.38	0.53	0.71	1.5

NEQS, National Environmental Quality Standard for Irrigation.

3.3. Concentrations of heavy metals in groundwater

Ground and surface water both are dirtied with heavy metals by several anthropogenic activities such as municipal, industrial waste into water-bodies and use of various chemicals in agriculture, that is, pesticides, fertilizers, insecticides, and fungicides. Numerous heavy metals are vital, in trace elements for human being health. Conversely, in greater concentrations they induce water-contamination and can be lethal, posing severe health problems. In Pakistan, noxious heavy metals in the groundwater often noticed the higher than WHO suggested permissible limits [2,10,29,30]. The observed levels of all selected metals in Lahore, Karachi and Sialkot groundwater samples are presented in Table 3. The level of Cr 2.02 mg L^{-1} in Lahore, 2.09 mg L^{-1} in Karachi and 2.29 mg L^{-1} in Sialkot observed is significantly higher in comparison to recommended limit (0.05 mg L^{-1}) for drinking-water by NSDWQ Pakistan and WHO. Seemingly, higher metal concentrations in the soil affect the groundwater. The lower concentrations in the groundwater might be owing to inadequate flow of metals by 20–40 m deep soil-bed to ultimately reach the water-table. Also high level of lead (Pb) was noticed in the groundwater samples of all three study areas (0.236 mg L^{-1} in Lahore, 0.263 mg L^{-1} in Karachi and 0.286 mg L^{-1} in Sialkot). Considerably higher compared to permissible limit recommended by NSDWQ Pakistan (0.05 mg L^{-1})

Table 2
Statistical parameters for assessment of heavy metals (mg kg^{-1}) in contaminated soil of Lahore, Karachi and Sialkot

	Fe	Ni	Cd	Cr	Pb	Zn	Co	Mn
				Lahore				
Maximum	171.3	63.87	33.7	2754	23.61	37.64	41.25	16.47
Minimum	76.3	17.91	11.4	1731	6.17	1.43	13.26	3.16
Mean	123.8	40.89	22.5	2242.5	14.89	19.53	27.25	9.81
Median	112.05	33.49	17.8	2134	16.17	7.71	27.56	9.09
SD	28.64	16.29	8.24	321.5	6.43	12.94	9.18	3.92
AAD	22.86	12.56	7.26	248	5.53	10.71	7.11	3.05
Skewness	0.56	0.75	0.44	0.51	–0.15	1.12	–0.09	0.18
				Karachi				
Maximum	187.7	66.98	39.7	3,018	22.34	39.64	43.87	15.94
Minimum	75.01	16.31	10.3	1,676	5.11	2.03	10.74	4.19
Mean	131.35	41.64	25	2,347	13.72	20.83	27.3	10.06
Median	112.95	33.35	19.15	2,260.5	12.23	8.34	25.66	9.18
SD	33.67	17.18	9.68	449.23	6.07	15.04	12.10	3.77
AAD	25.36	13.93	7.36	370.6	5.07	12.86	10.34	3.04
Skewness	0.86	0.6	0.97	0.17	0.28	0.98	0.18	0.32
				Sialkot				
Maximum	191.7	67.97	20.1	3,274	18.39	41.39	44.15	16.74
Minimum	51.03	14.18	9.2	1,793	6.17	3.89	11.08	5.07
Mean	121.36	41.07	14.65	2,533.5	12.28	22.64	27.61	10.09
Median	98.41	32.35	16.2	2,119	10.57	9.59	25.46	9.71
SD	47.17	16.92	3.46	532.63	3.57	14.59	12.50	3.31
AAD	35.24	13.17	2.82	436.14	2.78	12.41	11.01	2.53
Skewness	0.96	0.82	–0.5	0.96	0.65	0.98	0.18	0.44

AAD, Average absolute deviation;
SD, Standard deviation.

and WHO (0.01 mg L^{-1}) for drinking-water. Uptake of the elevated level of lead over a long duration of the time has several negative impacts on the public health [31–35]. Correspondingly, iron (Fe) was detected at higher amount in all selected cities (1.107 mg L^{-1} in Lahore, 1.231 mg L^{-1} in Karachi and 1.118 mg L^{-1} in Sialkot). These detected concentrations are higher than allowable limit set by WHO (0.3 mg L^{-1}) for drinking-water. The levels of other metals are also greater in groundwater in all the study areas compared to permissible limits set through World Health Organization for drinking-water. This might be because of seepage of pollutants from tanneries effluents contaminated soil to the groundwater over long period. Groundwater impurities due to release of tanneries effluents into open land and natural water resources was presented in recent studies [9,36–39]. The findings of the groundwater exploration also reflect un-normal distribution of the metals in groundwater, as evinced by higher values of the average absolute deviation, standard deviation, as well as skewness. A correlation between metals level observed in the groundwater in this research and their allowable limits in the drinking-water set by EU, Japan, Pakistan, USA-EPA and WHO is revealed in Table 4. The levels of Pb, Cd, Ni, Fe, and Cr are higher compared to recommended maximal concentrations. Conversely, amount of Zn was noticed at a lower level compared to maximum concentrations set by USA-EPA, Pakistan, and WHO but greater than those suggested by EU. The level of Pb, Cd, and Cr were 4–13, 3–15 and 12–25 times higher compared to recommended limits, correspondingly. A sturdy positive relationship was noticed for Pb–Fe, Pb–Cr, Fe–Cr, Co–Pb, Zn–Cd and Zn–Ni pairs (shown in Tables 5a–c) proposing that metals in soil of all three research areas have a common origin. This showed a mutual level dependence of the metals in soil organization under analysis. For the groundwater, metal-to-metal correlations matrix emphasizes numerous substantial positive correlations, representing the same origin of the groundwater pollution in research areas. This might because of fact that groundwater samples were taken from points situated in very adjacent locality to tanneries effluent affected areas (Shown in Tables 6a–c). The concentrations of selected metals in groundwater and soil samples were likened with their corresponding background concentrations are revealed in Figs. 2 and 3, respectively. This showed that all analysed metals displayed enormously high levels in the tanneries effluent polluted

Table 3
Statistical parameters for assessment of heavy metals (mg L^{-1}) in groundwater of Lahore, Karachi and Sialkot

	Fe	Ni	Cd	Cr	Pb	Zn	Co	Mn
				Lahore				
Maximum	1.107	0.198	0.106	2.02	0.236	0.191	0.147	0.127
Minimum	0.319	0.053	0.014	0.41	0.033	0.014	0.034	0.034
Mean	0.713	0.125	0.06	1.21	0.134	0.102	0.131	0.08
Median	0.441	0.113	0.087	1.22	0.115	0.082	0.093	0.082
SD	0.271	0.037	0.037	0.64	0.064	0.063	0.033	0.034
AAD	0.201	0.033	0.033	0.54	0.049	0.052	0.025	0.03
Skewness	1.636	–0.436	–0.44	–0.106	0.041	0.229	0.013	–0.002
				Karachi				
Maximum	1.231	0.199	1.46	2.09	0.263	0.197	0.157	0.131
Minimum	0.314	0.064	0.026	0.35	0.036	0.018	0.065	0.033
Mean	0.738	0.131	0.080	1.22	0.149	0.111	0.131	0.082
Median	0.443	0.114	0.087	1.21	0.114	0.101	0.093	0.050
SD	0.327	0.048	0.042	0.67	0.07	0.063	0.027	0.036
AAD	0.236	0.041	0.035	0.56	0.05	0.052	0.019	0.032
Skewness	1.511	0.242	0.094	–0.02	0.087	0.025	0.079	0.063
				Sialkot				
Maximum	1.118	0.201	0.108	2.29	0.286	0.141	0.171	0.112
Minimum	0.217	0.031	0.017	0.31	0.037	0.034	0.041	0.031
Mean	0.667	0.116	0.062	1.45	0.159	0.104	0.106	0.071
Median	0.367	0.066	0.055	0.605	0.092	0.076	0.087	0.042
SD	0.328	0.055	0.035	0.84	0.071	0.036	0.040	0.030
AAD	0.257	0.041	0.030	0.68	0.040	0.030	0.030	0.048
Skewness	1.239	1.238	0.218	1.102	2.308	0.239	0.664	1.112

Table 4
Comparison of the average metals levels (mg L^{-1}) with various international drinking-water quality standards

	Present study	USA-EPA	Japan	EU	Pakistan	WHO
			Lahore			
Fe	1.107	0.3	0.3	0.2	–	0.3
Cr	2.02	0.1	0.05	0.05	0.05	0.05
Cd	0.106	0.005	0.01	0.005	0.01	0.003
Ni	0.198	0.1	0.01	0.05	0.02	0.02
Zn	0.191	5.0	–	0.1	5.0	5.0
Pb	0.236	0.015	0.05	0.05	0.05	0.01
Mn	0.127	0.05	0.05	0.05	0.5	0.5
Co	0.147	–	–	–	–	–
			Karachi			
Fe	1.231	0.3	0.3	0.2	–	0.3
Cr	2.09	0.1	0.05	0.05	0.05	0.05
Cd	0.146	0.005	0.01	0.005	0.01	0.003
Ni	0.198	0.1	0.01	0.05	0.02	0.02
Zn	0.191	5.0	–	0.1	5.0	3.0
Pb	0.263	0.015	0.05	0.05	0.05	0.01
Mn	0.131	0.05	0.05	0.05	0.5	0.5
Co	0.157	–	–	–	–	–
			Sialkot			
Fe	1.118	0.3	0.3	0.2	–	0.3
Cr	2.29	0.1	0.05	0.05	0.05	0.05
Cd	0.108	0.005	0.01	0.005	0.01	0.003
Ni	0.201	0.1	0.01	0.05	0.02	0.02
Zn	0.141	5.0	–	0.1	5.0	3.0
Pb	0.286	0.015	0.05	0.05	0.05	0.01
Mn	0.112	0.05	0.05	0.05	0.5	0.5
Co	0.171	–	–	–	–	–

water and soil in contrast to their background concentrations, hence confirming the pollution of groundwater and soil via wastewater released from leather industries.

3.4. Exposure assessment and cancer risk assessment

Table 7 shows the health risk assessment of all the metals with respect to ADD for the people who are using heavy metals-polluted groundwater for drinking purpose in Lahore, Karachi and Sialkot. In this study, ADD ranged from (Fe 0.101, Ni 0.112, Cd 0.27, Cr 1.36, Pb 0.169, Zn

Table 5a
Metal to metal correlation coefficient matrix for tested heavy metals in polluted soil of Lahore

	Cr	Fe	Ni	Cd	Pb	Zn	Mn	Co
Fe	1.00							
Cr	0.684	1.00						
Cd	0.381	0.396	1.00					
Ni	–0.449	0.137	0.482	1.00				
Zn	0.689	0.689	0.475	0.578	1.00			
Pb	0.263	–0.492	0.649	0.687	0.557	1.00		
Mn	0.393	0.597	0.441	–0.379	–0.429	0.304	1.00	
Co	0.016	–0.187	0.646	0.356	0.698	0.211	0.463	1.00

Table 5b
Metal to metal correlation coefficient matrix for tested heavy metals in polluted soil of Karachi

	Cr	Fe	Ni	Cd	Pb	Zn	Mn	Co
Cr	1.00							
Fe	0.804	1.00						
Ni	0.512	0.394	1.00					
Cd	–0.637	0.151	0.472	1.00				
Pb	0.691	0.633	0.479	0.541	1.00			
Zn	0.261	–0.491	0.618	0.689	0.563	1.00		
Mn	0.339	0.539	0.452	–0.370	–0.422	0.301	1.00	
Co	0.021	–0.131	0.671	0.342	0.688	0.219	0.461	1.00

Table 5c
Metal to metal correlation coefficient matrix for tested heavy metals in polluted soil of Sialkot

	Cr	Fe	Ni	Cd	Pb	Zn	Mn	Co
Cr	1.00							
Fe	0.845	1.00						
Ni	0.501	0.347	1.00					
Cd	–0.673	0.148	0.489	1.00				
Pb	0.670	0.693	0.415	0.541	1.00			
Zn	0.281	–0.441	0.611	0.689	0.597	1.00		
Mn	0.331	0.548	0.459	–0.370	–0.436	0.368	1.00	
Co	0.023	–0.209	0.664	0.342	0.651	0.276	0.401	1.00

0.102 µg kg^{-1} d^{-1} Lahore), (Fe 1.021, Ni 0.079, Cd 0.183, Cr 2.02, Pb 0.139, Zn 0.129 µg kg^{-1} d^{-1} Karachi), and (Fe 0.558, Ni 0.108, Cd 0.084, Cr 1.01, Pb 0.130, Zn 0.113 µg kg^{-1} d^{-1} Sialkot) with a mean concentration. The mean ADD value of Cr was higher in Karachi (2.02 µg kg^{-1} d^{-1}) as compared to other two cities Lahore (1.18 µg kg^{-1} d^{-1}) and Sialkot (1.01 µg kg^{-1} d^{-1}). In this study, almost all the samples, Cr metal, exceeded the typical toxic risk index 1.00. This showed possible health hazards in nearly leather industries areas of these cities with respect to the use of groundwater for drinking purpose. Recently, [39] also reported high HQ

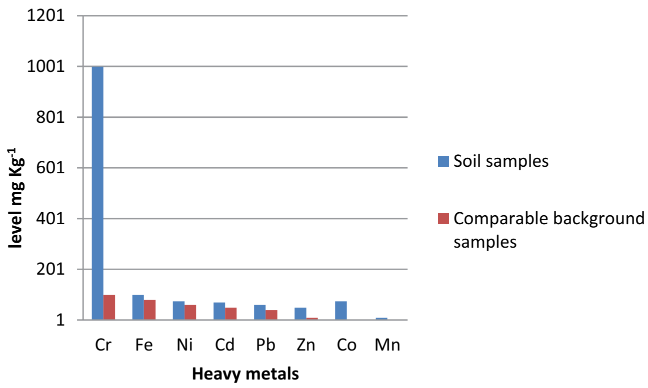

Fig. 2. Comparison of metals concentration of soil samples with background samples. Bars show the 95% confidence interval for mean values.

Table 6a
Metal to metal correlation coefficient matrix for tested heavy metals in ground-water samples from tannery premises (Lahore)

	Cr	Fe	Ni	Cd	Pb	Zn	Mn	Co
Cr	1.00							
Fe	0.191	1.00						
Ni	0.475	0.076	1.00					
Cd	0.298	–0.387	0.195	1.00				
Pb	0.304	0.601	0.507	0.541	1.00			
Zn	–0.768	0.414	–0.329	0.769	0.568	1.00		
Mn	0.496	–0.597	0.594	–0.398	–0.636	0.303	1.00	
Co	0.417	0.387	–0.194	0.398	0.686	0.201	0.497	1.00

Table 6b
Metal to metal correlation coefficient matrix for tested heavy metals in ground-water samples from tannery premises (Karachi)

	Cr	Fe	Ni	Cd	Pb	Zn	Mn	Co
Cr	1							
Fe	0.181	1						
Ni	0.477	0.081	1					
Cd	0.288	–0.382	0.193	1				
Pb	0.309	0.612	0.509	0.542	1			
Zn	–0.735	0.413	–0.324	0.767	0.561	1		
Mn	0.493	–0.598	0.598	–0.399	–0.632	0.314	1	
Co	0.418	0.367	–0.193	0.334	0.688	0.205	0.498	1

(range 0.12–18.5) in rural areas of southern Punjab. They stated that the 75% samples in Chichawatni, 61% samples in Vehari, and 27% samples in Rahim Yar Khan were higher than the typical toxic risk index 1. Similar to ADD and HQ (Table 8), carcinogenic risk values also exceeded the US-EPA limit (10–6) for all the water samples. The results proposed that the people living in the study areas that are exposed to Cr via drinking water are at carcinogenic risk (Table 9). This implies that constant monitoring and remediation of

Table 6c
Metal to metal correlation coefficient matrix for tested heavy metals in ground-water samples from tannery premises (Sialkot)

	Cr	Fe	Ni	Cd	Pb	Zn	Mn	Co
Cr	1							
Fe	0.187	1						
Ni	0.472	0.083	1					
Cd	0.289	–0.380	0.19	1				
Pb	0.3	0.61	0.513	0.541	1			
Zn	–0.732	0.411	–0.328	0.769	0.56	1		
Mn	0.494	–0.599	0.59	–0.390	–0.636	0.318	1	
Co	0.411	0.368	–0.199	0.331	0.685	0.207	0.497	1

Cr level in groundwater is required, in order to protect people from health hazards due to the use of Cr-contaminated water.

4. Conclusion

In study areas of Lahore, Karachi, and Sialkot, where untreated leather industry effluents have been discharged for a long time, groundwater and soil were observed to be dirtied with extremely high concentrations of different heavy metals. As expected, the chromium level was extremely higher in the comparison to other metals, owing to the fact that high concentrations of chromium salts have been used for leather tanning in Lahore, Sialkot and Karachi tanneries. The concentration of Pb, Cd and Cr in groundwater samples

Table 7
Average daily dose of (Fe, Ni, Cd, Cr, Pb, Zn, Co, and Mn) in Lahore, Karachi and Sialkot

	Fe	Ni	Cd	Cr	Pb	Zn	Co	Mn
				Lahore				
Maximum	0.164	0.432	0.784	2.41	0.347	0.209	0.238	0.188
Minimum	0.087	0.097	0.109	1.03	0.067	0.021	0.075	0.087
Mean	0.101	0.112	0.207	1.36	0.169	0.102	0.167	0.079
Median	0.350	0.109	0.181	1.18	0.137	0.051	0.098	0.063
				Karachi				
Maximum	1.021	0.209	1.580	3.17	0.328	0.204	0.209	0.264
Minimum	0.421	0.079	0.921	2.11	0.058	0.033	0.077	0.089
Mean	0.697	0.107	0.183	2.02	0.139	0.129	0.142	0.097
Median	0.334	0.118	0.105	2.19	0.108	0.108	0.087	0.067
				Sialkot				
Maximum	1.217	0.139	0.408	2.77	0.297	0.153	0.193	0.167
Minimum	0.319	0.091	0.097	1.13	0.072	0.046	0.088	0.082
Mean	0.558	0.108	0.084	1.01	0.130	0.113	0.137	0.087
Median	0.167	0.088	0.089	1.31	0.083	0.097	0.078	0.097

Table 8
Hazard quotient (HQ) of (Fe, Ni, Cd, Cr, Pb, Zn, Co, and Mn) in Lahore, Karachi and Sialkot

	Fe	Ni	Cd	Cr	Pb	Zn	Co	Mn
				Lahore				
Maximum	27.37	33.9	16.31	42.9	17.15	19.14	13.36	13.14
Minimum	23.15	29.03	7.031	14.91	6.14	6.21	8.12	9.36
Mean	21.42	19.34	27.12	13.91	9.11	8.67	11.96	12.1
Median	14.31	27.11	11.39	12.35	9.36	12.31	11.25	11.32
				Karachi				
Maximum	31.61	39.36	18.36	44.36	19.32	21.35	13.69	13.21
Minimum	12.64	8.139	1.364	2.36	0.97	0.36	0.99	1.23
Mean	13.36	7.36	11.36	7.31	1.36	4.25	2.21	1.02
Median	11.36	11.63	13.64	6.36	4.21	3.69	4.36	3.65
				Sialkot				
Maximum	20.31	14.25	11.32	13.25	10.64	17.26	9.31	11.21
Minimum	1.25	0.94	0.78	0.91	0.68	0.87	0.51	0.89
Mean	2.36	6.21	3.21	3.94	6.32	7.21	2.11	5.21
Median	6.21	2.21	4.12	2.84	2.14	3.69	1.32	2.31

Table 9
Carcinogenic risk (CR) of (Fe, Ni, Cd, Cr, Pb, Zn, Co, and Mn) in Lahore, Karachi and Sialkot

	Fe	Ni	Cd	Cr	Pb	Zn	Co	Mn
Lahore								
Maximum	0.00016	0.00023	0.00047	0.00189	0.00069	0.00031	0.00023	0.00063
Minimum	0.00006	0.00012	0.00013	0.00046	0.00009	0.00008	0.00006	0.00006
Mean	0.00012	0.00010	0.00021	0.00019	0.00036	0.00014	0.00014	0.00023
Median	0.00010	0.00013	0.00016	0.00016	0.00042	0.00011	0.00019	0.00013
Karachi								
Maximum	0.00103	0.0099	0.00059	0.00309	0.00089	0.00087	0.00100	0.00078
Minimum	0.00074	0.00049	0.00003	0.00073	0.00015	0.00008	0.00072	0.00001
Mean	0.00045	0.00087	0.00013	0.00067	0.00010	0.00019	0.00047	0.00026
Median	0.00061	0.00070	0.00021	0.00042	0.00018	0.00014	0.00084	0.00012
Sialkot								
Maximum	0.00079	0.00097	0.00067	0.00259	0.00080	0.00100	0.00106	0.00089
Minimum	0.00031	0.00007	0.00009	0.00083	0.00010	0.00012	0.00021	0.00009
Mean	0.00021	0.00020	0.00015	0.00054	0.00019	0.00031	0.0087	0.00026
Median	0.00030	0.00014	0.00018	0.00021	0.00027	0.00038	0.00049	0.00019

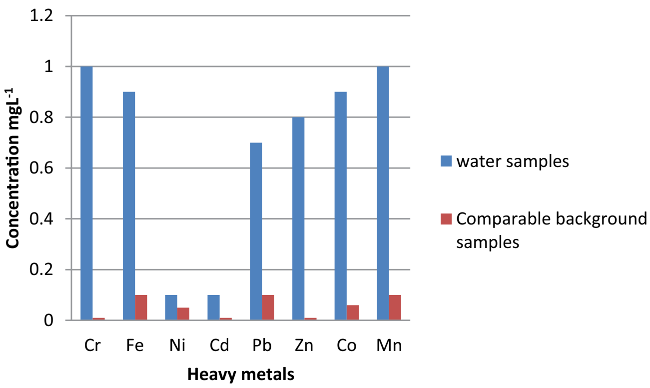

Fig. 3. Comparison of ground-water metals concentrations with background water samples. Bars show the 95% confidence interval for mean values.

not only outdid the recommended safe limits, rather these were 3–25 times greater than the drinking water quality standards. Correlation analysis demonstrated that the heavy metals in groundwater and soil have a common origin. The contamination in scrutinized areas, particularly with chromium needs an efficient treatment approach for remediation of groundwater and soil. A suitable remediation technique for such pollutants, heavy metals, chemical waste, Industrial waste, pharmaceutical waste, pesticides, nitrates, and fertilizers is phytoremediation and adsorption. Conversely, more issues require to be addressed in these study areas are availability and speciation of the metals, physio-chemical attributes of effluents, water and soil.

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Authors' contribution

Original draft wrote (Ghulam Murtaza); review and editing (Muhammad Usman)

Conflict of interest

Authors have no conflict of interest.

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