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Heavy metal analysis for assessing the quality of wastewater effluent samples collected from three major waste drains of Peshawar city, Pakistan

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ABSTRACT

Irrigation with wastewater is becoming a tradition due to increased demand of freshwater for industrial purposes. Therefore, it is vital to investigate the quality of wastewater effluents of Peshawar city at all points intended for irrigation purposes. Hence, trace metal contents in effluents from Peshawar city were assessed. A total of 24 samples on hourly basis for 24 h were collected one each from Shahi Khatta, Muhammad Zai drain, and Bara Gate effluents, respectively. These were then analyzed for metal contents like As, Cd, Cr, Pb, Fe, Mn, Ni, Ag, total phosphorus, and Zn. This study showed that the concentration of Cd, Pb, Ag, Mn, and Fe in the waste effluents at Shahi Khatta was much higher than the limits of National Environmental Quality Standards Pakistan. Almost similar trend was found in Bara Gate effluents except for Mn, while Muhammad Zai drain effluents exhibited all the metal values within the limits. Stringent precautionary measures are needed to not let these effluents into irrigation channels without treatments. Further, it is suggested to monitor the quality of Peshawar city waste effluents periodically.

Keywords: Wastewater quality; Trace elements; Baseline data

1. Introduction

From last few decades the industrial revolution is on its gallop in the developed and developing countries around the world. This sector in Pakistan is also on its gallop which has contributed to high economic growth, but at the same time it has also given rise to severe environmental problems. In the developed countries, the industrials effluents are properly treated; however, in the developing countries there are no stringent rules for the treatments of industrial effluents and directly discharged into main streams, where they are used for irrigation purposes. In future these will give rise to serious environmental problems. The water quality and human health are closely related to each other. In the developing countries, the domestic wastes from each building along with the effluent of small-scale as well as large-scale industries is disposed off into the open drains and gutters which ultimately enter into the rivers, resulting in the deterioration of river water quality [1–4].

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Wastewater from manufacturing or chemical processing industries contributes to water pollution. Industrial wastewater usually contains specific and readily identifiable chemical compounds. It is found that one-third of the total water pollution comes in the form of effluent discharge, solid wastes, and other hazardous wastes. Unfortunately, the industrial waste effluents in one-third of the world countries are directly disposed into surface waters without pretreatment. It has been found that almost all rivers are polluted in most parts of the world by one or the other kind of industries [5–8]. Although all industries in Pakistan work under the strict guidelines of the Environmental Protection Agency, the environmental situation is far from satisfactory. As a result, in Pakistan there are sufficient evidences available related to the mismanagement of industrial wastes [8–11]. Most of these defaulting industries are chemical industries, sugar mills, distilleries, leather processing industries, paper mills, agrochemicals, pesticides manufacturing industries, and pharmaceutical industries. The problem of water pollution has worsened due to toxic heavy metals (HMs) [12,13]. The increasing trend in concentration of HMs in the environment has attracted considerable attention of the ecologists globally during the last decades. Untreated or allegedly untreated industrial effluents and sewage water contain variable amounts of HMs such as arsenic, lead, nickel, cadmium, copper, manganese, iron, zinc, and chromium [14–16]. Most of these metals are notorious for having the potential of contaminating crops when irrigated with these industrial and city waste effluents. HMs have a marked effect on the aquatic flora and fauna which through bio-magnification enter into the food chain and ultimately affect the human beings. Incidence of HM accumulations in fish, oysters, sediments, and other components of aquatic ecosystems has also been reported [17–26]. They enter into aquatic environment in free metal ion forms where they form soluble complexes as well and are thus available for uptake by organisms [23]. They also adsorb on particulate matter. The metals associated with particulate material are also available for biological uptake [26] and are also deposited in estuarine sediments [27]. Once deposited, binding by sulfides and/or iron hydroxides immobilizes trace metals until a change in redox or pH occurs [21,22]. Thus, the surficial sediments, particularly the fine fraction, accumulate trace metals and provide means for evaluating the long-term accumulation of contaminants [24,28].

Wastewater irrigation is a widespread practice in the world and recently a number of articles have been published on wastewater-irrigated soils contaminated with HMs [14,16,17]. Excessive accumulation of HMs in agricultural soils through wastewater irrigation may not only result in soil contamination, but also leads to elevated HMs uptake by crops, and thus affects food quality and safety [18,29–31]. In turn, water pollution is transferred to agricultural soils, passed on to plants and then to cattle feed being grown in the areas which ultimately transfer HMs to the bodhy of the animals which are major producers of our dairy products [30,31].

In Pakistan, about 26% of national vegetable crops are irrigated with wastewater. With the growth in population and the increase in consumption of freshwater in domestic activities, the use of wastewater is bound to increase in agriculture for the production of food crops. Around 70% of the water utilized in cities is refused as wastewater and its volume has increased with increase in population and economic development [19].

The problem of environmental pollution due to HMs has begun to cause concern now in most of the major metropolitan cities of Pakistan including Peshawar. The present, day-by-day increasing tremendous industrial pollution has prompted us to carry the systematic and detailed study of pollution due to toxic HMs in effluent samples collected from the selected areas of Peshawar. This study was aimed to investigate the wastewater pollution load in terms of HMs and to find out whether these wastewaters are fit for irrigation or not.

2. Materials and methods

2.1. Area of study

The study was carried out at the wastewater drains at the outskirts of Peshawar city which is one of the most rapidly developing and heavily polluted industrial belts of Khyber Pakhtunkhwa, Pakistan. In order to investigate the overall effect of the waste effluents, sampling strategy was devised in such a way to include the effluents of the nearby cottage industries also in addition to the large-scale Hayatabad industrial estate effluents. As there are a lot of industries such as small-scale dying, tanning, carpet, leather, vulcanizing, hospitals, automobile, jewelry, and pottery industries also ultimately join these effluent drains. The study area lies between latitude 34° 16' 54" North and 71° 41' 17" East. The main water source for the industrial consumption is Kabul River coming from Shah Kas tributary. The industrial area utilizes about 35,000 m^3/d of freshwater. The treated and untreated effluent discharge amounts to 28,750 m^3/d, that is, 64% of the total industrial effluents. This has created health hazards not only for local population but has also resulted in disturbance of the aquatic life of Kabul River flowing in the area.

2.2. Glasswares and chemicals

All the glasswares used for the analyses were carefully cleaned with nitric acid followed by thorough rinsing with double-distilled water. All of the reagents used were of analytical grade.

2.3. HM analysis

The collected water samples were analyzed for the HMs including As, Cd, Cr, Pb, Fe, Mn, Ni, Ag, and Zn using an air acetylene flame mode except As for which hydride formation mode was used which is the preferred method [32,33].

The analysis was carried out using atomic absorption spectrophotometer Z-2000, Hitachi, Japan. The calibration curves were drawn separately for all the metals by running different concentrations of standard solutions. A reagent blank sample was analyzed and subtracted from the samples to correct for reagent impurities.

2.4. Sample collection and preparation of wastewater effluents

The industrial wastewater effluent samples were collected from three different effluent discharge points namely Shahi Khatta, Muhammad Zai drain, and Bara Gate. The sampling was performed for 24 h, each after 1-h interval, in polythene bottle of 2-L capacity. Water sampler was used to collect the wastewater samples from the drains (number of samples collected, $n = 24$). Weather conditions were specially considered during sampling periods in order to avoid any disturbances due to rain and other environmental conditions in the region. During raining, the sampling was postponed till normal flow conditions of the wastewater effluents were attained again. The bottles were thoroughly cleaned with hydrochloric acid, washed with tape water to render free of acid, washed with distilled water twice, again rinsed with the water sample to be collected, and then filled up the bottle with the sample leaving only a small air gap at the top. The samples were concentrated to 10-fold on a water bath and subjected to nitric acid digestion and then kept for further analysis.

3. Results and discussion

3.1. HM contents of waste effluents

The National Environmental Quality Standards (NEQS) limits are given in Table 1, while the data for HMs in three different waste drains, that is, Shahi Khatta, Muhammad Zai drain, and Bara Gate effluents, have been presented in Tables 2–4, respectively. For the sake of comparison, NEQS limits have been graphically presented in Fig. 1 along with

Table 1
Pakistan National Environmental Quality Standards (NEQS) for wastewater effluents

Sr. no.	Parameters	Method no.	Units	Pakistan NEQS
1	Cadmium as Cd	3500-Cd	mg/L	0.10
2	Chromium as Cr	3500-Cr	mg/L	1.00
3	Lead as Pb	3500-Pb	mg/L	0.50
4	Nickle as Ni	3500-Ni	mg/L	1.00
5	Silver as Ag	3500-Ag	mg/L	1.00
6	Total phosphorus	4500-P	mg/L	–
7	Arsenic as As	3500-As	mg/L	1.00
8	Manganese as Mn	3500-Mn	mg/L	1.50
9	Iron as Fe	3500-Fe	mg/L	2.00
10	Zinc as Zn	3500-Zn	mg/L	5.00

Table 2
Heavy metals concentrations (mg/L) in Shahi Khatta effluents

Time	Cd	Cr	Pb	Ni	Ag	P	As	Mn	Fe	Zn
9:00 AM	1.16	0.09	0.62	0.19	1.02	0.63	0.12	1.69	2.53	2.42
10:00 AM	1.18	0.07	0.62	0.19	1.01	0.62	0.13	1.53	2.59	2.39
11:00 AM	1.16	0.08	0.63	0.2	1.03	0.67	0.12	1.62	2.95	2.39
12:00 PM	1.18	0.08	0.65	0.19	1.03	0.67	0.12	1.61	3.05	2.38
1:00 PM	1.19	0.08	0.61	0.19	1.02	0.68	0.08	1.68	3.12	2.49
2:00 PM	1.19	0.08	0.6	0.2	1.02	0.65	0.11	1.69	2.58	2.58
3:00 PM	1.16	0.07	0.65	0.2	1.01	0.64	0.12	1.58	2.6	2.62
4:00 PM	1.16	0.09	0.64	0.21	1.01	0.72	0.1	1.6	2.62	2.47
5:00 PM	1.19	0.09	0.68	0.22	1.04	0.68	0.09	1.65	2.61	2.79
6:00 PM	1.18	0.08	0.61	0.21	1.02	0.76	0.1	1.67	2.69	2.58
7:00 PM	1.13	0.08	0.63	0.2	1.01	0.64	0.08	1.45	2.57	2.11
8:00 PM	1.05	0.07	0.49	0.19	1.03	0.63	0.05	1.6	2.53	1.93
9:00 PM	1.09	0.09	0.48	0.19	1.02	0.6	0.06	1.59	2.43	2.1
10:00 PM	1.09	0.06	0.49	0.18	1.01	0.61	0.07	1.35	2.51	1.84
11:00 PM	1.07	0.08	0.47	0.18	1.01	0.62	0.07	1.23	2.39	1.89
12:00 AM	1	0.08	0.46	0.16	1	0.63	0.06	1.35	2.57	1.92
1:00 AM	0.8	0.06	0.48	0.19	1	0.67	0.05	1.4	2.42	1.89
2:00 AM	1.02	0.05	0.45	0.16	1	0.63	0.08	1.6	2.45	1.68
3:00 AM	0.9	0.05	0.47	0.15	1	0.57	0.07	1.43	2.51	1.79
4:00 AM	0.95	0.06	0.48	0.17	1.01	0.61	0.06	1.3	2.47	1.68
5:00 AM	0.9	0.05	0.46	0.12	1.01	0.63	0.08	1.4	2.43	1.79
6:00 AM	1.07	0.05	0.45	0.15	1.01	0.62	0.07	1.3	2.48	1.98
7:00 AM	1.09	0.06	0.5	0.12	1	0.62	0.05	1.6	2.42	1.96
8:00 AM	1.01	0.05	0.48	nd	nd	0.62	0.07	1.4	2.49	1.79
Min.	0.80	0.05	0.45	0.12	1.00	0.57	0.05	1.23	2.39	1.68
Max.	1.19	0.09	0.68	0.22	1.04	0.76	0.13	1.69	3.12	2.79
Mean	1.08	0.07	0.55	0.18	1.01	0.64	0.08	1.51	2.58	2.14
SD	0.11	0.01	0.08	0.03	0.01	0.04	0.03	0.14	0.19	0.34
Range	0.39	0.04	0.23	0.10	0.04	0.19	0.08	0.46	0.73	1.11
CV	0.10	0.20	0.15	0.15	0.01	0.06	0.30	0.09	0.07	0.16

SD, standard deviation; CV, coefficient of variation; nd = not determined..

Table 3
Heavy metals concentrations (mg/L) in Muhammad Zai effluents

Time	Cd	Cr	Pb	Ni	Ag	P	As	Mn	Fe	Zn
9:00 AM	0.06	0.06	0.13	0.03	nd	1.4	0.02	0.08	1.23	4.21
10:00 AM	0.03	0.07	0.12	0.03	0.01	1.3	0.03	0.08	0.57	3.69
11:00 AM	0.05	0.06	0.15	0.04	0.02	1.3	0.03	0.07	1.29	3.89
12:00 PM	0.06	0.08	0.12	0.03	0.02	1.2	0.04	0.05	0.49	4.23
1:00 PM	0.02	0.07	0.12	0.05	0.02	1.3	0.05	0.06	0.69	3.79
2:00 PM	0.05	0.08	0.13	0.04	0.01	1.3	0.02	0.08	1.32	4.26
3:00 PM	0.06	0.07	0.12	0.02	0.02	1.4	0.03	0.09	0.46	3.68
4:00 PM	0.06	0.06	0.11	0.01	0.01	1.3	0.02	0.08	0.63	3.86
5:00 PM	0.05	0.05	0.13	0.02	0.02	1.4	0.04	0.09	1.32	4.23
6:00 PM	0.03	0.05	0.06	0.03	0.02	1.25	nd	0.03	0.36	2.58
7:00 PM	0.02	0.04	0.08	0.02	nd	1.2	0.02	0.04	0.53	3.24
8:00 PM	0.02	0.03	0.09	0.02	nd	0.85	nd	0.05	0.29	2.56
9:00 PM	0.03	0.03	0.05	0.02	0.01	0.95	0.02	0.03	0.31	3.25
10:00 PM	0.02	0.02	0.07	0.03	nd	0.85	nd	0.02	0.18	1.84
11:00 PM	0.02	0.03	0.06	0.02	0.01	1.1	0.02	0.04	0.4	2.35
12:00 AM	0.03	0.03	0.05	0.02	0.01	0.89	0.02	0.04	0.17	1.92
1:00 AM	0.03	0.02	0.06	0.02	0.01	0.79	0.02	0.03	0.16	2.36
2:00 AM	0.02	0.03	0.08	0.01	0.01	0.86	nf	nd	0.18	1.68
3:00 AM	0.03	0.03	0.08	0.02	nd	0.83	0.02	0.02	0.09	2.68
4:00 AM	0.02	0.02	0.04	0.01	nd	0.95	0.01	nd	0.13	3.21
5:00 AM	0.03	0.03	0.08	0.02	nd	0.93	nd	0.03	0.81	2.65
6:00 AM	0.03	0.02	0.09	0.02	nd	0.89	0.02	nd	0.36	1.98
7:00 AM	0.02	0.03	0.08	0.02	nd	0.87	nd	0.03	0.21	2.64
8:00 AM	0.03	0.04	0.06	0.02	nd	0.86	0.01	0.02	0.15	1.79
Min.	0.02	0.02	0.04	0.01	0.01	0.79	0.01	0.02	0.09	1.68
Max.	0.06	0.08	0.15	0.05	0.02	1.40	0.05	0.09	1.32	4.26
Mean	0.03	0.04	0.09	0.02	0.01	1.08	0.02	0.05	0.51	3.02
SD	0.02	0.02	0.03	0.01	0.01	0.22	0.01	0.02	0.40	0.88
Range	0.04	0.06	0.11	0.04	0.01	0.61	0.04	0.07	1.23	2.58
CV	0.44	0.46	0.35	0.41	0.36	0.20	0.43	0.49	0.78	0.29

nd = not determined.

mean HMs concentrations in collected effluents, collected on hourly basis from the three collecting sites.

In addition, Figs. S1–S3 (supplementary figures) exhibit graphically the trends of variations in the selected HMs concentrations for three sites, during 24 h.

3.1.1. Cadmium

Cadmium (Cd) is a very toxic metal and can cause serious health problems. Recently, attention has been focused for its availability in the water, soil, milk, medicinal plants, herbal drugs, etc. A vast amount of literature exist which document the adverse health effects of acute and chronic exposure to cadmium in both humans and animals [3]. From the data given in Table 2, it can be seen that Cd content in Shahi Khatta wastewater sample is higher at an average, that is, 1.08 mg/L than Bara Gate effluent samples 1.04 mg/L (Table 3) followed by Muhammad Zai drain (Table 4) which is 0.03 mg/L. The higher amount of Cd in Shahi Khatta and Bara Gate effluents may be due to input from city domestic waste effluents in addition to industrial wastes coming from Hayatabad Industrial Estate which further increase the waste load. From the results, it can be seen that Cd concentration was higher during working hours (9:00 AM–5:00 PM) which decreased gradually during late night hours, and in the morning it was shifted toward minimum values in samples of all the three drains. However, Muhammad Zai drain has mean Cd value of 0.03 mg/L (Table 2).

3.1.2. Chromium

Chromium (Cr) is one of the known environmental toxic pollutants in the world. The main sources for Cr contamination are tanneries and steel industries, sewage sludge applications, and fly ash. Besides these, Cr plating and alloys in motor vehicles are considered to be a more probable source of Cr [34]. At elevated concentrations, it could be toxic for plants and animals. From the data in Table 2, it can be seen that Cr in Shahi Khatta effluents ranged between 0.05 and 0.09 mg/L with mean value of 0.07 mg/L while Muhammad Zai drain (Table 3) have Cr content in the range of 0.02–0.08 mg/L with mean Cr value of 0.04 mg/L. Similarly, Bara Gate effluents (Table 4) have designated range of 0.04–0.09 mg/L with mean

Table 4
Heavy metals concentrations (mg/L) in Bara Gate effluents

Time	Cd	Cr	Pb	Ni	Ag	P	As	Mn	Fe	Zn
9:00 AM	1.13	0.05	0.62	0.18	1.01	3.29	0.05	0.21	2.69	3.12
10:00 AM	1.15	0.06	0.59	0.16	1.02	2.92	0.04	0.09	3.4	2.69
11:00 AM	1.08	0.07	0.82	0.15	1.17	3.95	0.05	0.15	3.26	2.36
12:00 PM	1.09	0.06	0.8	0.17	1.16	3.58	0.04	0.21	2.94	2.68
1:00 PM	1.07	0.07	0.49	0.21	1.37	3.24	0.03	0.23	3.02	1.68
2:00 PM	1.32	0.06	0.57	0.21	1.25	3.1	0.04	0.24	2.15	1.92
3:00 PM	1.21	0.07	0.64	0.24	0.99	2.59	0.04	0.21	3.08	2.56
4:00 PM	1.08	0.06	0.59	0.26	1.56	3.26	0.03	0.22	2.36	3.95
5:00 PM	1.13	0.06	0.57	0.18	1.08	3.68	0.04	0.21	3.29	2.68
6:00 PM	1.05	0.09	0.39	0.16	1.07	1.39	0.04	0.11	2.43	2.1
7:00 PM	1.12	0.06	0.54	0.09	nd	1.54	nd	0.09	2.25	1.86
8:00 PM	1.02	0.08	0.41	0.16	0.92	0.95	nd	0.08	2.31	1.75
9:00 PM	1.08	0.07	0.49	nd	0.83	0.89	0.03	0.05	2.16	1.63
10:00 PM	1	0.06	0.41	0.15	nd	1.21	0.02	0.11	2.21	1.25
11:00 PM	nd	0.07	0.38	0.13	0.93	1.24	nd	0.07	2.31	1.64
12:00 AM	0.86	0.09	0.51	nd	0.84	1.23	0.04	0.09	2.16	1.32
1:00 AM	0.92	0.06	0.53	0.16	0.92	1.32	0.03	0.08	2.21	1.21
2:00 AM	nd	0.08	0.56	0.12	0.89	nd	0.02	0.09	2.13	1.12
3:00 AM	0.86	0.06	0.58	nd	0.93	1.27	nd	nd	2.26	0.98
4:00 AM	0.87	0.08	0.36	0.13	nd	1.24	0.02	0.11	2.42	1.34
5:00 AM	0.83	0.05	0.47	0.12	0.95	0.89	nd	0.13	0.95	1.21
6:00 AM	nd	0.04	0.43	nd	0.79	nd	0.01	nd	2.19	1.21
7:00 AM	0.97	0.04	0.28	0.12	nd	1.32	nd	0.08	1.29	1.23
8:00 AM	nd	0.04	0.25	0.09	0.78	nd	0.04	0.09	1.24	1.14
Min.	0.83	0.04	0.25	0.09	0.78	0.89	0.01	0.05	0.95	0.98
Max.	1.32	0.09	0.82	0.26	1.56	3.95	0.05	0.24	3.40	3.95
Mean	1.04	0.06	0.51	0.16	1.02	2.10	0.03	0.13	2.36	1.86
SD	0.13	0.01	0.14	0.05	0.20	1.10	0.01	0.06	0.62	0.76
Range	0.49	0.05	0.57	0.17	0.78	3.06	0.04	0.19	2.45	2.97
CV	0.12	0.22	0.27	0.28	0.19	0.52	0.32	0.47	0.26	0.41

nd = not determined.

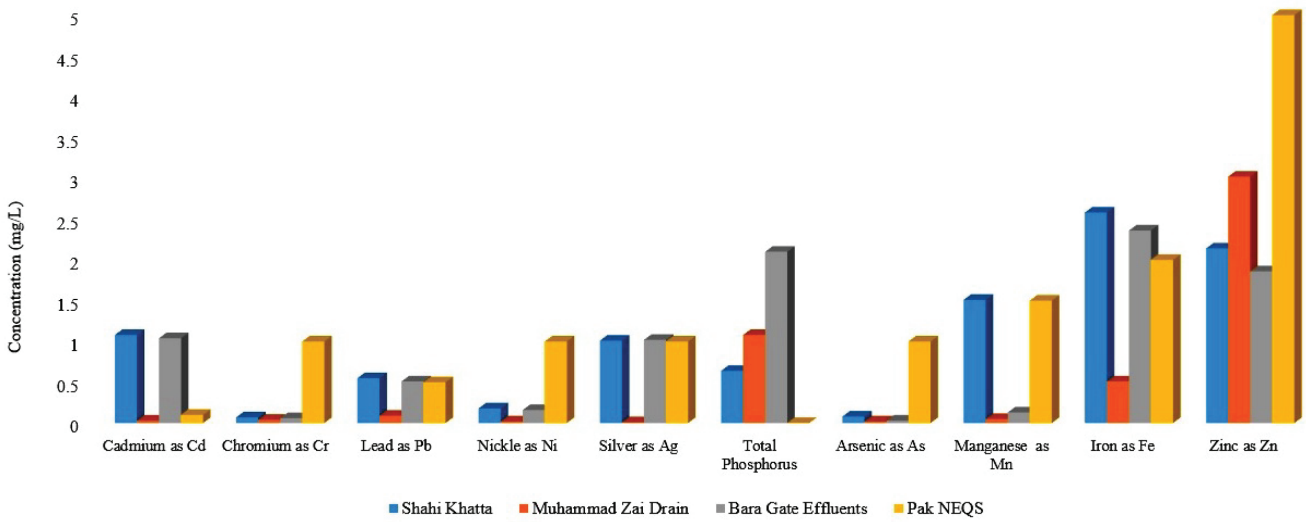

Fig. 1. Comparison of Peshawar city waste effluents (mg/L) to Pakistan National Environmental Quality Standards (Pakistan NEQS).

Cr value of 0.06 mg/L. Elevated concentration pattern of metal (Cr) during working hours was seen which was later on followed by gradual decrease in evening and night hours. The problems that are associated with Cr exposure are skin rashes, upset stomachs and ulcers, respiratory problems, weakened immune system, kidney and liver damage, alterations in genetic material, lung cancer, and may be death also. Besides, it has some benefits too, for example, it enhances the removal of glucose from the blood [35]. It also acts as an activator of several enzymes. Chromium deficiency decreases the antidiabetic enzyme insulin efficiency leading to increased sugar and cholesterol levels in blood [36]. Cr availability may be attributed to the presence of larger number of tannery industries present in the surroundings of Peshawar city.

3.1.3. Lead

Lead (Pb) is regarded as very hazardous for plants, animals, and humans. The sources of Pb pollution are Pb mines, fuel combustion, sewage sludge applications, and farmyard manure. The maximum acceptable concentration for foodstuffs is around 1 mg/kg [26]. From the data in Table 2, it can be seen that Pb contents in Shahi Khatta waste effluent ranged from 0.45 to 0.68 mg/L with mean value of 0.55 mg/L, for Muhammad Zai drain 0.04–0.15 mg/L having mean of 0.09 mg/L, and for Bara Gate effluent these lie between 0.25 and 0.82 mg/L having mean Pb concentration of 0.51 mg/L.

As high as 0.82 mg/L Pb content in wastewater has been investigated at 11:00 AM while it was gradually decreased during evening, and in early morning it was at minimum. Long-term exposure to Pb can result in a buildup of Pb in the body and has more severe symptoms. These include anemia, pale skin, a blue line at the gum margin, decreased hand grip strength, abdominal pain, severe constipation, nausea, vomiting, and paralysis of the wrist joints. Prolonged exposure may also result in kidney damage, and it may also affect nervous system.

3.1.4. Nickel

Nickel (Ni) is an abundant element and is found in all soils. Ni is emitted from volcanoes and airborne industrial effluents. Ni dust or the Ni of asbestos dust inhaled in occupational exposure may cause bronchial cancer and dermatitis [37,38]. Mean Ni concentration found in Shahi Khatta drain was (0.18 mg/L) followed by Bara Gate effluents (0.16 mg/L) and Muhammad Zai drain (0.02 mg/L). Maximum value of Ni (0.22 mg/L) at Shahi Khatta drains was found at 5:00 PM, whereas at Muhammad Zai drain (0.05 mg/L) and Bara gate effluents (0.26 mg/L) the maximum concentrations of Ni were found at 1:00 PM and 4:00 PM, respectively.

3.1.5. Silver

Data in Tables 2–4 show that mean (Ag) metal concentration in Bara Gate effluents (1.02 mg/L) was higher than that in Shahi Khatta (1.01 mg/L), and both these have crossed the NEQS limit for Ni (1.00 mg/L). However, Muhammad Zai drain (0.01 mg/L) was found within the permissible limit. Higher silver metals at Shahi Khatta and Bara Gate effluents may be due the nature of industrial waste coming from Hayatabad and medium-sized industries in the area, especially pottery industry and traditional utensils factories. Besides this the jewelry shops are also located in that area which may also contribute to the Ag pollution into the city effluents.

3.1.6. Total phosphorous

Form the data in Tables 2–4, it can be seen that at an average Bara Gate effluents (2.10 mg/L) had higher phosphorous (P) content than Muhammad Zai drain (1.08 mg/L) followed by Shahi Khatta (0.64 mg/L). This higher phosphorus content may be due to agricultural soil run off in the area upon which different phosphate-based fertilizers are applied in addition to the waste effluents of the city areas and the industrial effluents [34]. However, the maximum concentration at Shahi Khatta (0.76 mg/L), Muhammad Zai drain (1.4 mg/L), and Bara Gate effluent drain (3.95 mg/L) was investigated at 5:00 PM, 5:00 PM, and 11:00 AM, respectively (Tables 2–4). The reasons for maximum P concentration at the two points mentioned earlier at 5:00 PM may be due to different industries randomly located, while in Bara Gate effluents it may be attributed to numerous match manufacturing industries effluents and certain other chemical industries at its peak working hours at 11:00 AM (Table 4).

3.1.7. Arsenic

Arsenic (As) is recognized as the probable carcinogen [37,38]. It is not needed by our body in any form. However, its industrial uses are abundant. It is used in fertilizers, insecticides, and as wood preservative. Form the data in Tables 2–4, it can be seen that Shahi Khatta drain effluents have (0.18 mg/L) as content > Bara Gate effluents (0.165 mg/L) > Muhammad Zai drain (0.02 mg/L). This higher As content was found within the NEQS limit (1 mg/L); however, it may endanger the situation if its concentration increases further in future.

3.1.8. Manganese

Major sources of manganese (Mn) are soil, fertilizers, and fuel oils. Mn in the air may have adverse effects on health, for example, it may cause Parkinson's disease and progressive deterioration of the central nervous system [39]. Shahi Khatta drain has Mn content in the range of 1.23–1.69 mg/L with mean value of 1.51 mg/L, Muhammad Zai drain ranges from 0.02 to 0.09 mg/L, having mean Mn content of 0.05 mg/L while that of Bara Gate effluents were found in the range of 0.05–0.24 mg/L with mean value of 0.13 mg/L (Tables 2–4). At all the three effluent drains, maximum Mn contents were found during working hours and followed by a gradual decrease toward minimum during break/rest hours. Mn in the effluents of Shahi Khatta crossed the Pakistan NEQS limit (1.5 mg/L) for each sample collected during every working hour (9:00 AM–5:00 PM) as well as at 6:00 PM, 8:00 PM, and 9:00 PM after working hours (Table 2).

3.1.9. Iron

Iron (Fe) is another essential element. It is found in body tissues and helps in energy metabolism. It facilitates the oxidation of carbohydrates, proteins, and fats to control body weight, which is a very important factor in diabetes [39]. Tables 2–4 demonstrated Fe concentrations in effluents of Shahi Khatta, Muhammad Zai, and Bara Gate, respectively.

At an average the highest Fe concentration 2.58 mg/L was found in Shahi Khatta wastewater sample having minimum and maximum values of 2.39–3.12 mg/L. The lowest mean concentration of Fe was found in Muhammad Zai Drain (0.51 mg/L), being below the NEQS limit (2.0 mg/L). Bara Gate effluents were within the range of 0.95–3.4 mg/L with mean Fe content of 2.36 mg/L. It is clear from Table 2 (Shahi Khatta effluents) and Table 4 (Bara Gate drain) that both these waste effluents are above the limit of Pakistan NEQS. It may cause health problems through multiple exposure paths including crops irrigation, which may ultimately be transported to the consumer's body.

3.1.10. Zinc

About 85% of zinc (Zn) in blood combines with protein for transport after its absorption, and its turnover is rapid in the pancreas. Deficiency of Zn is known to cause diabetic hyposmia, hypogeusia, or coma [18,39,40]. It is obvious from the data in Tables 2–4 that Zn concentration in Shahi Khatta wastewater ranged between 1.68 and 2.79 mg/L with mean value of 2.14 mg/L. Similarly, Zn contents in Muhammad Zai drain were in the range of 1.68–4.26, with mean of 3.02 mg/L. However, among these three drains, the lowest concentration of Zn was found in Bara Gate waste effluents, which was in the range of 0.98–3.95 mg/L and the mean value for Zn was found as 1.86 mg/L. Although these concentrations are within the permissible range (5.0 mg/L) of NEQS but with the increasing demand of the increasing population, ultimately the Zn metal load may increase in future. Whatsoever, the greater concentration of Zn found in Muhammad Zai drain samples may be attributed to abundance of brick-making units in suburbs of the city, as well as to other mud/clay-made utensils because worn out tires are frequently used for baking these clay-made products, and Zn is an essential constituent of tires.

4. Conclusions

This study was aimed to evaluate the HMs level in industrial waste effluents. From the results, it was concluded that Shahi Khatta and Bara Gate wastewater effluents were highly contaminated with toxic metals such as Cd, Pb, Ag, Mn, and Fe and their concentrations were high from the limits of Pakistan NEQS, while Muhammad Zai drain effluents were found within NEQS limits. The Shahi Khatta and Bara Gate effluents are of much concern, as these effluents are used by the inhabitants of Peshawar for irrigating their fields and kitchen gardens. The HMs are potential threats to all kinds of life and through food chain eventually, it will reach to human body. There is need for stringent precautionary measures to not let these effluents without treatment to main streams. Detailed environmental impact assessment studies must be made mandatory prior to the installation of any new industry, small or large, to avoid contamination of HMs in irrigation channels. Further studies are needed to investigate the level of HMs in vegetables, fruits, and cereals of these areas. This will be helpful in avoiding secondary health problems due to toxic metals in the inhabitants of these areas.

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Supplementary

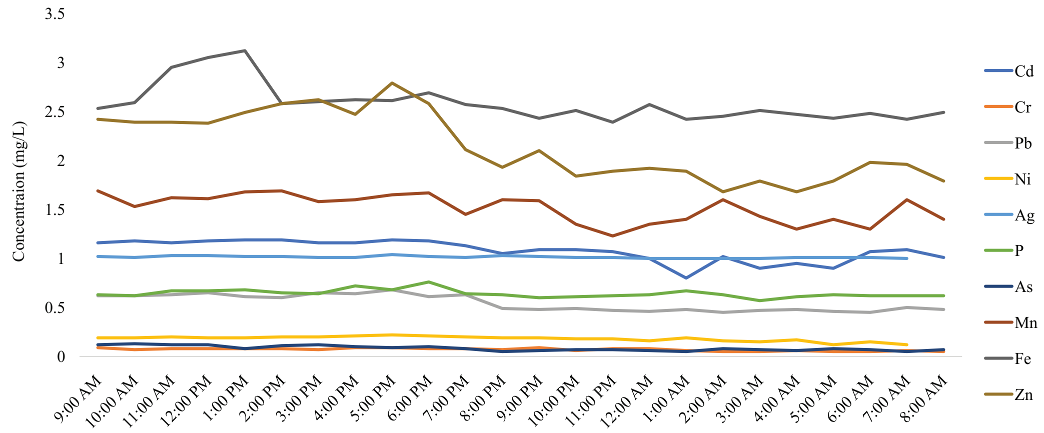

Fig. S1. Concentration of heavy metals in Shahi Khatta drain effluents.

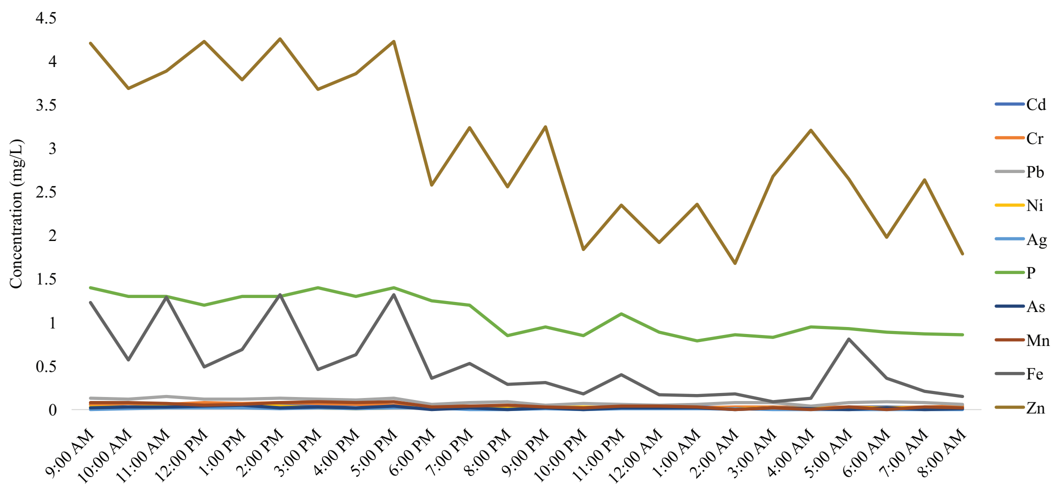

Fig. S2. Concentration of heavy metals in Muhammad Zai drain.

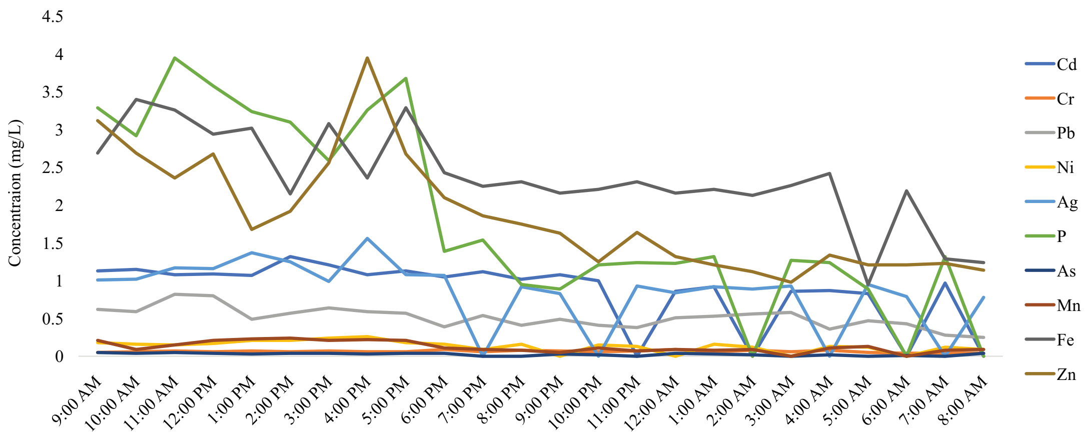

Fig. S3. Concentration of heavy metals in Bara Gate Drain.