Characterization, Distribution and Comparison of Selected Metals in Textile Effluents, Adjoining Soil and Groundwater

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Summary: This paper reports characterization and distribution, along with international comparison, of the concentration levels of twelve selected metals in effluents, adjoining soil and groundwater samples taken from three textile industries located in Hattar Industrial Estate, NWFP, Pakistan. Metal analysis in these media was done by FAAS System using automatic background compensation. The results show elevated levels of Cr, Pb, Ni, Co, Fe, Ca, Na, K and Zn in these media, following the order: soil > effluent > groundwater. Comparison with background and international data revealed that the textile effluents are contaminating the soil and groundwater. Cr and Pb were dominant toxic metals in soil samples having concentrations of 5.96 mg kg^{-1} and 4.46 mg kg^{-1}, respectively while other toxic metals such as Co, Cd, Zn, Ni, Mn and Fe, were found to be higher than background levels. Descriptive statistics, along with correlation coefficient and linear regression supported the fact that various elevated metal concentrations emerged from the textile industrial effluents ultimately leading to contamination of the soil and groundwater in their proximity thus adversely affecting the local environment.

Introduction

Industrialization, all over the world, is causing degradation of environmental quality, resulting in serious long-term adverse health effects [1]. The problem of environmental pollution arising from essential industrial growth is, in practical terms, the problem of disposal of industrial waste, whether solid, liquid or gaseous. These wastes have the potentiality of ultimately polluting soil and groundwater they come in contact with. Studies have shown that areas in close proximity of industrial activities are marked by contamination of soil, water and agricultural fields, downstream [2-3]. The effluent based soil and groundwater pollution aspects have thus remained the main focus point of several studies on the distribution of heavy toxic metals in effluents in relation to their impact on groundwater quality, depth of aquifer, type of soil and human activities in and around the target area. To this effect, relevant data are reported in literature for K, Na, Cd, Cu, Pd, Ni, and Zn [4-7]. An earlier research evidences that boosted up industrial production give rise to saturation levels of Cr, Cu, Zn, and Ni in the environment in areas close to industrial estates [8]. Specific studies on evaluating the toxicity caused by textile effluents rich in the toxic metals have also been carried out [9-10].

As in any developing country, the industrial growth in Pakistan has been currently boosted up to substantially enhance the economic growth without implementation of regulatory control measures for effluent quality. The Industrial Estate, Hattar, NWFP, (Figure 1) houses a large number of textile units wherefrom the effluents rich in organic and inorganic contents as well as heavy metals, have been found to result in toxic effects on nearby plants and vegetation

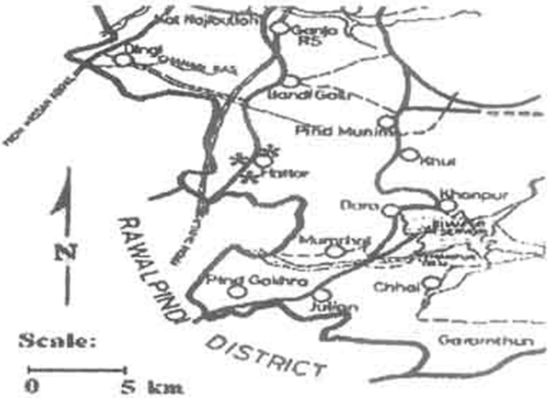

Fig. 1: Location map of the study area showing the sampling points (.) in Hattar Industrial Estate, NWFP.

[11-12]. The environmental contamination situation in the area is becoming more serious day by day. This situation demands a strict treatment program for the effluents from textile industry involving safe disposal of the effluents so that the soils are safeguarded

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against elevated levels of the toxic metals, as reported for other parts of the world [13-16]. It is high time that characterization and distribution of toxic metals in textile effluents be monitored to evolve data that might be used in futuristic effluent management and control studies, as reported earlier [17-20].

The present study was undertaken keeping in view the environmental significance of the potential influence of toxic textile effluents on nearby soil and water system. Metal characterization and distribution constitute important aspects of a study dealing with environmental degradation, usually evaluated through inter-correlation patterns existing between various metals in the effluents and soil (Na, K, Ca, Mg, Fe, Mn, Co, Ni, Pb, Cr, Cd, and Zn). It is anticipated that the study would provide the baseline for a workable policy to combat with effluents affected soil and would thus help to evolve a pollution abatement program on realistic grounds with flexibility of applica-

Data on metal distributions in the three media on the basis of mean metal concentrations in effluent samples show Na, Ca, Mg, K, and Fe as dominant metals, with highest mean concentration of Na, followed by Ca, Mg, K and Fe, at 606.5, 124.9, 33.81, 17.91 and 2.14 mg L^{-1}, respectively. The standard deviation (SD) values related to the distribution of these metals in the soil samples show a very high dispersion around the mean metal concentrations. The salient findings from these data on soil samples was relatively very high concentration of Cr, which exhibited about 34.0 mg kg^{-1} Cr in some soil samples, against an average level of 5.96 mg kg^{-1} as the mean value. The highest concentration of Cr found in groundwater samples along with other toxic

metals (Co, Cd, Ni, Pb, Zn) being used in these industries from underground reservoir stands at 0.94 mg L^{-1}, against 0.22 mg L^{-1} as the mean value for the groundwater samples and 0.097 mg L^{-1} as the background level calculated (n = 30).

Statistical correlation study of the data pertaining metal-to-metal relationships in the three media was conducted on mutually inclusive basis. The metal-to-metal correlation coefficient evaluation yielded r values > 0.322 or < -0.322 as significant at tions to futuristic studies on the trends of distribution of metal concentrations in effluents and soils so that safety considerations are incorporated in keeping with the internationally laid down safe standards for levels of toxic metals in the media [21-22].

Results and Discussion

The data pertaining to the distribution of selected metals in the effluent, soil and groundwater samples from three textile industries are reported in Table-1 as descriptive statistical parameters. In total, these data represent 90 samples pertaining to the three media for each industry.

$p < 0.001$, revealing that there was a significant correlation between Fe and Cr (r = 0.359), Fe and Ni (r = 0.430) and Ni and Co (r = 0.488) in the effluent samples as shown in Table-2. For the soil matrix, the correlation study brought out some positive correlations between pairs of metals (Table-2). The listed r-values bring out a strong relationship of Cr with Ni, at (r = 0.556). The Ni concentration related to Fe in the effluent samples and to Cr in the soil samples indicated highly dependent concentration levels of the metals in the two media. The third correlation aspect between metal pair in groundwater system

Table 1: Basic descriptive statistics of selected metals in effluent (mg L^{-1}), soil (mg kg^{-1}) and groundwater (mg L^{-1}) samples from three textile industries (n= 90).

Metals	Effluents					Soil					Groundwater				
	Min	Max	Mean	SD	Skew-ness	Min	Max	Mean	SD	Skew-ness	Min	Max	Mean	SD	Skew-ness
Na	71.00	3127	606.5	473.5	2.940	1116	37460	12069	14357	0.750	7.500	325.0	201.1	122.8	-0.640
K	2.200	62.80	17.91	12.18	1.580	0.260	1716	409.8	551.7	0.920	0.290	62.80	7.520	10.47	2.400
Ca	0.300	313.6	124.9	42.44	0.660	124.0	6120	1263	1096	1.960	17.80	103.2	67.15	20.48	-0.090
Mg	6.200	87.00	33.81	19.60	0.420	0.780	296.0	98.62	75.55	0.290	0.100	93.80	31.42	29.32	0.780
Fe	0.039	30.39	2.140	4.280	4.250	0.780	196.0	15.02	26.44	4.380	0.005	1.070	0.110	0.210	3.530
Mn	0.011	0.970	0.160	0.200	3.040	0.020	7.000	1.210	1.450	2.040	0.004	0.180	0.040	0.030	1.630
Cr	0.023	2.671	0.710	0.620	1.030	0.240	34.06	5.960	6.650	2.410	0.010	0.940	0.220	0.250	1.320
Co	0.046	1.703	0.460	0.410	1.440	0.100	18.40	2.750	3.200	2.850	0.001	0.465	0.080	0.080	2.550
Cd	0.004	0.181	0.040	0.030	1.710	0.020	1.400	0.170	0.190	3.840	0.001	0.210	0.020	0.040	3.920
Ni	0.013	2.482	0.260	0.400	4.320	0.020	18.40	1.510	3.000	4.470	0.009	0.585	0.080	0.100	3.270
Pb	0.013	2.340	0.280	0.320	3.800	0.020	23.02	4.460	5.420	1.580	0.001	2.340	0.260	0.330	3.570
Zn	0.014	2.482	0.260	0.420	3.810	0.020	49.64	2.610	6.030	5.840	0.007	1.340	0.180	0.260	2.520

shows significant relationship between Mg and Mn (r = 0.463), Cr and Mg (r = 0.392), Fe and K (r = 0.337) and Na and Mg (r = 0.327). An important cross-correlation (r = 0.442) also exists for effluent-soil system for Pb and Cd. The corresponding effluent-water relationship emerged as significantly positive, between Fe and Mg (r = 0.247), Cr and Ca (r = 0.260), Fe and Mn (r = 0.276) and Co and Fe (r = 0.229). A similar correlation study also conducted on metal-to-metal interdependence for the soil-water system.

The study based on metal-to-metal correlations was further substantiated by the linear regression relationships given in Table-2, which lists only significant linear regression equations in terms of pairs of metals for the three media. The metal-to-metal correlation studies could provide a meaningful interpretation of the data based on variation in entire samples of the three media. It was revealed by correlation and regression analyses that Cr, Fe, Pb and Cd are enriched in soil and groundwater samples by the industrial effluents.

Table 2: Significant correlation and linear regression analyses for effluent, soil and groundwater samples from three textile industries (n = 90).

Matrix	Regression Equation	Correlation (r)
Effluent	Zn = 4.564Cd + 0.092	0.313
	Cr = 0.052Fe + 0.603	0.359
	Ni = 0.040Fe + 0.176	0.430
	Pb = 0.243Co + 0.171	0.311
	Ni = 0.476Co + 0.045	0.488
Soil	Ca = 1.135K + 797.9	0.571
	Ni = 5.743Cd + 0.542	0.368
	Pb = 9.011Cd + 2.940	0.320
	Ni = 0.250Cr + 0.020	0.556
	Zn = 0.308Cr + 0.775	0.340
	Fe = 0.022K + 5.868	0.466
	Mg = 0.002Na + 69.14	0.464
Groundwater	Cr = 0.004K + 4.105	0.375
	Fe = 0.007K + 0.057	0.337
	Cr = 0.003Mg + 0.109	0.392
	Mg = 0.078Na + 15.74	0.327
	Mn = 0.005Mg + 0.025	0.463

Comparison is made between the mean metal levels in the soil (Table-3) and groundwater (Table-4) from textile industry in relation to the corresponding background concentration levels of the metals in samples taken from remote locations near the industrial units and various environmental regulatory agencies around the world.

From the results of mean metal concentration, it is evident that Na, Ca, Mg, K, and Fe emerge as dominant metals in the three media. The concentrations of these metals are highest in soil samples in agreement with a previous finding reported in literature [23-24]. The study reveals moderately high metal concentrations in the effluent samples and marginally low concentrations in the groundwater samples. The distribution, therefore, indicates a large flux of these metals accumulated in the soil in close vicinity to the industries. The SD values related to the distribution of these metals in the soil samples show a high dispersion around the mean metal concentrations, following, on the average, the order: soil > effluents > groundwater. Though empirical in nature, this relationship indicates the role of effluents towards enhanced metal accumulation in nearby soil systems. Therefore, the possible contribution of the effluents towards contamination of groundwater in the area cannot be ruled out. To support this observation, the mean metal concentrations in groundwater samples from textile industry were compared with those for background water taken from distant areas from the industry, indicating increased concentrations of toxic metals such as Cr Cd, Ni, Pb and Zn (Table-3)

The order of distribution of these metals in relation to in relevant effluent, soil and groundwater samples is worth consideration. For the effluent samples, the highest mean concentration was that of Na, followed by Ca, Mg, K and Fe. A small variation in the pattern of concentration distribution was observed in the case of soil samples where Na, Ca and Fe remained at their respective concentration ranking, while K and Mg exchanged their ranking positions with effluent samples. This observation could probably be explained on the basis of possible chemical exchange processes among cations, under given condition of pH and temperature [25]. To support this view point, the background concentration level of metals for virgin soil were analysed and compared with those in the soil samples understudy (Table-4). The comparison indicated that the soil in the adjoining area of the industries accumulated enhanced levels of toxic metal like Cr, Cd, Ni, Pb and Zn, which also manifested higher concentration levels in the groundwater samples. The study, therefore, confirms the view that the soils in proximity to the industries have accumulated toxic metals such as Cr, Co, Cd, Ni, Pb and Zn, with concentrations in the three media far exceeding the limits for their safe use laid down by the different international environmental agencies [21-22, 26].

Table-3: Comparison of metal levels (mg L^{-1}) in groundwater investigated in the present study with the background and international data

Metals	Hattar	Background	WHO	US-EPA	EU	Canada-EPA	UK	Russia	Japan	Pak.NEQ's
Na	201.1	12.42	200	20	150	-	150	-	200	-
K	7.520	2.270	10.0	-	12.0	12.0	10	-	-	-
Ca	67.15	16.60	75	-	-	-	-	-	-	-
Mg	31.42	5.690	50	-	-	-	-	-	-	-
Fe	0.110	0.030	0.3	0.3	0.2	0.3	0.2	0.3	0.3	8.0
Mn	0.040	0.020	0.1	0.05	0.05	0.05	0.05	0.5	0.01	1.5
Cr	0.220	0.097	0.05	0.1	0.05	0.05	0.05	0.05	0.05	1
Co	0.080	0.020	0.1	-	-	-	-	-	-	-
Cd	0.020	0.003	0.003	0.005	0.005	0.005	0.05	0.003	0.01	0.1
Ni	0.080	0.022	0.02	0.1	0.05	-	0.05	0.02	0.01	0.5
Pb	0.260	0.175	0.01	0.015	0.05	0.01	0.05	0.01	0.01	0.5
Zn	0.180	0.006	3.0	5.0	0.1	5.0	-	1.0	-	5.0
Ref.	Present study	Present study	22	21	26	26	26	26	26	26

Table-4: Comparison of metal levels (mg kg^{-1}) in soil investigated in the present study with the background and international data

Metals	Hattar	Background	WHO	Canada-EPA	EU	UK
Na	12069	568.0	-	-	-	-
K	409.8	12.00	-	-	-	-
Ca	1263	209.0	-	-	-	-
Mg	98.62	50.00	-	-	-	-
Fe	15.02	0.140	-	-	-	-
Mn	1.210	1.200	18	-	-	-
Cr	5.960	2.080	15	20	600	-
Co	2.750	0.320	5.0	10	-	-
Cd	0.170	0.060	0.4	0.5	3.0	1-3
Ni	1.510	0.244	20	25	-	30-75
Pb	4.460	1.520	20	20	500	50-300
Zn	2.610	0.400	60	60	-	150-300
Ref.	Present study	Present study	22	26	26	26

The evaluation of metal-to-metal correlation coefficient pertaining to the effluent data showed that the concentrations of Fe, Co, Cr and Ni mutually depend on each other, possibly because of the fact that they originate from a single source. For the soil matrix, the correlation study showed that K was significantly related to Ca, Fe, Cr, Cd, Ni, Pb and Zn (Table-2), supported by an earlier study [27]. However, no other metal showed such a strong correlation behavior, perhaps due to the fact that the K salts are used in these industries in large bulk during various chemical processes, thus overwhelmingly outweighing other metal salts towards saturation of the soil. In the case of soil samples, Cr was found to have a strong relationship with Ni. However, Ni related to Fe in the effluent samples, and Cr in the soil samples indicated a high concentration correlation with Cr in the two media. Another correlation aspect in groundwater system showed stronger relationship between Mg and Mn (r = 0.463), Cr and Mg (r = 0.392), Fe and K (r = 0.337 and Na and Mg (r = 0.327). The water medium, therefore, is influenced by the positive correlation between these metal pairs. A cross-correlation study between effluent and soil multiple-metal correlations showed that in the effluent-soil system Pb and Cd (r = 0.442) were strongly correlated. The corresponding effluent-water relationship emerged out to be signifycantly positive, for the following metal pairs: Fe and Mg (r = 0.247), Cr and Ca (r = 0.260), Fe and Mn (r = 0.276) and Co and Fe (r = 0.229). Despite the fact that these correlations were significantly strong, they indicated a positive interrelationship between effluent and groundwater metal concentrations, especially for Cr, Mg, Fe, and Co. Correlation study conducted for the soil-water system showed a strong positive correlation between various pairs of metals including Na, Mg, Fe, Cd, Pb and Zn. It may be anti-cipated that the soil system rich in these metals could substantially affect the groundwater concentration.

The above observation based on metal-to-metal correlations was further substantiated by the linear regression equations in terms of pairs of metals with respective concentrations in the three media. The regression equations (Table-2) support the correlation coefficient analysis earlier described and discussed in terms of an intimate concentration dependence of various pairs of metals, notably Ca-K, Cr-Mn, Pb-Cd, Zn-Ni, Pb-Cr, etc.

The average metal levels recorded for soil and groundwater during the present study were evaluated on a comparative basis as shown in Table-3 and 4, respectively. For the purpose, the present metal data of groundwater was compared with those reported by WHO, USEPA, EU, Canadian EPA, UK, Russia, Japan and national environment quality standards (NEQ's) of Pakistan. Except Mg and Zn, the data revealed 10-30 fold higher mean levels of selected metals compared with those internationally accepted values. In comparison with NEQ's, of Pakistan, which are among the highest in the world, the present values are within the acceptable limits. Similarly the soil metal levels were also compared with those reported by WHO, Canadian EPA, EU and UK (Table-4). The present metal levels are found to be within the acceptable limits.

Experimental

Study Area

The study area, Hattar (33° 51' 1N, 72° 51' 8E) housing the textile units, included in the present study, is located in the North West Frontier Province (NWFP) of Pakistan. Hattar is a mountainous range, with plains elevated to 500 m altitude and at a distance of some 55 km from federal capital, Islamabad and 145 km from provincial capital, Peshawar. A survey of hazardous waste producing industries in NWFP, lists 348 industrial units including textile [28]. Other industrial units adjoining the textile units include paper/pulp, paint/varnishes, rubber/plastics, oil/soap, chemicals and petroleum products. The effluents from these units are discharged independently but they are ultimately flushed out from a main drain that opens in adjoining land.

Sampling and Analysis

Following standard analytical procedures and sampling guidelines [23, 29-30], a total of 30 effluents and as many soil and groundwater samples were collected during September to December 2002 from three textile industries, namely, Sac Textiles, Unitech Textiles and DS Textiles. The effluent samples were collected in duly labeled strong polythene bottles (1L) from the main discharge point of the individual industries. The surface soil (1-5 cm) samples, considered to be affected by the effluents, were collected up to 50 m from the discharge point. Prior to sampling, the soil samples were cleaned manually for any leafy, dry foreign matter. A 250 g portion of the soil was collected in zip-mouthed polyethylene bag. A 25.0 g portion of a soil sample was exracted in 500 mL of distilled water and stirred mechanically on an electric shaker for 2 minutes and allowed to settle subsequently for 30 minutes [31-32]. The supernatant layer of the solublized metal matrix was separated by filtration and used for the direct estimation of heavy metals, using Flame AAS system (Shimadzu Model-AA 670). The effluents filtered through 0.5 μm cellulose filters were directly aspirated without the addition of any pH adjusters and stabilizers. Where required the sample solutions were diluted with distilled water appropriately in case if the concentration of a metal in the effluent was too high. In a similar fashion, background samples for groundwater and soils were collected and analyzed for comparison purpose. Standard calibration method was applied for quantification. STATISTICA software was used to compute the relevant statistical analysis of the data [33].

Reagents and Glassware

All chemicals and reagents used in the study were of analytical and spectroscopic grade (certified minimum 99.9 % purity), procured from E. Merck, Germany or BDH, England. Pyrex glassware was used for processing of samples, dilution and making up the volume, etc. Distilled water made in all-glass apparatus was used throughout the work. Standard optimum analytical conditions were maintained during the work, as recommended by the manufacturer to ensure optimal accuracy and precision. Inter-laboratory comparison of the furnished data was conducted at Nutrition Division, NIH, Islamabad, Pakistan. Standard reference material (SR-96 OL) was used periodically to have a check on the accuracy of the results and the precision of the instrument.

Conclusions

In conclusion the present study revealed that the textile effluents are posing a great threat by contaminating the adjacent soils and relevant water bodies. The correlation and regression studies showed that the toxic metals like Co, Cd, Pb, Zn, with some other metals such as, Cr, Mn, Ni, Fe, Ca, Na, K and Mg, find common origin in all the three media, manifesting that these metals originate from textile effluents. Comparison of the background levels of soil and groundwater samples with the textile industry samples revealed that enhanced levels of Cr, Cd, Ni and Pb are posing a great threat to the health of the people inhabiting the area. International comparison of the data manifested a gross pollution of groundwater by the industrial effluents. There is a dire need to implement strict regulatory procedures for the safe discharge of effluents from the industries. Towards this effect, the relevant authorities must ensure recycling of effluents along with mandatory quality assurance requirements. It is high time that the issue of environmental contamination in the area adjoining the textile units be kept under constant monitoring and surveillance as proposed by world health bodies [21-22].

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