Distribution of Heavy Toxic Metals in Industrial Effluents and Relevant Soils from Selected Oil and Ghee Industries in Hattar

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Summary: Industrial effluents and relevant soils collected from five oil and ghee industries, Hattar Industrial Estate, NWFP, Pakistan, were analyzed and examined for distribution of heavy toxic metals, Cr, Fe, Cd, Ni, Pb and Zn for their probable impact on relevant soils. On the average basis, elevated levels were observed for Ni, Zn and Cr in the effluents with concentrations 0.327, 0.349 and 0.432 mg L^{-1}, respectively. All metals exhibited randomized variation in their levels, evidenced by a large scatter around the mean, and with widely varying kurtosis and skewness factors. The observed average distribution pattern for these metals followed the increasing concentration order: Cd < Fe < Pb < Ni < Zn < Cr. The temporal study on the effluents evidenced high concentration levels of Cr, Cd and Pb in the afternoon, for all industries with the exception of just one industry. The soil samples from the area adjoining the discharge point of these industries showed the maximum mean concentration of 1.082 mg kg^{-1} (Fe) and 0.370 mg kg^{-1} (Cr) with a non-symmetrical distribution pattern. The background concentration of Fe and Cr in the soil samples taken 500 m away from the main effluent drain, were found to have concentrations of 0.065 and 0.093 mg kg^{-1}. The observed order of increasing metal concentration in soil samples followed the pattern: Cd < Zn < Pb < Ni < Cr < Fe. Significant correlation was observed between Pb-Ni (r = 0.299) in the effluent matrix and Ni-Zn (r = 0.467) in the soil matrix. The statistical one-tail t-test revealed the same metal origin for effluent and soil samples.

Introduction

The major factors threatening the quality of the hydrosphere and biosphere in the world are rapid population growth, urbanization, expansion of rural settlements, industrial activity, intensively irrigated agriculture, pesticide consumption and continuous dumping of hazardous waste [1]. The demand for metals and chemicals continues to grow with the growth of our industrial society and ultimately the discharge of these substances poses many harmful consequences. Some of the toxic substances cause different acute and chronic diseases such as skin burns, rashes, bone abnormalities, lungs and digestive system disorderness [2-6].

Consequently the assessment of wastewater or effluent discharges remains the main focus of several studies towards reduction of specific pollutants or hazardous substances within the framework of their emission policies recognized worldwide [7]. With known limitations of an assessment program for the pollutants entering the environment, it is understood that the growing burden of heavy metals and effluents in the soil and water and its implication towards sustaining the agrifood system has become a matter of immediate concern [8, 9].

In Pakistan, as elsewhere in other developing countries, the issues related to unregulated discharge of industrial effluents has emerged as a critical environmental problem, especially from the view-point of health hazards associated with the dispersion of heavy toxic metals into water and soils. Some earlier work has evidenced that industrial effluents are deteriorating the soil quality towards crop production [10, 11]. Another study on interrelation-ship between industrial wastewater and soil reported the potential toxicity threat to the environment [12]. Increased levels of heavy metals like Pd, Cr, Cd, Ni, Fe, and Zn were assessed for effluents and soils of textile and metal finishing industries [13-15]. The currently boosted up produc-tion in metallurgical units has given rise to increased levels of Cu, Zn, and Ni in the environment in areas close to industrial estates [16]. Levels of Cr, Fe, Pb and Cd in industrial wastes and soils are also evaluated in other parts of the world in order to ascertain the quality parameters for different environ-mental samples as per require-ment laid down by WHO [17, 18].

Keeping in view the environmental signifi-cance of the potential influence of the industrial

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effluents on the nearby soils, the present investigation was undertaken to assess, in first place, the current levels of heavy toxic metals in industrial effluents coming out of Hattar Industrial Estate and then to examine their possible impact on relevant soils. It is anticipated that this study would provide the baseline data for the local environmentalist to evolve agricultural related pollution abatement program and could motivate some realistic futuristic studies on the trends of the metal concentration distribution in effluents and soils as a function of distance from the main effluent drain. The metals included in this study are: Cr, Fe, Cd, Ni, Pb and Zn

Results and Discussion

The levels of selected metals and the distribution parameters related to the relevant effluent and soil samples are given in Tables 1 through 4. All concentrations are averaged over triplicate samples, both for effluents and soils. Table 5 provides the correlation coefficient matrix for the pairs of metals in corresponding effluent and soil samples, while the t-Test results on the comparison of the averages for the two media are given in Tables 6 and 7.

An examination of Table 1 shows that the metal distribution in the effluent samples is both divergent and specific for various metals. In the case of effluents, Cd showed the minimum concentration of 0.017 mg L^{-1} and the Cr, a maximum concentration of 0.432 mg L^{-1} on average basis, indicating Cr as the most dominant metal in the effluents. Zinc and Ni followed Cr with concentration of 0.349 and 0.327 mg L^{-1} respectively; the remaining metals, however, ranged between 0.2-0.3 mg L^{-1}. The data indicated largest dispersion in the distribution of Zn, followed by that of Ni, with ± 0.555 and ± 0.564 as SD in mg L^{-1}, respectively (Table 3). The metal distribution in effluent samples did not follow normal distribution, as evidenced by widely varying kurtosis and skewness factors. The results thus indicated that the distribution of Zn and Ni in effluents is a random phenomenon while other metals, such as Cr and Pb stood at a comparable SD level. This could be attributed to the individual batch processes underta-

Table-1: Levels ($\bar{X}$, mg/L) of selected metals in various effluent samples from oil and ghee industries, Hattar Industrial Estate, NWFP, Pakistan.

Sr.#	Location	Industry Name	Sample Code	Metal Concentration					
				Cr	Fe	Cd	Ni	Pb	Zn
1	Plot # 44	Hafeez Iqbal Oil & Ghee Mills Ltd	1ES1-1	0.383	0.059	BDL*	0.055	0.026	3.014
2	Phase 1&2		1ES1-2	0.391	0.153	0.003	0.034	0.167	0.392
3			1ES1-3	0.557	0.087	BDL	0.034	0.051	0.426
4			1ES1-4	0.474	0.189	0.005	0.061	0.101	0.640
5			1ES1-5	0.656	0.434	0.009	0.431	0.342	0.432
6			1ES1-6	0.334	0.082	0.002	0.043	0.242	0.328
7	Plot # 63/1	Pan Asia Foods Ltd	2ES1-1	0.798	0.097	0.031	0.089	0.459	0.441
8	Phase 1&2		2ES1-2	0.568	0.019	0.022	0.150	0.381	0.140
9			2ES1-3	0.483	0.194	0.021	0.101	0.344	0.553
10			2ES1-4	0.559	0.144	0.013	0.159	0.420	0.658
11			2ES1-5	0.504	0.101	0.020	0.159	0.411	0.811
12			2ES1-6	0.486	0.124	0.020	0.146	0.351	0.642
13	Plot # 2B	Waheed Hafeez Oil & Ghee Mills Ltd	3ES1-1	0.35	0.136	0.016	0.09	0.257	0.116
14	Phase 1&2		3ES1-2	0.550	0.167	0.004	0.086	0.299	0.023
15			3ES1-3	0.386	0.121	0.005	0.155	0.346	0.038
16			3ES1-4	0.665	1.174	0.016	0.146	0.559	0.348
17			3ES1-5	0.530	0.182	0.069	0.161	0.337	0.039
18			3ES1-6	0.464	0.153	0.031	0.213	0.297	0.183
19	Plot # 2/2	Chiniot Enterprises	4ES1-1	0.203	0.024	0.008	0.099	0.299	0.009
20	Phase 1&2		4ES1-2	0.138	0.078	0.005	0.096	0.358	0.006
21			4ES1-3	0.492	0.036	0.008	0.083	0.274	0.075
22			4ES1-4	0.151	0.199	0.005	2.381	0.742	0.047
23			4ES1-5	0.411	0.356	0.005	0.684	0.204	0.048
24			4ES1-6	0.381	0.273	0.007	0.093	0.283	0.064
25	Plot # 62	B & B Oil Mills Ltd	5ES1-1	0.504	0.316	0.018	0.061	0.253	0.120
26	Phase 1&2		5ES1-2	0.230	0.251	0.027	0.091	0.208	0.165
27			5ES1-3	0.371	0.323	0.034	1.212	0.245	0.136
28			5ES1-4	0.440	0.413	0.033	2.000	0.162	0.076
29			5ES1-5	0.237	0.966	0.039	0.543	0.151	0.092
30			5ES1-6	0.275	0.385	0.026	0.142	0.251	0.421

*BDL = Below detection limit

Table-2: Levels ($\bar{X}$, mg/kg) of selected metals in various soil samples of oil and ghee Industries, Hattar Industrial Estate, NWFP, Pakistan

Sr.#	Location	Sampling Industry	Sample Code	Metal Concentration Cr	Fe	Cd	Ni	Pb	Zn
1	Plot # 44	Hafeez Iqbal Oil & Ghee Mills Ltd	1SS1-1	0.263	1.642	BDL*	0.041	0.03	0.019
2	Phase 1&2		1SS1-2	0.292	1.521	0.005	0.128	0.128	0.023
3			1SS2-1	0.5	5.11	0.011	0.039	0.05	0.055
4			1SS2-2	0.485	4.831	0.008	0.063	0.093	0.046
5			1SS3-1	0.446	0.091	0.001	0.061	0.041	0.019
6			1SS3-2	0.394	0.153	0.011	0.158	0.118	0.047
7	Plot # 63/1	Pan Asia Foods Ltd	2SS1-1	0.281	0.28	0.018	0.236	0.274	0.052
8	Phase 1&2		2SS1-2	0.293	0.371	0.015	0.173	0.246	0.056
9			2SS2-1	0.156	0.067	0.019	0.223	0.014	0.016
10			2SS2-2	0.185	0.258	0.013	0.173	0.087	0.029
11			2SS3-1	0.468	0.953	0.017	0.269	0.218	0.045
12			2SS3-2	0.49	0.882	0.004	0.183	0.283	0.061
13	Plot # 2B	Waheed Hafeez Oil & Ghee Mills Ltd	3SS1-1	0.147	0.33	0.005	0.196	0.308	0.065
14	Phase 1&2		3SS1-2	0.202	0.361	0.009	0.082	0.217	0.048
15			3SS2-1	0.183	2.728	0.006	0.241	0.286	0.077
16			3SS2-2	0.212	2.742	0.009	0.216	0.243	0.081
17			3SS3-1	0.021	0.189	0.002	0.261	0.329	0.052
18			3SS3-2	0.137	0.298	0.007	0.283	0.255	0.048
19	Plot # 2/2	Chiniot Enterprises	4SS1-1	0.381	0.953	0.024	0.235	0.02	0.091
20	Phase 1&2		4SS1-2	0.269	0.842	0.135	0.218	0.056	0.063
21			4SS2-1	0.709	0.578	0.032	0.353	0.021	0.075
22			4SS2-2	0.696	0.564	0.012	0.294	0.159	0.067
23			4SS3-1	0.372	1.066	0.03	0.262	0.082	0.077
24			4SS3-2	0.292	1.021	0.011	0.244	0.101	0.086
25	Plot # 62	B & B Oil Mills Ltd	5SS1-1	0.431	0.054	0.019	0.037	0.262	0.053
26	Phase 1&2		5SS1-2	0.395	0.138	0.015	0.133	0.167	0.029
27			5SS2-1	0.574	0.159	0.038	0.153	0.329	0.064
28			5SS2-2	0.587	0.244	0.012	0.213	0.281	0.059
29			5SS3-1	0.612	2.028	0.032	0.09	0.273	0.058
30			5SS3-2	0.616	1.992	0.004	0.148	0.108	0.074

*BDL = Below detection limit

Table-3: Some statistical distribution parameters for selected heavy metals in effluents (n=30)

Parameter	Cr	Fe	Cd	Ni	Pb	Zn
Minimum	0.138	0.019	0.000	0.034	0.026	0.006
Maximum	0.798	1.174	0.069	2.381	0.742	3.014
Mean	0.432	0.241	0.017	0.327	0.294	0.349
Median	0.452	0.160	0.015	0.122	0.290	0.153
Std. Deviation	0.154	0.254	0.015	0.564	0.144	0.555
Std. Error	0.028	0.046	0.003	0.103	0.026	0.101
Kurtosis	0.080	7.260	3.514	7.752	2.373	19.343
Skewness	0.014	2.576	1.542	2.853	0.847	4.059

Table-4: Some statistical distribution parameters for selected heavy metals in soils (n=30)

Parameter	Cr	Fe	Cd	Ni	Pb	Zn
Minimum	0.021	0.054	0.000	0.037	0.014	0.016
Maximum	0.709	5.110	0.135	0.353	0.329	0.091
Mean	0.370	1.082	0.017	0.180	0.169	0.055
Median	0.377	0.571	0.012	0.190	0.163	0.056
Std. Deviation	0.180	1.304	0.024	0.085	0.106	0.020
Std. Error	0.033	0.238	0.004	0.015	0.019	0.004
Kurtosis	-0.771	3.791	20.183	-0.730	-1.546	-0.503
Skewness	0.175	1.984	4.181	-0.197	-0.021	-0.314

ken in the industries dealing with the former metals and a continuous processing involving the latter. The observed average distribution pattern for the metals was found to follow the increasing order: Cd < Fe < Pb < Ni < Zn < Cr. This indicated that Cr was present in the effluents as a dominant metal. This result is obviously not indicative of the source of the metal in oil and ghee industries, as Cr is not commonly

involved in the chemical processing carried out in these industries. In fact, the effluents from most chemical industries are carried from upstream to the downstream drain point, which after admixing are discharged into the grand main drain, wherefrom all the samples for the present study were obtained. For the case of Cd, the present low levels could be attributed to the residual levels of the metal in a large flux of industrial effluents for other units mixed together towards the main drain.

The data on soil samples (Table 2) also reflected a similar metal distribution behavior, with Fe having maximum mean concentration of 1.082 mg kg^{-1}, followed by 0.370 mg kg^{-1} for Cr; against the background concentration of 0.065 and 0.093 mg kg^{-1} determined independently during the present study, respectively while rest of the metals were found to have far lower levels. These values suggested that the local soil adjoining the industrial estate contained elevated levels of both Fe and Cr. This again could be attributed to metal contamination arising from industrial effluents discharged collectively from the adjoining metallurgical, chemical and tannery industries that dumped their effluents into the open land in the adjoining areas. As before, no normal distribution of metals in soil was encountered in this case, evidenced by large kurtosis and skewness factors (Table 4). The observed order of increasing metal concentration in the soil followed the pattern: Cd < Zn < Pb < Ni < Cr < Fe. Here, in this case, both Cr and Fe emerged as the dominant metals in soil of the area adjoining the industrial discharge points. The mean metal levels in the soil samples from adjoining areas extending to 50 m away from the industries were found to be far above the normal background levels of the metals in soils from locations unaffected by the effluents, thus going up by a factor of 5 to 20-fold in many cases.

An important aspect of the present study was to follow the selected metal concentration on temporal basis. For this purpose a time schedule was defined for the sampling initiated in the morning at 9:00 am and running through 12:00 midnight with three hour interval in between. An examination of Table 1 reveals that for these industries, the levels of metals build up in the morning hours where the normal working shift starting in the morning, as the case with Pan Asia Foods Ltd showing highest levels of Cr, Cd and Pb encountered in the morning with concentrations 0.798, 0.031 and 0.459 mg L^{-1} respectively. In the case of other industries, the overwhelming majority exhibited concentrations of the selected metals in the afternoon as typically shown by Hafeez Iqbal oil & Ghee Mills Ltd, Waheed Hafeez Oil & Ghee Mills Ltd., Chiniot Enterprises and B & B Oil Mills Ltd.

The statistical correlation coefficient data were obtained for various metal pairs in the effluent and soil samples at $p < 0.05$ (Table 5). Some significant correlations ($r > 0.215$) were observed in the effluent matrix for Ni-Pb ($r = 0.299$) and Fe-Cd ($r = 0.253$), while few negative correlations were also observed, as for Pb-Zn ($r = -0.308$), Cr-Ni ($r = -0.276$) and Cd- Zn ($r = -0.225$). This furnished the information that the metal levels in the effluents were randomly distributed and they were not correlated together viably. In the case of soil samples, the correlation coefficient matrix (Table 5) evidenced strong correlation between Ni-Zn ($r = 0.467$), followed by a significant correlation between Cr-Zn ($r = 0.228$), while an inverse significant correlation was observed for Fe-Ni ($r = -0.340$). The rest of the correlations were too insignificant to warrant any stronger inter-relationship between the metals.

The objective behind the correlation study between the effluent (e) and soil (s) was to find out possible common source of the metals in the two media (Table 5). The strong correlations were observed for Cd(e)-Zn(s) ($r = 0.497$) and Cd(e)-Cr(s) ($r = 0.423$). Significant correlations for Cd($r = 0.253$) and Fe($r= 0.216$) in the two media evidenced some common source of these metals in effluents and soils Some other metal pairs exhibited significant correlations in the two media: these include Zn(s)-Fe(e), Zn(s)-Ni(e) and Zn(s)-Pb(e) at $r = 0.339$, $r = 0.232$ and $r = 0.244$, respectively. Similarly Cd(e)-Ni(s) were correlated at $r = 0.395$, followed by Fe(e)-Pd(s) ($r = 0.291$) and Zn(e)-Fe(s) ($r = 0.256$). Few metal pairs also exhibited inverse correlation in the two media, e.g., Zn(e)-Ni(s) ($r = -0.481$), Cd(e)-Pb(s) ($r = -0.325$) and Zn(e)-Zn(s) ($r = -0.320$). Thus for the soils, Cd, Fe, Cr and Zn emerged to play a significant role towards contamination by the relevant effluents, with a common source.

The origin of the selected trace metals in effluents and soil samples was checked through one tail t- Test by comparing the averages of the sets of metal data for the two media. The comparison was made between the metal distributions in the effluents

Table-5: Metal to metal correlation coefficient matrix for various samples of effluents (e) and soils (s)

Metals	Cr (s)	Fe (s)	Cd (s)	Ni (s)	Pb (s)	Zn (s)	Cr(e)	Fe(e)	Cd(e)	Ni(e)	Pb(e)
Fe (s)	0.165										
Cd (s)	0.072	-0.097									
Ni (s)	-0.073	-0.340	0.171								
Pb (s)	-0.144	-0.205	-0.188	0.095							
Zn (s)	0.228	0.173	0.196	0.467	0.194						
Cr(e)	-0.252	0.110	0.126	0.114	-0.229	0.186					
Fe(e)	-0.029	0.216	-0.120	0.099	0.291	0.339	0.070				
Cd(e)	0.423	0.107	0.253	0.395	-0.325	0.497	0.139	0.253			
Ni(e)	0.037	-0.072	-0.011	0.145	-0.143	0.232	-0.276	0.195	0.134		
Pb(e)	0.105	0.116	0.114	0.024	-0.109	0.244	0.112	0.102	0.084	0.299	
Zn(e)	-0.112	0.256	-0.186	-0.481	-0.259	-0.320	0.126	-0.144	-0.225	-0.201	-0.308

Values of $r > + 0.215$ or $r < - 0.215$ are significant at $p < 0.05$

Table 6: t-Test* for the comparison of average metal levels in effluents and soil samples

Metals	t-Stat (0 m soil)	t-Stat (25 m soil)	t-Stat (50 m soil)
Cr	2.664	0.175	0.866
Fe	3.155	3.591	4.739
Cd	0.912	0.033	0.665
Ni	0.991	0.590	0.609
Pb	2.480	2.381	1.908
Zn	1.693	1.566	1.546

*t-Stat against 1.686 t-critical one-tail value

Table 7: Typical result of t-Test for Ni at 0 m soil; Two-Sample Assuming Equal Variances

	Ni (e)	Ni (s)
Mean	0.327	0.148
Variance	0.318	0.006
Observations	30	10
Pooled Variance	0.244	
Hypothesized Mean Difference	0	
df	38	
t Stat	0.991	
P(T<=t) one-tail	0.164	
t Critical one-tail	1.686	

versus the metal concentration in soil in aqueous phase, expressed in mg L^{-1} of the leached soil solutions. The t values obtained for various metals are listed in Table 6 against the critical t-value, rated at 1.686 for the given degree of freedom (f =38). The data indicated that both effluent and the soil samples on the whole had a common metal origin, especially Ni and Cd at 0m soil/effluent and for Cr, Cd, Ni and Zn at 25m and 50m soil/effluent. The one-tail t-test for Ni was a typical case studied (Table 7), exhibited a common origin of the metals in effluent and soil samples thereby showing that Ni from these industries was contaminating both effluents and soils alike.

Experimental

Following the standard sampling guidelines and analytical procedures [19, 20], a total of 30 effluent and as many soil samples were collected from five ghee and oil industries (Figure 1) with the following order: Hafeez Iqbal Oil & Ghee Mills Ltd (Industry 1), Pan Asia Foods Ltd (Industry 2), Waheed Hafeez Oil & Ghee Mills Ltd (Industry 3), Chiniot Enterprises (Industry 4) and B & B Oil Mills Ltd (Industry 5). The effluent sample codes appended to these industries are listed in Table 1, with following significance: 1ES1-1 means industry 1, effluent sample (ES), outlet number (1), sampling time running from 1 to 6, from 9:00 am to 12:00 midnight with 3-hour interval in between. The effluent samples were collected in 1L strong polythene bottles from the collective discharge point of the relevant industries. For soil samples, a similar coding was used. For example 1SS1-1 signifies industry 1, soil sample (SS), soil sampling site distance from the outlet (1) and the sample number (1). The top surface soil (1-5 cm deep) samples were collected in proximity (0-50 m) from the drainage point. About 250 g portions of the soil were collected in strong zip-mouthed polyethylene bags. These samples were cleaned manually for any leafy and/or dry foreign matter. A portion of 25.0 g of a soil sample was dissolved in 500 mL of distilled water and stirred mechanically on a electric shaker for 2 minutes and allowed to settle for 30 minutes. After getting the solubilized matrix, the supernatant layer of the soil solution was separated through filtration and used for the direct estimation of heavy metals using Shimadzu Atomic Absorption Spectrophotometer, Model-AA 670. The effluents were filtered using cellulose filter paper of 0.5 μm porosity and the filtrates were directly aspirated. Where required these samples were diluted with distilled water appropriately in case the concentration of a metal in the effluent was too high. Standard calibration method was applied for quantification. As many as 30 underground water samples were also analyzed for Ni by the AAS method.

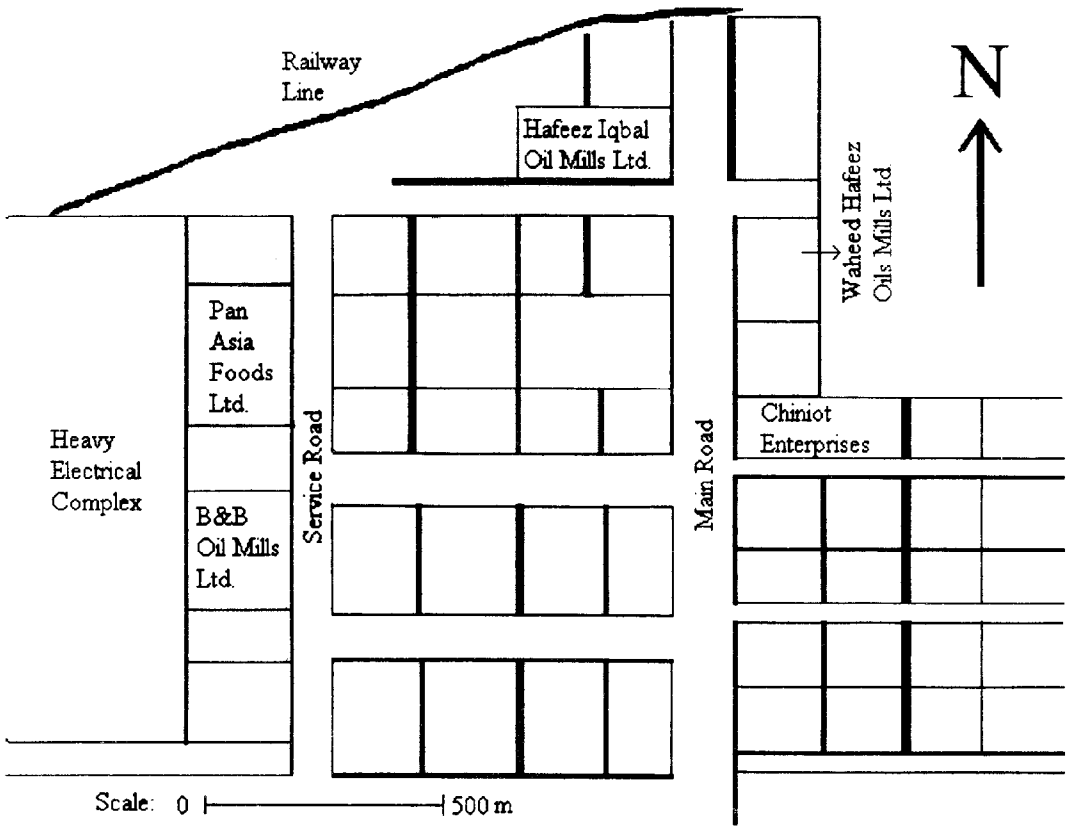

Fig.1: Location site of the oil and ghee industries, Hattar Industrial Estate.

All chemicals and reagents used in the study were of analytical and spectroscopic grade (certified minimum 99.9 % purity), procured from E.Merk, 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. Standard reference material (SR-90) was used periodically to have a check on the accuracy of the results and the precision of the instrument.

Conclusions

The present investigation showed a direct contamination of the soils by industrial effluents of the oil and ghee industries. On the average Ni, Cr and Fe emerged as dominant contaminants in the relevant industrial effluents. Although Cr and Fe compounds are not used directly in the manufacture of oil and vegetable ghee, it is believed that they find their way in to the effluents from other adjoining industries that truncate the common washouts at the main drain housed close to the oil and ghee industries. The observed elevated concentrations of Ni in both effluent and soil samples far exceed the upper allowed safe limit laid down for the metals by WHO at 0.1 mg L^{-1} (5). The study therefore showed that this limit is being seriously violated in the case of local industrial effluents. For ground water, the mean concentration of Ni was found to be 0.191 mg L^{-1}, which also exceeds the upper allowed limit. This necessitates proper measures to be adopted to recycle the effluents before they are discharged from the industries so that the elevated metal levels do not directly affect the vegetation and plantation in the area, and thus the human health is safeguarded against the ill effects of these toxic metals. The

present situation also calls for implementation of proper legislation to regulate and guard the discharge of the industrial effluents.

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