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Seasonal Variation and Seepage Identification of Chromium from Tanneries Effluent into Groundwater in District Kasur Pakistan

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Abstract: Groundwater in the district Kasur, Pakistan has become highly contaminated due to the percolation of tanneries effluent into the subsurface. Chromium was investigated for its concentrations in the wastewater, soil and groundwater in the affected area. In this regard initially groundwater samples were collected from existing sources randomly. 2 soil bores were conducted to find chromium concentration in soil by using Aqua regia digestion. In order to identify the presence of chromium in the groundwater from the tanneries effluent, 8 monitoring wells were bored for periodic groundwater sampling. Wastewater samples analysis for chromium was used to correlate its seepage with existence in the groundwater. Seasonal variation of chromium in the wastewaters was also investigated.

Key words: Groundwater contamination · Chromium · Tanneries · Monitoring wells · Wastewater analysis

INTRODUCTION

Due to improper industrial waste management the quality of groundwater resources has deteriorated to such an extent that it has become havoc for the human health in the developing countries. Pakistan, on its way to progress, is also facing severe environmental hazards, mainly caused by the untreated effluent from the industries.

This research document is based on the initial investigations carried out in the region dominated by the tanning industry situated in the district Kasur, Pakistan. Tanning industry is recognized as a serious environmental hazard throughout the world and in Pakistan it is causing severe environmental problems [1, 2].

In the district Kasur, Pakistan, there are about 230 tanneries out of the total 650 in the country [3]. According to United Nations Industrial Development Organization (UNIDO), at present the tanneries in Kasur discharge around 13,000 cubic meters per day of heavily polluted tannery wastewater [3]. Due to the lack of any proper industrial zone in the district Kasur, the tannery units are increasing in number and penetrating into the residential areas thus becoming a more exposed threat to the inhabitants of the entire region. Atleast 50,000 workers and inhabitants, living in and around the polluted areas are at a direct risk of vital and chronic diseases related to drinking water from groundwater resources and air which have become polluted due to tanneries.

Chrome tanning method is the most widely used process in tannery units in Pakistan however vegetable method is considered to be more environmental friendly [4]. Both methods are sometimes used in combination. Chrome tanning is currently preferred technique as it is more rapid process of leather production [4]. Chromium is considered to be major contaminant in tannery industry [5]. In the southwestern part of Dhaka, Bangladesh, where tanneries are located, surface accumulation of trivalent chromium reaching as high as 28,000 mg/kg have been encountered at a distance of 1 km from the waste lagoons [6]. Large variation in chromium concentration in the soil was observed in the leather tannery district Italy, ranging from 42.9 to 10,594 mg/kg having mean of 610.54 mg/kg [5]. In district Kasur, maximum concentration of chromium in the effluent is found to be 3,956 mg/L, high enough to pose serious pollution stress to the environment in the proximity of the tanneries [1]. In district Kasur, level of Chromium (Cr), Iron (Fe) and Lead (Pb) in the groundwater samples, was found to be many times higher than the recommended limit for water quality by WHO, US-EPA, EU and Japan. The elevated levels of chromium (Cr),

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recorded as 21-42 fold higher as compared with the recommended values, were believed to have origin from tannery industries [7, 8]. Environmental Protection Department Punjab also conducted research showing higher concentrations of chromium (Cr) in groundwater samples taken from different existing sources including tube wells and hand pumps. It was observed that concentration of chromium (Cr) ranged between 0.02 to 0.2 mg/L [3, 9].

This research document will encompass the wastewater analysis results, carried in the research area in the district Kasur and groundwater samples results which were collected after boring and soil sampling from peripheral area of the effluent carrying drains. It was aimed to correlate the groundwater contamination with the untreated tannery effluent.

MATERIALS AND METHODS

Study Area: The research work was conducted in the surrounding area of the tanneries units located in the district Kasur, in the province of Punjab, Pakistan. It is adjacent to the Indian border, about 55 kilometers on south eastern side from Lahore, capital of Punjab. The area selected for research purpose constitutes of about 230 tanneries, a biological wastewater treatment plant and 4 drains in total. There are two drains, which carry wastewater from the tanneries area to the treatment plant and are named as *Drain 1* and *Drain 2* in this paper. At the time of sampling *Drain 1* was flowing while *Drain 2* was not in flow. *Drain 3* carries the treated effluent from the treatment plant and it also contains the diverted untreated effluent from the tanneries, in order to compensate the over flow into the treatment plant. The fourth drain is *Drain Rohi* named as *Drain 4*, which carries municipal and tanneries effluent both and it passes through the center of the city. There is a junction of *Drain 4* and *Drain 3* at the Debal Pur Road from where onwards the wastewater is carried through underground sewer for final disposal into another drain which is about 7 kilometers distance from the treatment plant.

Sampling and Methodology: Based on the initial results of the 22 groundwater samples analysis (Figure 1), further methodology was planed. Total Chromium in 20 samples was below detection limit but in the two samples in which it was detected, the concentration was extremely alarming i.e. 10 and 90 mg/L, far more than the permissible limit of 0.05 mg/L for the drinking water [10]. Soil was explored by conducting 2 soil bores in the area near the junction of *Drain 4* from city and *Drain 3*, which is coming from the treatment plant, at Debal Pur Road. The locations of the two soil bores are shown in the Figure 1. The soil bore 1, which was up to the depth of 18.29 meters, 13 samples were collected at the every depth of 1.52 meters (Table 1). For the soil bore 2, which was bored up to the depth of 24.38 meters, 17 soil samples were collected at the every depth of 1.52 meters (Table 2).

From all the four drains in the area, wastewater samples were collected twice a year, firstly in June and second time in January in order to find out the seasonal variation by observing peak and minimum production variation trends. The samples were examined for basic chemical parameters and total chromium concentrations in the wastewaters.

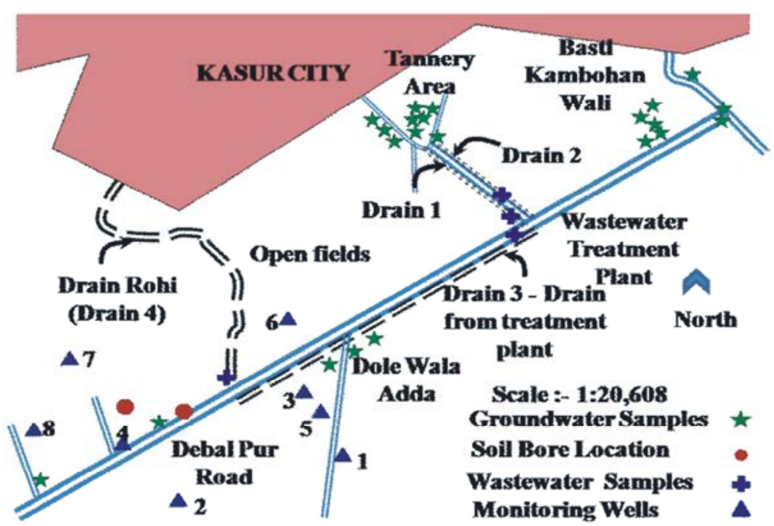

Fig. 1: The study area in district Kasur with sampling locations

Table 1: Hexavalent Chromium and Total Chromium (mg/kg) retained in soil for Soil Bore 1

Sample	Depth (m)	Cr (VI) mg/kg	Total Cr mg/kg	Soil Type: Sand	Silt	Clay	Texture	Field Remarks
SC-1	0	3.60	12.72	61	31	8	Sandy Loamy	
SC-2	3.05	4.66	42.40	21	57	22	Silt Loam	
SC-3	4.57	5.72	6.36	98	0	2	Sand	
SC-4	6.10	6.15	6.36	99	0	1	Sand	
SC-5	7.62	5.09	6.36	99	0	1	Sand	
SC-6	8.53	6.15	48.76	94	6	0	Sand	Changed soil colour
SC-7	9.14	7.84	8.48	98	2	0	Sand	
SC-8	10.67	5.94	6.36	98	2	0	Sand	
SC-9	11.58	8.06	10.60	98	2	0	Sand	Water Table
SC-10	13.72	7.84	10.60	99	1	0	Sand	
SC-11	15.24	7.63	8.48	98	2	0	Sand	
SC-12	16.76	3.82	8.48	97	3	0	Sand	
SC-13	18.29	4.66	6.36	97	3	0	Sand	

Table 2: Hexavalent Chromium and Total Chromium (mg/kg) retained in soil for Soil Bore 2

Sample	Depth (m)	Cr (VI) mg/kg	Total Cr mg/kg	Soil Type: Sand	Silt	Clay	Texture	Field Remarks
SC-1	0	2.54	10.60	38	52	10	Silty Loam	
SC-2	1.52	2.97	10.60	65	30	5	Sandy Loam	
SC-3	3.05	3.82	25.44	18	71	11	Silty Loam	
SC-4	4.57	4.67	12.72	96	2	2	Sand	
SC-5	6.10	4.24	8.48	96	2	2	Sand	
SC-6	7.62	3.82	8.48	96	2	2	Sand	
SC-7	9.14	5.72	10.60	96	2	2	Sand	
SC-8	10.67	6.57	10.60	96	2	2	Sand	
SC-9	11.58	6.78	10.60	96	2	2	Sand	Water Table
SC-10	13.72	6.78	12.72	96	2	2	Sand	
SC-11	15.24	6.78	12.72	96	2	2	Sand	
SC-12	16.76	4.66	25.44	19	46	35	Silty Clay Loam	
SC-13	18.29	4.24	19.08	33	48	19	Loam	
SC-14	19.81	2.54	12.72	50	38	12	Loam	
SC-15	21.34	3.18	8.48	84	14	2	Loamy Sand	
SC-16	22.86	4.24	10.60	90	8	2	Sand	
SC-17	24.38	4.66	10.60	92	6	2	Sand	

Further 8 soil bores were conducted in order to install monitoring wells so as to observe the periodic variation in the groundwater quality regarding chromium concentrations (Figure 1). The points were selected in the surrounding areas of the drains.

The amount of total chromium and hexavalent chromium, retained in the soil, existing in both solid phase (solid grain) and the liquid phase (pore water), for all the soil samples collected at the every depth of 1.52 meters was determined by Aqua regia digestion [11]. These soil samples were also analyzed for the particle size distribution analysis by hydrometer method so as to know the soil nature for each sample.

The wastewater samples were analyzed for the chemical parameters, pH, BOD_5, COD, TDS, TSS, Chloride, sulphate, sulfide and total chromium by using the standard techniques as described in the Standard methods for examination of water and wastewater [12]. Total chromium in groundwater samples were measured by using Atomic Absorption Spectrophotometer method by method described in Standards methods for examination of water and wastewater [12].

RESULTS AND DISSCUSSIONS

Soil Analysis: For the soil bore 1, the total chromium and hexavalent chromium concentrations along with particle size distribution are shown in Table 1. The variation trend of the concentrations along the sampling depth is presented in Figure 2. It can be observed from Table 1 that hexavalent chromium ranges from 3.6 to 8.06 mg/kg, while total chromium ranges between 6.36 and 48.76 mg/kg. Hence the first finding is that both hexavalent chromium and total chromium retained in the soil are within the permissible limit of 250 mg/kg [13].

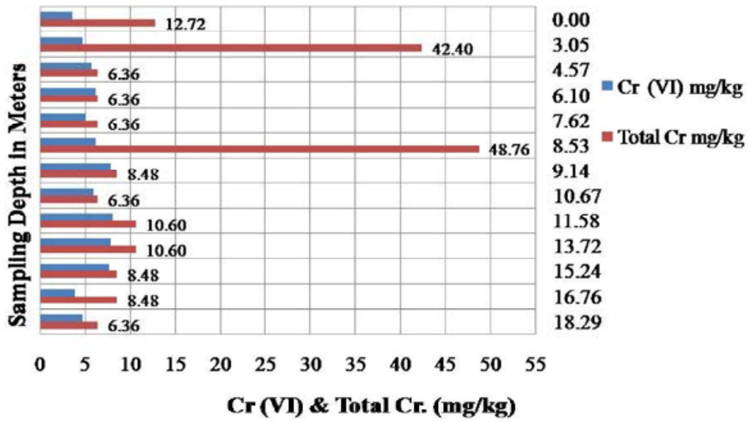

Fig. 2: Hexavalent Chromium and Total Chromium in mg/kg for Soil Bore 1 plotted against depth (m)

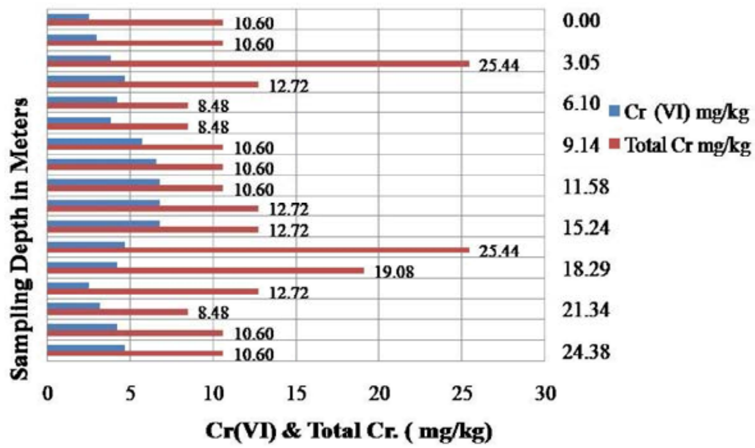

Fig. 3: Hexavalent Chromium and Total Chromium in mg/kg for Soil Bore 2 plotted against depth (m)

It can be seen from Table 1 as well as from Figure 2 that the higher values of total chromium and hexavalent chromium are in relation with the higher silt and clay proportion. The value 42.4 mg/kg has maximum silt and clay proportion to be 79%.

For the samples from soil bore 2, Aqua regia digestion results are shown in Table 2. The hexavalent chromium varies from 2.54 to 6.78 mg/kg and total chromium content retained in soil varies from 8.48 to 25.44 mg/kg. All the values for both hexavalent and total chromium are within the standard limit i.e. 250 mg/kg [13]. The bar chart in Figure 3 shows a variation trend somewhat dependant on the soil nature. The highest values 25.44 mg/kg, obtained for total chromium retained in soil for the soil samples at the depths of 3.05 and 16.76 meters are in proportion with and justified by the highest silt & clay contents i.e. 82 and 81% respectively throughout the sampling depth. Thus the higher the silt and clay proportion, the higher will be the retention in the soil [14].

Wastewater Analysis

Analysis During Tanneries Peak Production Season: Four wastewater samples were collected from the four drains flowing in the nearby vicinity of the tanneries. The results obtained are compared with the National Environmental Quality Standards Pakistan [15], which has been developed for the industrial and municipal wastewaters. In order to compare the seasonal variation, the samples were taken twice a year, first in the month of June, which is the peak production time, secondly in January when the tanneries are operating at their minimum production level. Figure 4 shows the comparison of the chemical parameters analyzed for wastewater samples obtained from the four drains with NEQS.

The pH was the only parameter which was found to be within permissible limit of NEQS, it ranged from 7.1 to 7.7 where the standard limit ranges from 6 to 9. The values of biochemical oxygen demand (BOD) ranged from 300 to 2,760 mg/L whereas the standard limit for BOD as permitted by NEQS is 80 mg/L. The values of chemical

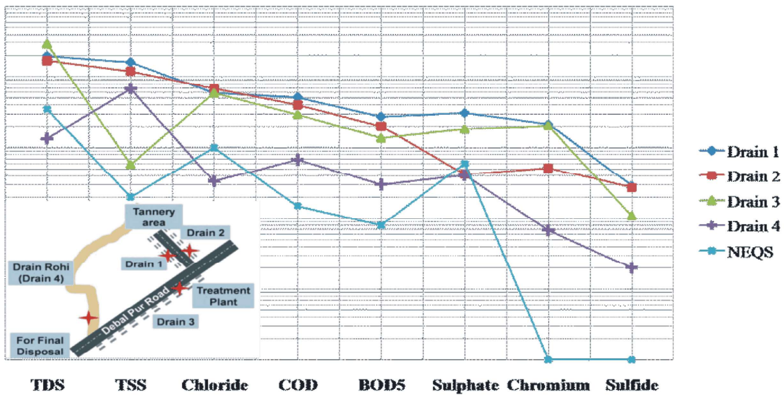

Fig. 4: Wastewater analysis during Peak Production Season, in comparison with NEQS

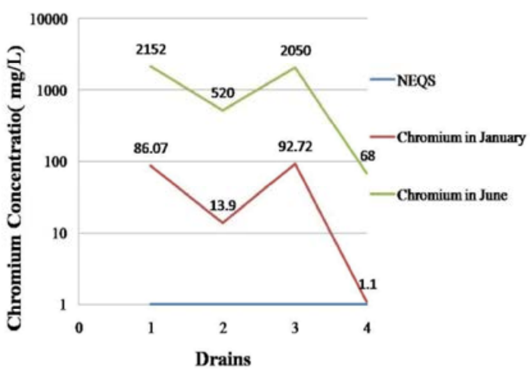

Fig. 5: Seasonal variation in the chromium concentration in comparison with the NEQS

oxygen demand (COD) ranged from 680 to 5,152 mg/L, whereas the standard limit for COD as permitted by NEQS is 150 mg/L. Total dissolved solids has the standard limit of 3,500 mg/L as recommended by NEQS but the samples values for TDS ranged from 1340 to 28,740 mg/L with only one sample within permissible limit i.e. 1,340 mg/L. Total suspended solids has the standard limit of 200 mg/L, while the values obtained for the wastewater samples ranged from 580 to 16,020 mg/L.

According to NEQS, standard limit for chloride in wastewaters is 1,000 mg/L and the value of chloride obtained for the wastewater samples ranged from 335 to 6,808 mg/L, with only one sample within the limit having value 335 mg/L. Sulphates having the permissible limit of 600 mg/L, obtained the values ranging from 407 to 3,106 mg/L, with two samples having values within the limit i.e. 407 and 424 mg/L. Sulfide has the permissible limit of 1.0 mg/L and the values of sulfide obtained for the wastewater samples are all beyond this limit ranging from 20 to 288 mg/L. The heavy metal chromium has the permissible limit of 1.0 mg/L and all the wastewater samples have values of chromium exceeding the permissible limit, ranging from 68 to 2,152 mg/L. It depicts greater potential risk of seepage of the high concentrations of chromium into the soil ultimately mixing with the groundwater.

Analysis During Tanneries Minimum Production Season: In the month of January, when most of the tannery units were on vacations, wastewater samples were again collected from the same locations as earlier. This time only total chromium was analyzed for these wastewater samples. Figure 5 shows the comparison of total chromium concentration for both the seasons with the National Environmental Quality Standards.

The concentrations at all four drains exceeded the National Environmental Quality Standards limits even in the minimum production seasons. It can be observed from Figure 5 that although the chromium concentrations for all the four drains, during minimum production season is far less than those obtained for the peak production season, the trends of differences in the concentration at the four drains are very similar between the peak and minimum production seasons.

Monitoring Wells Samples Analysis for Chromium: Based on the findings of the possible sources of groundwater contamination and locations of the effluent carrying drains, furthers 8 points were selected in order to install monitoring wells for periodic groundwater sampling. These monitoring points were in the nearby vicinity of the drains.

While conducting bore holes for the installation of monitoring wells, soil samples were also collected at the every depth of the 1.52 meters. These samples would be analyzed for total chromium and hexavalent chromium in the soil.

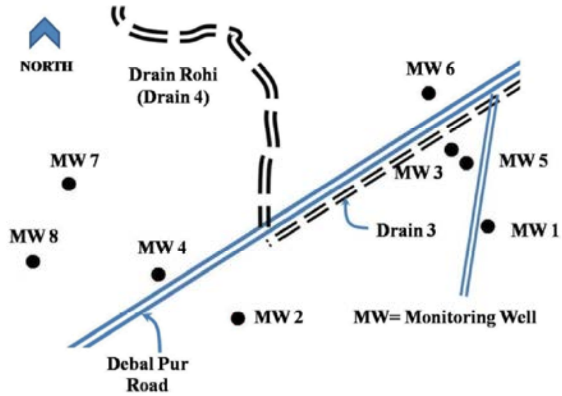

Fig. 6: Zoomed view of the 8 monitoring wells location

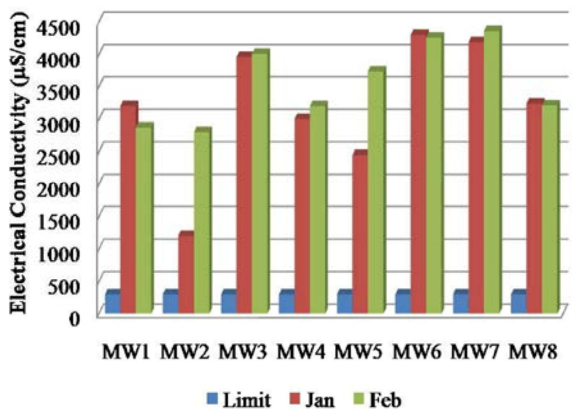

Fig. 7: Electrical conductivity and the standard limit for the monitoring well samples analysis

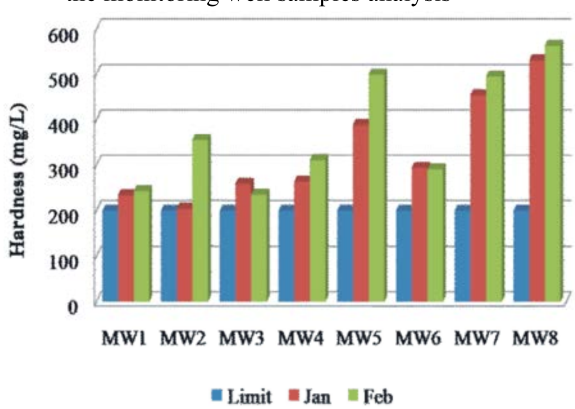

Fig. 8: Hardness and the standard limit for the monitoring well samples analysis

The location of these monitoring points is shown in Figure 1 and a detailed view of these locations can be seen in Figure 6. All the monitoring wells were installed at the same depth of 30.48 meters so as to have fixed parameter of sampling depth. It was planned to collect the groundwater samples from these monitoring points on monthly basis so that the variation could be observed for a specific period of time. So far the results for only the first two months have been obtained as the research work is still in process.

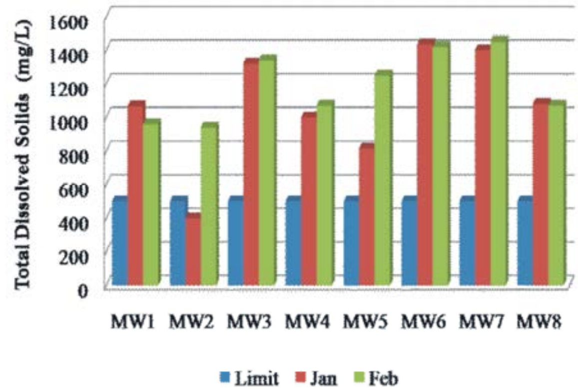

Fig. 9: TDS and the standard limit for the monitoring well samples analysis

The groundwater samples collected from these 8 monitoring wells were analyzed for electrical conductivity, hardness as calcium carbonate, total dissolved solids and total chromium. From Figure 7 to 10, the results obtained for the two repetitions of the groundwater sample analysis of all the monitoring wells are shown for the parameters in comparison with the permissible limits.

The results of electrical conductivity for the 8 monitoring wells are shown in Figure 7 for the two months, January and February, 2010. The values range between 1,198 and 4,300 µS/cm for the first sampling month, January while for the second month, February, the values range between 2,800 and 4,360 µS/cm.

When compared with the standard limit for the electrical conductivity i.e. 300 µS/cm [16, 17] all the values obtained are far more than this limit. The results for the total hardness as $CaCO_3$ are shown in Figure 8. The values for the sampling in the month of January ranged between 205 to 532 mg/L while for samples in February it ranged between 236 to 564 mg/L. The permissible limit for the hardness is 200 mg/L [10] and all the values obtained from the samples are exceeding it. The values of TDS obtained for the samples in both the sampling months, are plotted in Figure 9, along with the permissible limit 500 mg/L (EPA, 1992). All the TDS values are higher than the standard limit except one sample from the MW 2 in the month of January. The TDS values for the month of January ranged between 400 and 1,435 mg/L while for February it ranged between 940 and 1,450 mg/L. In Figure 10 the result of the total chromium analysis for the samples obtained in the months of January and February from the monitoring wells are

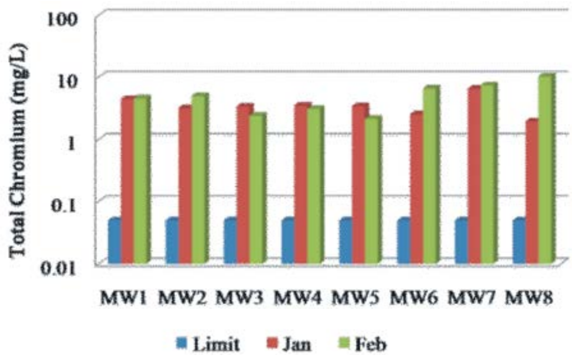

Fig. 10: Total Chromium and the standard limit for the monitoring well samples analysis

shown in comparison with the permissible limit i.e. 0.05 mg/L [10]. Total chromium concentrations in the groundwater samples for the month of January ranged between 1.98 and 6.56 mg/L while for the month of February it ranged between 2.44 and 10.37 mg/L. It can be observed that all these values are extremely high in comparison to the WHO permissible limit for the drinking water i.e. 0.05 mg/L. Overall an increasing trend can be observed for all the parameters analyzed in every sample. However the most significant trend can be observed in the case of total chromium. In three of the monitoring wells, MW2, MW6 and MW8, the chromium concentration changed relatively higher as compared to the other monitoring wells. These monitoring wells are highlighted in the Figure 11 by circles so that the significance of these wells can be understood in relation to the most probable sources of the groundwater contamination. It can be observed that the junction of the Drain 3 and Drain 4 at the Debal Pur Road is likely to be very significant in contaminating the groundwater in the surrounding area.

CONCLUSION

The research work conducted can be summarized as follows

The results of the soil analysis showed that soil has not been seriously contaminated due to the tannery effluent in the surrounding areas of the drains. None of the soil sample has exceeded the recommended limit of the 250 mg/kg for total or hexavalent chromium. However samples with higher silt and clay proportions have shown relatively higher concentrations for the total chromium. Deeper layers have even lower concentrations of total chromium and hexavalent chromium. It may be due to high sand proportions up to 98% in these layers.

The analysis of wastewater samples depict alarming situation as BOD_5, COD, TDS, TSS, Sulphates, sulphides and total chromium all are far more than the permissible limits for the wastewater according to the National Environmental Quality Standards. Pakistan (NEQS). There are higher risks of the existence and transportation of total chromium in subsurface, especially groundwater, as there is huge amount of total chromium in the wastewaters, ranging from 68 to 2,152 mg/L, which may percolate down into the soil to contaminate the groundwater. This concentration was observed during the peak season of production in tanneries i.e. from May to September. The wastewater carrying drains, even during the season of minimum production, have the concentration of total chromium exceeding the standards set by the National Environmental Quality Standards, Pakistan.

The groundwater samples collected from the installed monitoring wells exhibit the most threatening results regarding the total chromium concentrations. In all the samples the chromium concentration is exceeding the permissible limit of 0.05 mg/L many folds. The chromium concentration is in the range of 1.98 and 10.37 mg/L. Such high concentrations are even more vital when the source is used for drinking purposes and for daily use as well. It can result into number of health related problems to the inhabitants of the area.

Due to higher concentration of total chromium in groundwater than in the soil, it can be concluded that there is direct interference of wastewater with the groundwater. By focusing on the seepage prevention of the untreated effluent from the drains or leakage from the concrete made sewers, groundwater contamination could be controlled up to a large extent.

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REFERENCES

1. Saadia, R.T., M.H. Shah, Shaheen N. *et al*., 2005. Multivariate analysis of selected metals in tannery effluents and related soil, Journal of Hazardous Materials, 122: 17-22.

2. Hyder, S. and J.A. Aziz, 2009. Characterization and treat ability studies of tannery wastewater using chemically enhanced primary treatment (CEPT) – A case study of Saddiq Leather Works, Journal of Hazardous Materials, 163: 1076-1083.
3. Atiq, R., 2004. Evaluation of technical and social aspects of environmental infrastructure projects, Journal of Architect and Planning, 578: 99-107.
4. Saadia, R.T., M.H. Shah and Shaheen, N. 2009. Comparative statistical analysis of chrome and vegetable tanning effluents and their effects on related soil. Journal of Hazardous Materials, 169: 285-290.
5. Bini, C., L. Maleci and A. Romanin, 2008. The Chromium issue in soils of the leather tannery district in Italy, Journal of Geochemical Exploration, 96: 194-202.
6. Shams, K.M., G. Tichy, M. Sager, *et al*., 2009. Soil contamination from tannery wastes with emphasis on the fate and distribution of tri- and hexavalent chromium. Water Air and Soil Pollution, 199: 123-137.
7. Saadia, R.T., M.H. Shah, N. Shaheen, *et al*., 2008. Statistical source identification of metals in groundwater exposed to industrial contamination, Environmental Monitoring and Assessment, 138: 159-165.
8. Mehrjardi, R.T., M.Z. Jahromi, S. Mahmodi and A. Heidari, 2008. Spatial distribution of groundwater quality with geostatistics (Case study: Yazd-ardakan plain). World Applied Sciences Journal, 4(1): 09-17.
9. Environment Protection Department, EPD Punjab. Environmental Protection Department Government of Punjab, 1997. Pakistan.http:// www.soc.titech.ac.jp/ ~sakano/ atiq/kasur/epdreport97.html.
10. WHO 2008. Drinking Water Quality Standards, http:// www.who.int/ water_sanitation_health/ dwq/ fulltext.pdf.
11. Hindu, A.K., 2008. Enhancement of heavy metal removal from clay by acoustics, PhD dissertation, Tokyo Institute of Technology, Tokyo Japan.
12. Standard Methods for Examination of Water and Wastewater 20th ed. 1998. APHA AWWA WEF.
13. Ministry of Environment, MOE Japan 2003. Soil Contamination Prevention Law http:// www.env.go.jp/ en/water/soil/contami_cm.pdf.
14. Armienta, M.A. and A. Quere, 1995. Hydrogeochemical Behavior of chromium in unsaturated zone and in the aquifer of Leon Valley, Water Air and Soil Pollution, 84: 11-29.
15. National Environmental Quality Standards for the Municipal and Liquid Industrial Effluents, the Gazette of Pakistan, Ministry of Environment, Local Government and Rural Development, Islamabad, SRO, 549 (I)/2000.
16. Jain, P., J.D. Sharma, D. Sohu and P. Sharma, 2006. Chemical analysis of drinking water of villages of Sanganer tehsil, Jaipur District, International Journal of Environmental Science and Technology, 4: 373-379.
17. Iqbal, M., M. Qasim, K.K. Abida, R. Rehana, N. Sadia, Qaisar, Mahmood and K. Jamil, 2009. Surface Water Quality Risk Assessment through UV-Visible Spectrophotometer, World, Applied Sciences Journal, 7(9): 1195-1202.