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Research Article

Comparative Assessment of Heavy Metals in Water, Sediment and Adjacent Soil of Hudiara Drain

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Abstract: Industrial effluents cause contamination of water resources especially when it is discharged untreated in waterways. This study was conducted to measure the concentration of different heavy metals (Chromium, Nickel, Lead, Manganese and Copper) in wastewater, sediment and irrigated soil. Samples were collected from Hudiara drain near Gajomatta, Lahore. Experiments were done for the identification of heavy metals concentration in samples. In first step acid digestion, using hot plate was done of all samples. In second step Heavy metals analysis was carried out using FAAS. In wastewater heavy metals was present in order of copper (28.01ppm) >Manganese (9.81ppm)>Nickel (0.79ppm)> Chromium (0.43ppm) >Lead (0.36ppm). In top soil the order was Copper (77.51ppm)> Manganese (9.93ppm)> Chromium (3.71ppm)> Nickel (0.71ppm) >Lead (0.57pm). In subsoil the heavy metal order was Copper (27.19ppm) >Manganese (11.94ppm) > Chromium (5.25ppm) Nickel (1.01ppm) >lead (0.61ppm). In sediment the heavy metals were observed as follows Manganese (8.43ppm)> Chromium (5.85ppm) > Copper (1.46ppm) > Nickel (0.89ppm) > Lead (0.79ppm). The results were compared with National Environment Quality Standards (NEQS) Pakistan, Canadian soil quality guidelines for agricultural soil and Canadian Sediment Quality Guidelines for the Protection of Aquatic Life (2002). Heavy metal contents of water and soil aretransferred to vegetables and crops, which cause serious health hazards on their consumption so industrial effluent should be treated at source.

Keywords: Heavy metals, Sediment, Wastewater and Soil.

1. INTRODUCTION

Heavy metal poisoning occurs by long-term exposure to these metals. These may cause acute or chronic diseases in human body. Various vital organs of the body such as brain, spinal cord, kidneys and liver are negatively affected by these metals [1, 2].Continuous exposure can cause more serious diseases like Alzheimer's disease, Parkinson's disease, allergies and even cancer in some cases. Some heavy metals are more toxic even in trace amounts or just above their threshold concentration [3, 4]. Use of wastewater for the irrigation is not an efficient approach. It not only increase heavy metals content in soil but also increases the health risk by taking vegetables and fruits as food grown in the soil irrigated by wastewater [5, 6]. In order to measure aquatic pollution sediment study is an important part as sediments act as a pool for heavy metals. Sediments also provide information about the geochemical record of watershed. Heavy metals including lead, copper and mercury are listed as very toxic pollutants for aquatic life [7, 8].

Anthropogenic activities related to industries are increasing contents of heavy metals in the water [9]. Heavy metals in soil effect the plants growth depending on the plant species. Some plants have capability to accumulate heavy metals in much higher quantities as compared to other plant species [10,11]. Discharge from industries and municipal waste which are directly dumped to the natural water resources also contaminate the sediments. These effluents contain hazardous elements which can accumulate in the soil and sediments. These can be absorbed by aquatic organisms, thus entering the

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food chain. Fish can absorb metallic ions from gills from water under acidic conditions [12].

Irrigation in Pakistan is mostly carries out by contaminated water discharged from households and industries. The application of wastewater for agricultural practices is increasing because of increasing salinity, unsustainable agricultural practices and less availability of suitable irrigation water. Heavy metals also have negative impacts on plant growth which may be in the form of inhibition of growth, chlorosis, and decrease ability to uptake of nutrients and water. In some cases heavy metals also damage the enzyme system. Long term intakes of heavy metals have high damaging impacts on humans and other life [13, 14]. Heavy metals are persistent in the environment so their long term exposure may have detrimental impacts by decreasing body's ability to store iron, vitamin and other vital elements and in severe cases these metals also cause immunological and mental problems [15, 16].

Hudiara drain is included in one of the main tributaries of river Ravi. More than 120 industries in Pakistan are located on Hudiara drain which discharges their effluents into it. In addition it also carries municipal water from the city of Lahore and other nearby areas. Contaminated water of this drain is used for irrigation throughout its range [17]. Studies showed that there were high metals (Cr, Cd and Mn) concentration in Hudiara drain water [18].The main objective of this study was to assess heavy metal contents found in industrial effluent flowing through Hudiara drain and deposition of these metals from water to sediments and soil irrigated from this drain.

2. MATERIALS AND METHODS

The current study was carried out to measure the heavy metal concentration in wastewater, sediment and irrigated soil of Hudiara drain.

2.1 Collection of samples

Representative samples of wastewater, sediment and soil were collected from Hudiara drain near Gajomatta Lahore. Samples were collected in plastic bags in case of sediment and soil while wastewater samples were collected in pre-cleaned plastic bottles. Samples were stored at 4°C until further analysis.

2.2 Collection of Wastewater samples, Sediments and Irrigated soil:

Wastewater samples were collected from three different sites named as site A, site B and site C. Representative samples of about 1 liter were collected from each site. Sediment samples were collected from three different sites named as site A, site B and site C. From each site representative sample of about 1kilogram was collected. Irrigated soil samples were collected from three different sites named as site A, site B and site C. From each site surface soil and 6cm deep soil samples of about 1kilogram were collected. Soil samples were also collected from water channel from which pumped wastewater is applied to the fields.

3. PRIMARY TREATMENT

3.1. Filtration, Oven drying and Blending of samples

Wastewater samples were filtered before analysis with Whatmann filter paper no. 42 to remove suspended solids. The sediment and soil samples were first oven dried at 105°C for overnight to remove moisture contents. The oven dried samples of sediments and soils were crushed and ground. To get more fine particles crushed samples were passed through 60 mesh sized sieves. The samples were then preserved in polythene bags until further analysis.

3.2. Analysis of heavy metals

For the analysis of heavy metals wet acid digestion method was used.

3.3. Preparation of wastewater samples, Sediments and Soil samples

Wet digestion of filtered wastewater samples were done with HNO_3. 0.5ml of sample was taken into a digestion flask and 5ml of HNO_3 was added. It was placed on hot plate at 80-90°C for 2 hours. After 2 hours temperature was raised to 150°C and 3-5ml of HNO_3 and H_2O_2 were added and heated until a yellowish clear solution formed. Blank samples were also prepared in a flask without sample. For the analysis of heavy metals, 0.5g of prepared sample of sediments and soil were taken in the digestion flasks and 5ml of concentrated HNO_3 was added. Blank sample was also prepared by adding

5ml of concentrated HNO_3 in a digestion flask. The digestion flasks were then placed on hot plate at 80-90°C for 2 hours. The temperature was raised to 150°C and 3-5ml of HNO_3 and H_2O_2 were added in flasks and heated on hot plate until a yellowish clear solution appeared. Digested samples were cooled at room temperature and filtered with Whatmann filter paper no. 42. The volume of filtrate was made up to 25ml with distilled water. All reagents used were of analytical grade and all samples were prepared in triplicates.

3.4. Analysis by Flame Atomic Absorption Spectrophotometer

The prepared samples of water, sediment and soil were then analyzed for heavy metals content by using "FAAS, Shimadzu AA-7000F". Samples were analyzed for chromium, nickel, lead, manganese and copper.

4. STATISTICAL ANALYSIS

The One-way ANOVA was applied using SPSS version 19 to compare distribution of heavy metals in wastewater, sediment and irrigated soil.

5. RESULTS AND DISCUSSION

5.1. Concentration of Chromium

Chromium concentration was analyzed in samples collected from study sites by Atomic Absorption Spectrometry. The concentration of chromium analyzed in samples from wastewater, sediment, surface soil, 6-12cm deep soil and water channel soil were 0.43 ppm, 5.84 ppm, 3.71 ppm, 5.25 ppm and 9.31 ppm respectively. As shown in Figure 1, sites can be arranged as follows in accordance with decreasing chromium concentration, water channel soil>sediments>6-12cm deep soil>surface soil>wastewater. Chromium concentration in wastewater was low as compared to permissible values of NEQS. Previous study also measured chromium concentration in water that chromium value (2.5 µg/L) was higher than the concentration determined in the current study [12]. Some other researchers also measured chromium level in water and that chromium concentration (0.02-0.75µg/L and 0.45 mg/L respectively) was equal to the chromium level measured in the current study [15, 19]. Heavy metals content measured in another study, in Hudiara drain wastewater was observed to be higher for chromium and manganese as compared to heavy metals concentration measured in current study [18].

5.2. Concentration of Nickel

Nickel concentration was analyzed in samples collected from study sites by Atomic Absorption Spectrophotometry. Concentration of nickel in samples was 0.79 ppm, 0.88 ppm, 0.70 ppm, 1.01 ppm and 1.16 ppm for wastewater, sediment, surface

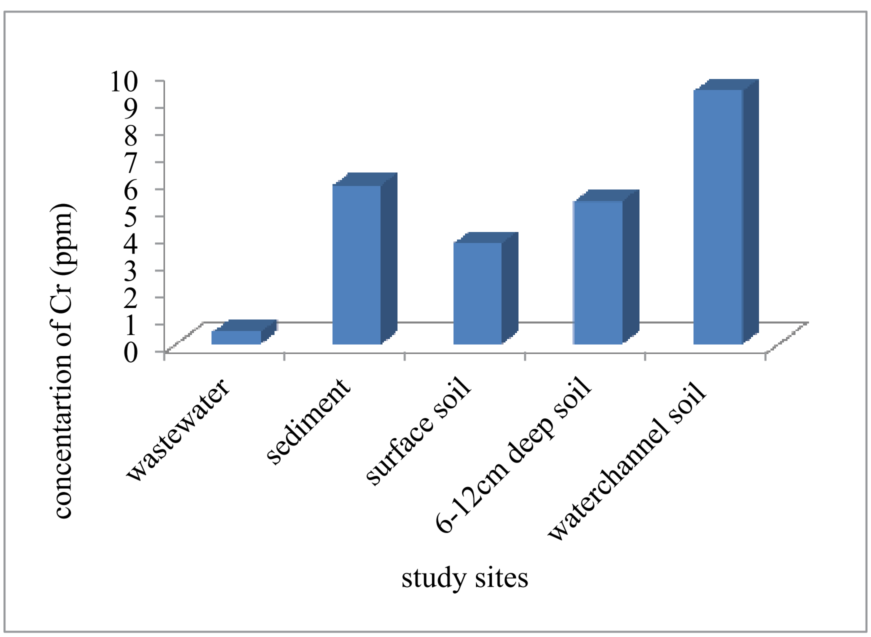

Fig. 1. Mean concentration of Chromium in different selected study sites.

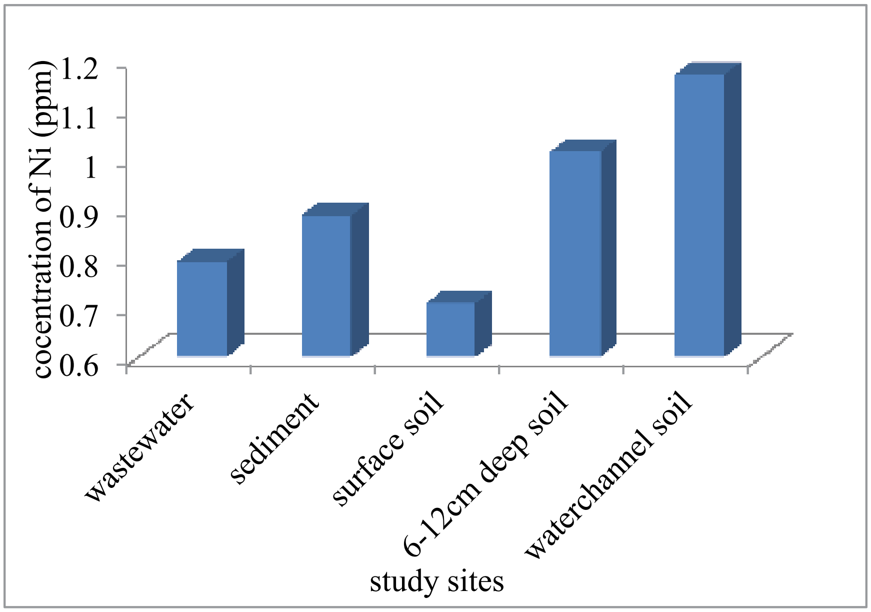

Fig. 2. Mean Nickel concentration in selected study sites.

soil, sub soil and water channel soil respectively (Figure 2). Nickel concentration measured in current study in wastewater was within permissible values of NEQS (2000). Ni level was also measured in irrigation water that Ni range (0.02-5.35 mg/L) was matched with concentration of Ni measured in current study [20]. Concentration of nickel in soil was within standard as compared to Canadian soil quality guidelines (50 mg/kg) for agricultural soil.

5.3. Concentration of lead

Atomic Absorption spectrophotometer was used to analyze lead concentration in samples collected from study sites. Concentration of lead in wastewater was 0.34ppm (Figure 4.3). Lead level in current study was within permissible value of NEQS [21]. Lead level was also measured in water and found that Pb value (0.03-0.20µg/L) was higher than Pb concentration measured in the current study [22].

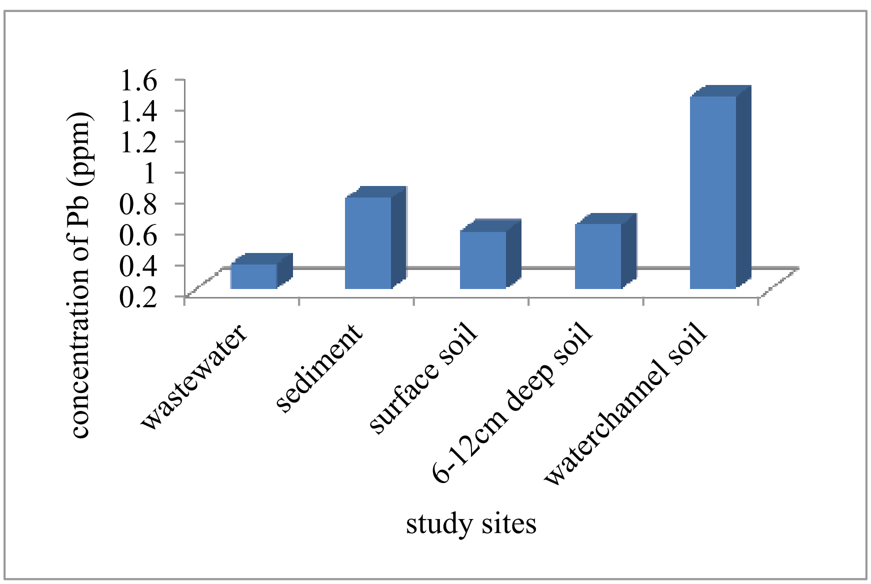

Fig. 3. Mean Lead concentration in selected study sites.

In soils concentration of lead was 0.57 ppm, 0.61 ppm, and 1.44 ppm for surface soil, 6-12cm deep soil and water channel soil respectively (Figure 3). Lead concentration in irrigated soil samples of Hudiara drain was within permissible of Canadian soil quality guidelines (70 mg/kg) for agriculture soil. Pb concentration in soil was measured and found that Pb value (47.7-52.6mg/kg) was high as compared to the Pb concentration measured in this study [23]. In sediments the Pb content was 0.78 ppm and it was within permissible limit while compared with the Canadian Sediment Quality Guidelines (35 mg/kg) for the Protection of Aquatic Life (2002) ISQG (Interim freshwater sediment quality guidelines).

5.4. Concentration of Manganese

The concentration of Manganese in wastewater was 9.81 ppm (Figure 4.4). Manganese concentration was higher than the permissible value of NEQS (2000) [21]. Mn concentration was also measured in water and found that value (1-467μg/L) was higher as compared to Mn concentration measured in current study [24]. Manganese concentration in surface soil, 6-12cm deep soil and water channel soil was 9.92 ppm, 11.93 ppm and 9.83 ppm respectively.

5.5. Concentration of Copper

In wastewater the concentration of copper was

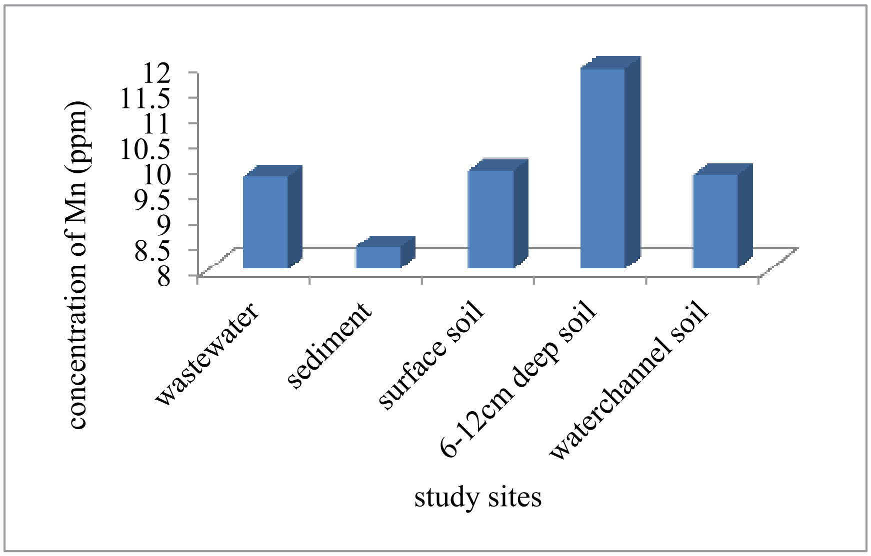

Fig. 4. Mean Manganese concentration in selected study sites.

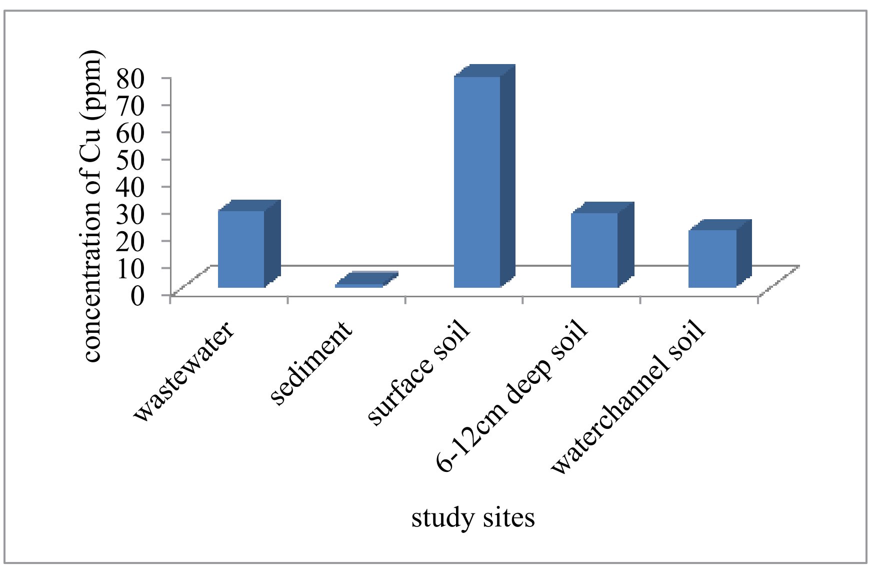

Fig. 5. Mean Copper concentrations in selected study sites.

28 ppm. Copper concentration was higher than permissible values of NEQS (2000) [21]. Cu concentration was also measured in water that range (0.005-1.19mg/L) was lower as compared to the Cu level measured in current study [20]. Cu concentration in surface soil, 6-12cm deep soil and water channel soil was 77.59 ppm, 27.19 ppm and 21.24ppm respectively (Figure 5). The values of copper in soils were higher than the Canadian soil quality guidelines (63 mg/kg) for agricultural soil.

5.6. One way ANOVA Analysis

Statistical analysis was done to measure the difference of metals (Cr, Ni, Pb, Mn and Cu) in all selected sites. One way ANOVA was applied at variance significance level of 0.05. Concentration of metals was compared in wastewater, sediment, water channel soil, surface soil and 6-12cm deep soil individually. Results showed (Table 2) high significance of all metals in the study sites which means that there was a difference in concentration of each metal in all sites. Lead level was measured in sediment and water and results showed no significant value for lead in samples [22]. A study measured Mn, Cr, Pb and Cu concentration in soil and found significantly high concentration of metals in study sites [25]. A researcher studied heavy metal pollution in soil and found significant level of Cu and Pb in samples [26].

6. DISCUSSION

Chromium level in wastewater was low as compared to Cr concentration measured in previous studies [27]. The concentration of chromium in wastewater was 0.43 ppm. In all samples the concentration of chromium was within standards. In current study Chromium concentration in soil was 3.70 ppm i.e., in surface soil, while in 6-12cm deep soil it was 5.25 ppm.Soil Chromium level in current study was higher as compared to Cr concentration measured in previous studies [28, 29]. In current study Chromium concentration in sediment was 5.85 ppm

Table 1. Comparison of heavy metals in wastewater, sediment and soil.

Sr. No	Heavy metals	Wastewater ppm)	Sediment (ppm)	Surface soil(ppm)	Subsoil (ppm)
1	Chromium	0.43 ± 0.03	5.84 ± 0.95	3.7 ± 0.4	5.25 ± 1.2
2	Nickel	0.79 ± 0.12	0.88 ± 0.13	0.7 ± 0.06	1.01 ± 0.46
3	Lead	0.36 ± 0.01	0.78 ± 0.05	0.57 ± 0.09	0.61 ± 0.05
4	Copper	28.0 ± 3.0	1.46 ± 0.22	77.59 ± 5.0	27.19 ± 2.5
5	Manganese	9.81 ± 1.8	8.43 ± 0.99	9.93 ± 1.5	11.94 ± 1.6

Table 2. One way ANOVA showing significance level of metals in selected sites at significance level 0.05

		Sum of Squares	df	Mean Square	F	Sig.
Chromium	Between Groups	125.524	4	31.381	439.364	.000
	Within Groups	.714	10	.071		
	Total	126.238	14			
Nickel	Between Groups	.401	4	.100	75.318	.000
	Within Groups	.013	10	.001		
	Total	.414	14			
Lead	Between Groups	2.041	4	.510	197.139	.000
	Within Groups	.026	10	.003		
	Total	2.067	14			
Manganese	Between Groups	18.818	4	4.704	546.484	.000
	Within Groups	.086	10	.009		
	Total	18.904	14			
Copper	Between Groups	9485.290	4	2371.323	178369.503	.000
	Within Groups	.133	10	.013		
	Total	9485.423	14			

and it was low as compared to Cr concentration measured by another researcher [30].

In current study concentration of nickel in wastewater samples was 0.79 ppm. Nickel concentration in wastewater was within permissible values in comparison with NEQS [21] and Ni values measured previously [15]. Nickel amount in current study was lower as compared to the values measured in other studies [31]. In current study Nickel concentration was 0.71 ppm, 1.01 and 1.17 ppm in soil samples. Concentration of nickel in water channel soil and irrigated soil was within standards. Concentration of lead in wastewater was 0.34 ppm and it was within permissible value as compared to NEQS. Lead concentration was lower as compared to the concentration measured by Begum [12]. Lead concentration in the current study was higher than Pb concentration measured by Guhathakurta and Kaviraj [22]. In soils, concentration of lead was 0.57 ppm, 0.61 ppm, and 1.44 ppm for surface soil, 6-12cm deep soil and water channel soil respectively.

The concentration of Manganese in wastewater was 9.81 ppm which was higher than values measured by Saif and Karadede and Unlu [31]. Manganese concentration in surface soil, 6-12cm deep soil and water channel soil was 9.93 ppm, 11.94 ppm and 9.84 ppm respectively. Manganese level in soils was lower than concentration measured by Yasmeen [19]. In sediment Mn concentration was 8.4316ppm. Manganese concentration was lower than Mn level measured by Karadede and Unlu [31].

In wastewater the concentration of copper was 28.01ppm. Copper concentration was higher than permissible values. Copper level in wastewater was also higher as compared to Cu concentration measured by Bhuiyan [32]. Cu concentration in surface soil, 6-12cm deep soil and water channel soil was 77.59 ppm, 27.19 ppm and 21.25 ppm respectively. The values of copper in soils were higher than standards.

7. CONCLUSION

The current study was conducted to investigate heavy metals pollution level in wastewater, sediment and irrigated soil of Hudiara drain. Samples were collected and after wet digestion method, analyzed for heavy metals (Cr, Ni, Pb, Mn and Cu) by atomic absorption spectrophotometer. Results of this study were compared with National Environmental Quality Standards (NEQS) 2000 of Pakistan, the Canadian soil quality guidelines for agriculture soil and Canadian Sediment Quality Guidelines for the Protection of Aquatic Life (2002). It was found that heavy metals content was within standards except for copper in wastewater (28 ppm) and in irrigated soil (77.5ppm in top soil and 27.1 ppm in 6-12cm deep soil).The use of wastewater has some benefits as well as may have some potential negative impacts. Negative impacts are the contamination of soil and vegetation by hazardous elements including heavy metals and also increase health risks to the population.

8. RECOMMENDATIONS

There is dire need to monitor industrial effluents and enforcement of National Environmental Quality Standards before discharge into water bodies.

- ✓ There must be proper monitoring and research on water quality of all drains.
- ✓ Detailed survey is needed to assess and monitor water quality and agricultural soil nearby Hudiara drain.
- ✓ Government and private sectors must cooperate in a productive way for further research and development.
- ✓ Farmers and local community must aware of hazards and health risk caused by the using wastewater for irrigation.
- ✓ As Hudiara drain enters from the India so there must be water quality investigation system which will measure the water quality of Hudiara drain before entering from India to Pakistan.

9. REFERENCES

1. Sin, S.H. Chua,W. Lo & L.M. Ng.Assessment of heavy metal cations in sediments of Shing Mun River, Hong Kong. *Environment International,* 26(5): 297-301 (2001).
2. Li, S. & Q. Zhang. Risk assessment and seasonal variations of dissolved trace elements and heavy metals in the Upper Han River, China. *Journal of hazardous materials*, 181(1): p. 1051-1058 (2010).
3. Cook, J., S. Andrew &M. S. Johnson. Lead, zinc,

cadmium and fluoride in small mammals from contaminated grassland established on fluorspar tailings. *Water Air and Soil Pollution.* 51: 43-54 (1990).

4. Rattan, R.,S. P. Datta, P. K. Chhonkar, K. Suribabu, & A. K. Singh.Long-term impact of irrigation with sewage effluents on heavy metal content in soils, crops and groundwater—a case study. *Agriculture, Ecosystems & Environment,* 109(3): 310-322 (2005).
5. Muchuweti, M., J.W. Birkett, E. Chinyanga, R. Zvauya, M. D.Scrimshaw & J. N. Lester. Heavy metal content of vegetables irrigated with mixtures of wastewater and sewage sludge in Zimbabwe: implications for human health. *Agriculture, Ecosystems & Environment*, 112(1): 41-48 (2006).
6. Igwe, J. & A. Abia.Abioseparation process for removing heavy metals from waste water using biosorbents.*African Journal of Biotechnology,* 5(11): 19-24 (2006).
7. Kishea, M. A.&J.F. Machiwa.Distribution of heavy metals in sediments ofMwanza Gulf of Lake Victoria, Tanzania.*Environment International*, 28: 619-625 (2003).
8. Arnason, J. G. &B. A.Fletcher. A 40-Yer record of Cd, Hg, Pb, and U deposition in sediments of Patroon Reservoir, Albany County, NY, USA. *Environmental Pollution*, 123(3): 383–391(2003).
9. Pérez-López, R. Evaluation of heavy metals and arsenic speciation discharged by the industrial activity on the Tinto-Odiel estuary, SW Spain. *Marine pollution bulletin,* 62(2): 405-411 (2011).
10. Baker, A. The possibility of in situ heavy metal decontamination of polluted soils using crops of metal-accumulating plants.*Resources, Conservation and Recycling,* 11(1): 41-49 (1994).
11. Ismail, B., K. Farihah, & J. Khairiah. Bioaccumulation of heavy metals in vegetables from selected agricultural areas. *Bulletin of environmental contamination and toxicology,* 74(2): p. 320-327 (2005).
12. Begum, A., S. Harikrishna& I. Khan. Analysis of heavy metals in water, sediments and fish samples of Madivala lakes of Bangalore, Karnataka. *International Journal of ChemTech Research*, 1(2): 245-249 (2009).
13. Audry, S., et al., Early diagenesis of trace metals (Cd, Cu, Co, Ni, U, Mo, and V) in the freshwater reaches of a macrotidalestuary. *GeochimicaetCosmochimicaActa*, 70(9): p. 2264-2282 (2006).
14. Moon, J.W. Evaluation of heavy metal contamination and implication of multiple sources from Hunchun basin, northeastern China.*Environmental Geology,* 39: p. 1039–1052 (2000).
15. Mushtaq, N. & K.S. Khan. Heavy metals contamination of soils in response to wastewater irrigation in Rawalpindi region.*Pakistan J. AgricultralScience,* 47(3): 215-224 (2010).
16. Farrell, L. Rehabilitation at Silvermines, Extract. Ind. *Ireland Ann. Rev.,* 41–45 (2002).
17. Yamin, M.T. & N. Ahmad. Influence of Hudiara drain water irrigation on trace elements load in soil and uptake by vegetables. *Journal of Applied Sciences and Environmental Management*, 11(2): (2007).
18. Yasar, A. The effect of industrial effluent stream on the groundwater.*1st International conference on ESDEV*, 2 (2005).
19. Yasmeen, K. Enhanced Metal Levels in Vegetables and Farm Soil irrigated with Industrial Waste. *Water Jounral of Application Science Environ. Manage*, 14(3): 95-99 (2010).
20. Saif, M.S. Heavy metals Contamination through industrial effluent to irrigation water and soil in Korangi area of Karachi (Pakistan). *International journal of Agriculture &Biology*, 07(4): 646-648 (2005).
21. National Environmental Quality Standards (NEQS), Ministry of environment, local government and rural development. The gazette of Pakistan, (2000).
22. Guhathakurta, H. & A. Kaviraj. Heavy Metal Concentration in Water, Sediment, Shrimp Penaeusmonod on and Mullet Liza parsiain Some Brackish Water Ponds of Sunderban, India*. Marine Pollution Bulletin*, 40(11): 914-920 (2000).
23. Khan, S. Health risks of heavy metals in contaminated soils and food crops irrigated with wastewater in Beijing, China. *Environmental Pollution*. 152 (3): 686-692 (2008).
24. Varol, M. & B. Şen. Assessment of nutrient and heavy metal contamination in surface water and sediments of the upper Tigris River, Turkey. *Catena*, 92: 1-10 (2012).
25. Muhammad, S., M. T. Shah & S. Khan.Heavy metal concentrations in soil and wild plants growing around Pb–Zn sulfide terrain in the Kohistan region, northern *Pakistan.Microchemical Journal*, 99(1): 67-75 (2011).
26. Ye, C. Assessing soil heavy metal pollution in the water-level-fluctuation zone of the Three Gorges Reservoir, China. *Journal of hazardous materials,*

191(1): 366-372 (2011).

27. Zarazua, G. Analysis of total and dissolved heavy metals in surface water of a Mexican polluted river by total reflection X-ray fluorescence spectrometry. *SpectrochimicaActa*, 61(B): 1180–1184 (2006).
28. Shallari, S. Heavy metals in soils and plants of serpentine and industrial sites of Albania. *The Science of the Total Environment,* 209: 133-142 (1998).
29. Gowd, S.S., M.R. Reddy& P. K. Govila. Assessment of heavy metal contamination in soils at Jajmau (Kanpur) and Unnao industrial areas of the Ganga Plain, Uttar Pradesh, India. *Journal of Hazardous Materials,* 174 : 113–121 (2010).
30. Wei, M. Heavy metal pollution in Tianjin Bohai Bay, China. *Journal of Environmental Sciences*, 20: 814–819 (2008).
31. Karadede, H. & E. Unlu. Concentrations of some heavy metals in water,sediment and fish species from the Ataturk Dam Lake (Euphrates), Turkey. *Chemosphere,* 41: 1371-1376 (2000).
32. Bhuiyan, M. A. H. Evaluation of hazardous metal pollution in irrigation and drinking water systems in the vicinity of a coal mine area of Northwestern Bangladesh. *Journal of Hazardous Materials*, 179(1-3): p. 1065-1077 (2010).