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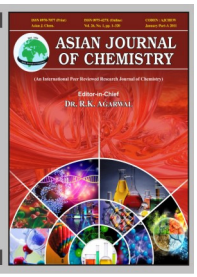

Comparative Study of Metal Contents in Soil and Plants Being Irrigated by Tannery Treated and Fresh Water

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Due to human activities level of metal ions circulating in the environment has been increasing continuously. It is important to understand the tolerance of plants species to high concentration of heavy metals. The present study compares the metal content in soil and plants irrigated with tannery treated and fresh water. The analysis of Kasur tannery treated water shows that high value of Cr 4.55 ± 0.01 mg/L and Fe 7.59 ± 0.02 mg/L that exceed National environmental quality standard. The result reveals that the concentration of Cu, Mn, Cr, Fe, Zn, Na, K concentration in soil, *Digitaria sanguinalis*, *Nerium oleander* and *Eucalyptus* samples taken from tannery irrigated water areas have high values as compared to fresh irrigated water.

Keywords: Heavy metals, Kasur tannery, *Eucalyptus*, *Nerium oleander*, Irrigated water.

INTRODUCTION

The problem of soil and water contamination in many countries has become major issue and thus immediate measures are necessary to avoid further environmental damage. Heavy metals and metalloids, which are toxic and carcinogenic to living organism, mainly enter into the soil and water system due to anthropogenic activities which includes metal processing, mining operations, refinery industries, tannery industries, army activities and landfills[1,2].

Leather industries in Pakistan produce all type of waste that is wastewater, solid waste and air emission. The discharge of untreated wastewater produces number of problems to local community, spoil the civic beauty of area and pollute water sources. The levels of chromium in soil near tannery areas were found beyond the safe limits[3]. Long term wastewater irrigation can cause accumulation of heavy metals in agricultural soil and plants. Heavy metals like zinc, manganese, nickel and copper act as micronutrients at lower concentrations however they become toxic at higher concentrations. Health risk due to heavy metal contamination of soil has been widely reported[4-6].

Heavy metals like chromium and lead may be tolerated in lower concentration but are harmful in higher concentration[7]. Plants are non-specific while taking-up metals from soil. Non-essential heavy metals such as arsenic, cadmium, chromium, mercury and lead present in soil would also be accumulated in different part of plants and vegetables along with the essential metals such as potassium, manganese, iron, cobalt, copper, zinc and selenium[8]. Accumulation of heavy metals in soil can caused due to two main processes. Firstly the inputs due to natural process such as weathering of rocks, erosion and floods. Secondly, the anthropogenic inputs associated with industrialization, mining activities, waste disposal, effluents discharge, vehicle exhaust, fertilizer and sewage sludge in agriculture land[9].

Leather industry is the main source of the high influx of chromium to the biosphere, accounting for 40 % of the total industrial use[10]. In effluent chromium occurs in less toxic trivalent form but when discharged into hydrosphere due to environmental condition Cr(III) is oxidized to toxic hexavalent Cr(IV) form[11,12].

Literature showed that the pollution load from tanning industries in cities like Sialkot, Kasur and Faisalabad were very high[13,14]. The damage to the environment by the hazardous tannery effluents is becoming an acute problem in the country. It is very important to determine the pollution level of toxic heavy metals in the wastewater, soil and plants due to tannery industries and their remedial measure were taken. In this study attempt has been made to inspect the quality of Kasur tannery wastewater and its impacts on soil and plants. This paper examines the metals concentration in tannery treated, fresh water and their irrigation effects on soil, *Digitaria sanguinalis*, *Nerium oleander* and *Eucalyptus* samples.

EXPERIMENTAL

The experimental site covers the area around Kasur tannery treatment plant. This treatment plant carries out only primary treatment of tannery effluent. There is no provision of removing chromium from effluent. All chemicals used in this study were of analytical grade.

Water and plants sampling: Treated effluent samples were collected from the outlet of treatment plant in a pre acid washed polyethylene bottles. The samples of *Eucalyptus*, *Digitaria sanguinalis* and *Nerium oleander* were collected from tannery irrigated water (TIW) areas. The purpose of sampling was to cover all types of vegetation that is herb, shrub and tree. For comparison control plants samples were collected from Kasur areas that were irrigated by fresh water. Firstly, samples were washed with fresh tap water to remove dust, dirt and possible parasites and then treated with deionized water.

Soil sampling: The soil samples were collected from the same site and location points as that of the plants sampling. The top 30 cm soil was collected near the plants roots. Soil samples were air dried, crushed, passed through a 2 mm mesh sieve and stored at ambient temperature for analysis. During sample preparation, necessary measures were taken in order to avoid any loss or contamination of heavy metal.

Acid digestion of plants and soil samples: Crushed and powdered portion of each plant part; leaf, bark and twig were placed in an oven at 110 ºC to remove moisture. The dried samples were charred and then heated in a furnace for 4 h at 550 ºC. The contents of crucible were cooled in desiccators and 5 mL concentrated HNO_3 was added into the dish to dissolve its contents. The solution was filtered and transferred to a 100 mL flask and diluted up-to the mark[15]. Total metal contents were extracted from soil samples by acid digestion[16].

Estimation of heavy metals in soil and plants sample was carried out on flame Atomic Absorption Spectrophotometer (Polarized Zeeman Hitachi 2000). The heavy metal analysis of tannery treated and fresh water were done by Inductive couple plasma (PerkinElmer optimum-5300). The Na and K were analyzed on flame photometer (Jenway PFP-7). Results obtained from the experiments (n = 3) are expressed as mean values ± SD (standard deviation).

RESULTS AND DISCUSSION

Metals analysis of Kasur tannery treated and fresh water were shown in Table-1. The value of Cr 4.55 ±0.01 mg/L and Fe 7.59 ± 0.02 mg/L in tannery treated water are very high as compared to NEQS value[17]. The high value of chromium is because in tanning process *ca.* 60-70 % of Cr reacts with hides while the remaining 30-40 % of chromium concentration are dispersed in the solid and liquid wastes[18] chromium ion in tanning wastewater varies from 2500 to 8000 mg/L[19]. The other metals like Mn, Pb, Cd, Se, Ni, Cu, Zn and Ba are in permissible range. All the metals in fresh water are below permissible range shown in Table-1. The level of heavy metals in soil and plants samples collected from tannery irrigated water (TIW) and fresh irrigated water (FIW) were shown in Figs. 1-4.

Toxicity caused by Cr in plants is found at multiple levels that is reducing yield, badly affected the root and leaf growth[20]. The maximum concentration of Cr in soil irrigated with tannery

TABLE-1
METALS CONCENTRATION IN FRESH AND TANNERY IRRIGATED WATER SAMPLES

Metals	Mean values of fresh irrigated water (mg/L)	Mean values of tannery irrigated water (mg/L)	NEQS Limits (mg/L)
Mn	0.062 ± 0.003	0.154 ± 0.002	1.5
Pb	*ND	0.040 ± 0.020	0.5
Se	0.002 ± 0.001	0.006 ± 0.002	0.5
Zn	0.009 ± 0.001	0.085 ± 0.001	5.0
Cr	ND	4.550 ± 0.010	1.0
Ni	0.002 ± 0.001	0.006 ± 0.002	1.0
Cu	0.003 ± 0.001	0.050 ± 0.010	1.0
Ba	0.015 ± 0.001	0.233 ± 0.004	1.5
Fe	0.125 ± 0.002	7.590 ± 0.020	2.0
Cd	ND	ND	0.1

*ND: Non-detected.

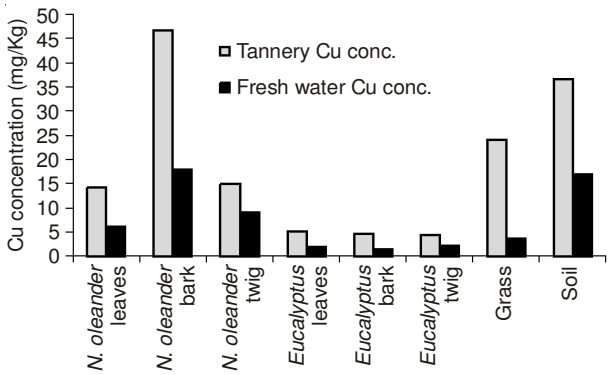

Fig. 1. Copper concentration in soil and plants of tannery irrigated water and fresh irrigated water samples

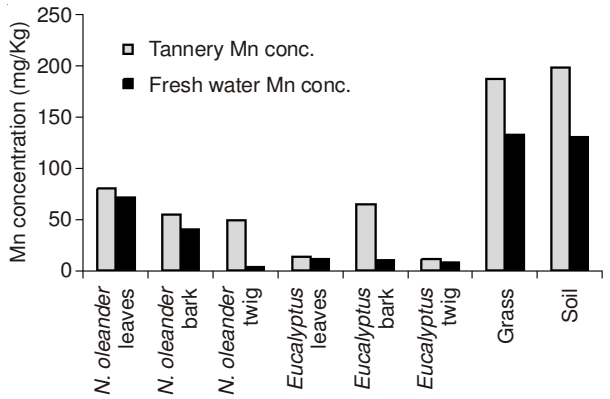

Fig. 2. Manganese concentration in soil and plants of tannery irrigated water and fresh irrigated water samples

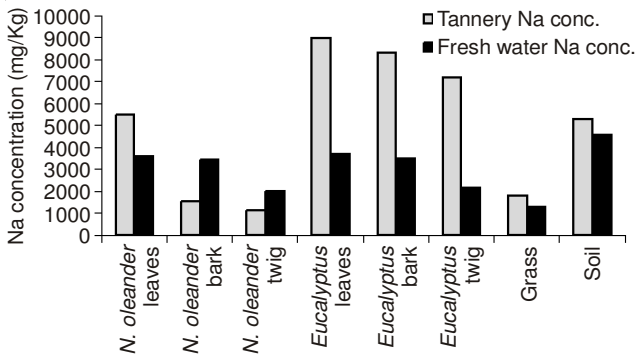

Fig. 3. Sodium concentration in soil and plants of tannery irrigated water and fresh irrigated water samples

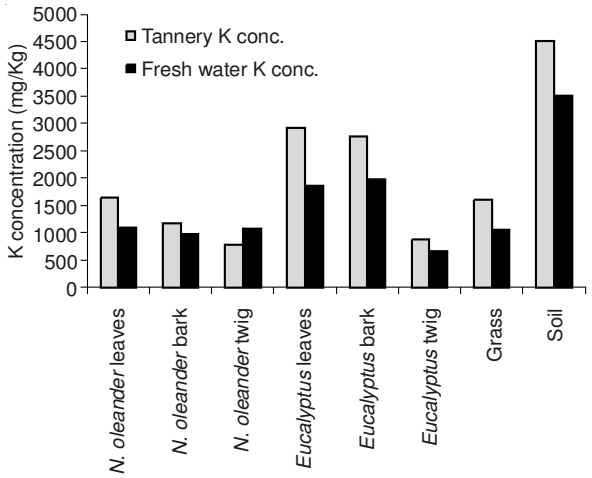

Fig. 4. Potassium concentration in soil and plants of tannery irrigated water and fresh irrigated water samples

treated water was 279.25 mg/kg. The concentration of Cr in tannery irrigated *Nerium oleander* leaves; twig and bark were in the range of 10.72-105.0 mg/kg. Concentration of Cr in tannery *Nerium oleander* leaves was (105.0 ± 1.02 mg/kg) found very high as compared to permissible limit of Cr which is 2.3 mg/kg[21]. The Cr uptakes in *Eucalyptus* leaves irrigated by tannery irrigated water were 49.35 ± 0.83 mg/kg and bark is 42.9 ± 0.55 mg/kg. However, fresh irrigated water *Eucalyptus* leaves contain Cr, 11.20 ± 0.35 mg/kg bark 10.4 ± 0.10 mg/kg and *Digitaria sanguinalis* 11.418 ± 0.3 mg/kg, which were considerably low as compared with tannery irrigated water. All the samples collected from tannery irrigated water soil having higher value than permissible level, which show that the surroundings of Kasur tannery treatment plant area were heavily polluted by Cr. The concentration of Cr in tannery treated water was 4.55 ± 0.01 mg/L, which exceed NEQS level. That is why bioaccumulation of Cr ions in soil and plants samples irrigated by tannery water samples was very high.

The concentration of Fe was found to be very high in tannery irrigated water soil and plants samples. The maximum amount of Fe ion in tannery irrigated water *Eucalyptus* bark was 986.0 ± 1.09 mg/kg in contrast the value found in fresh irrigated water soil 168.0 ± 1.05 mg/kg,. The Fe concentration in tannery soil was 359.0 ± 1.56 mg/kg presented in Table-2. The tannery irrigated water *Nerium oleander* contained remarkable Fe concentration and same pattern found in *Digitaria sanguinalis*. The result of iron in tannery effluent was 7.59 ± 0.02 mg/L, (Table-1) which exceed NEQS level. That is why bioaccumulation of Fe ions in soil and plants irrigated by tannery irrigated water were very high as compared to fresh irrigated water that considered as control sample.

Main source of Zn in *plants* is due to industries, composting materials and pesticides in agriculture[22]. The maximum Zn concentration was found in *Digitaria sanguinalis* of tannery irrigated water sample (72.8 ± 1.96 mg/kg). The Zn concentration in tannery irrigated water soil is very higher as compared to fresh irrigated water shown in Table-2. The fresh water threshold value prescribed for soil is 200 mg/kg[23]. The Zn concentration in tannery irrigated water *Nerium oleander* leaves 58.6 ± 1.25 was higher as compared to *Eucalyptus* leaves 39.21 ± 0.54. The study of Assareh *et al.*[24] showed that concentration of Zn and Cu uptake were found very high in different *Eucalyptus* species. Level of Zn metal was very high in tannery samples as compared to fresh water sample. The similar results were noticed in case of copper, manganese, sodium and potassium shown in Figs. 1-4, respectively. The study of Cheraghi *et al.*[25] showed that the heavy metals Pb, Cu, Mn and Zn uptake in vegetables and plants grown in wastewater were higher than grown in fresh water that were considered as control sample.

Correlation matrix (Table-3) of the trace metal data indicates strong positive correlations ($r^2 > 0.5$) between Cr-Cu-Zn and Cr-Mn-K and weak positive correlation ($r^2 \leq 0.5$) between Cr-Fe-Na. The significant positive correlations within these metals reveal their common source in tannery wastewater especially Cr of the study area. The positive correlation is also found in Cu-Zn-Mn. The bold values in Table-3 show strong positive correlation.

Conclusion

The present study showed that the soil, *Digitaria sanguinalis*, *Nerium oleander* and *Eucalyptus* samples taken from tannery irrigated water areas have high values of all metals as compared

TABLE-2
METALS ANALYSIS OF SOIL AND PLANTS OF FRESH AND TANNERY IRRIGATED WATER SAMPLES

Sample name	Cr (mg/kg)	Cu (mg/kg)	Zn (mg/kg)	Mn (mg/kg)	Fe (mg/kg)	Na (mg/kg)	K (mg/kg)
Tannery *Nerium oleander* leaves	105.0±1.02	14.29±0.35	58.6±1.25	80.3±1.02	560.2 ±1.98	5497.0±2.56	1649.12±1.56
Fresh water *Nerium oleander* leaves	22.17±0.10	6.15±0.45	42.88±1.09	70.9±1.05	434.1±2.74	3617.9±2.98	1085.44±1.34
Tannery *Nerium oleander* bark	56.53±0.29	46.78±1.20	31.86±1.00	54.87±0.78	520.03±2.98	1559.14±3.05	1169.05±1.57
Fresh water *Nerium oleander* bark	12.58±0.55	18.0±0.01	29.23±0.98	39.9±0.72	298.5±2.05	3445.3±2.55	976.01±1.53
Tannery *Nerium oleander* twig	10.72±0.32	15.0±0.25	39.86±0.17	49.24±0.05	500.8 ±1.05	1148.16±2.90	787.34 ±1.00
Fresh water *Nerium oleander* twig	0.71±0.10	9.0±0.15	12.87±0.18	2.81±0.02	402.0±1.79	2010.0±1.09	1072.0±2.01
Tannery *Eucalyptus* leaves	49.35±0.83	5.23±0.45	39.21±0.54	13.80±0.05	515.3±1.80	8990.0±0.46	2910.0±2.07
Fresh water *Eucalyptus* leaves	11.20±0.35	1.90±0.01	3.99±0.02	10.85±0.01	207.8±1.57	3717.0±1.98	1852.0±1.04
Tannery *Eucalyptus* bark	42.9±0.55	4.498±0.15	32.56±0.02	64.0±0.95	986.0±1.09	8304.0±2.90	2760.0±2.35
Fresh water *Eucalyptus* bark	10.4±0.10	1.46±0.20	16.2±0.01	10.55±0.35	394.4±1.34	3502.0±1.45	1984.0±3.55
Tannery *Eucalyptus* twig	11.06±0.34	4.31±0.15	33.01±1.02	11.12±0.04	605.2±1.54	7162.0±1.04	874.0±2.87
Fresh water *Eucalyptus* twig	0.25±0.01	2.12±0.25	10.83±1.00	7.77±1.00	200.7±2.08	2182.0±2.45	655.0±2.97
Tannery grass	140.63±1.2	24.01±0.29	72.8±1.96	186.6±1.02	615.8±2.05	1802.2±1.96	1605.0±0.09
Fresh water grass	11.418±0.3	3.6±0.27	53.45±1.09	132.2±1.95	425.4 ±1.06	1306.6± 1.23	1060.55±2.34
Tannery soil	279.25±2.1	36.5±0.98	58.25±1.65	190.5±1.60	359.0 ±1.56	5280.0±2.03	4500.0 ±2.57
Fresh water soil	37.6±0.25	17.0±1.00	46.0±1.05	130.5±1.20	168.0 ±1.05	4550.0 ±1.56	3500.0 ±1.98

TABLE-3
PEARSON'S PRODUCT MOMENT LINEAR CORRELATION COEFFICIENTS OF DETERMINED METAL ELEMENT IN SOIL AND PLANTS SAMPLES

	Cr	Cu	Zn	Mn	Fe	Na	K
Cr	1.00	–	–	–	–	–	–
Cu	0.62	1.00	–	–	–	–	–
Zn	0.64	0.54	1.00	–	–	–	–
Mn	0.74	0.59	0.84	1.00	–	–	–
Fe	0.11	0.01	0.31	0.07	1.00	–	–
Na	0.17	-0.26	0.06	-0.13	0.42	1.00	–
K	0.64	0.22	0.27	0.47	-0.01	0.51	1.00

to samples of these plants from fresh irrigated water of Kasur areas. Analysis of Kasur tannery treated water showed high value of Cr 4.55 ± 0.01 mg/L and Fe 7.59 ± 0.02 mg/L. Due to consequent the level of Cr and Fe were found very high in soil and plants samples of tannery irrigated water as compared to fresh irrigated water samples. The concentration of Cr was high in *Nerium oleander* leaves 105.0 ± 1.02 mg/kg and *Eucalyptus* 49.35 ± 0.83 mg/kg.

Tannery treated water is not suitable to use directly for irrigation purpose. Moreover suitable treatment and regular monitoring of Kasur tannery treated water is essential to prevent excessive build-up of these pollutants in soil and plants. The findings of this research could be helpful in monitoring the heavy metals in plants that grow in the vicinity of industrial areas.

REFERENCES

1. B.-G. Ryu, G.-Y. Park, J.-W. Yang and K. Baek, *Sep. Purif. Technol.*, **79**, 170 (2011).
2. D.H. Kim, B.G. Ryu, S.W. Park, C.I. Seo and K. Baek, *J. Hazard. Mater.*, **165**, 501 (2009).
3. S.R. Tariq, M.H. Shah, N. Shaheen, A. Khalique, S. Manzoor and M. Jaffar, *J. Hazard. Mater.*, **122**, 17 (2005).
4. G.E. Eriyamremu, S.O. Asagba, A. Akpoborie and S.I. Ojeaburu, *Bull. Environ. Contam. Toxicol.*, **75**, 278 (2005).
5. M. Muchuweti, J.W. Birkett, E. Chinyanga, R. Zvauya, M.D. Scrimshaw and J.N. Lester, *Agric. Ecosyst. Environ.*, **112**, 41 (2006).
6. S. Satarug, M.R. Haswell-Elkins and M.R. Moore, *Br. J. Nutr.*, **84**, 791 (2000).
7. B.J. Alloway and D.C. Ayres, Chemical Principles of Environmental Pollution, Blackie Academic and Professional, Chapman & Hall, London, edn. 2, pp. 208-211 (1997).
8. Y.-J. Cui, Y.-G. Zhu, R.-H. Zhai, D.-Y. Chen, Y.-Z. Huang, Y. Qiu and J.-Z. Liang, *Environ. Int.*, **30**, 785 (2004).
9. A. Maiga, D. Diallo, R. Bye and B.S. Paulsen, *J. Agric. Food Chem.*, **53**, 2316 (2005).
10. J. Barnhart, *Regul. Toxicol. Pharmacol.*, **26**, S3 (1997).
11. A.A. Ansari, I.B. Singh and H.J. Tobschall, *Chem. Geol.*, **162**, 245 (2000).
12. S. Srinivasa Gowd and P.K. Govil, *Environ. Monit. Assess.*, **136**, 197 (2007).
13. J.A. Bhalli and Q.M. Khan, *Pak. J. Biol. Sci.*, **9**, 418 (2006).
14. U. Rafique, A. Ashraf, K.A. Khan, S. Nasreen, R. Rashid and Q. Mahmood, *J. Chem. Soc. Pak.*, **3**, 644 (2010).
15. M. Radojevic, Vladimir Practical environmental analysis. Royal Society of Chemistry, Cambridge, UK, p. 366 (1999).
16. C.T. Sposito, The Chemistry of Soil, Oxford University Press, Oxford (1989).
17. The Gazette of Pakistan, Ministry of Environment Local Government and Rural Development, pp. 1289-1293 (2000).
18. K.J. Sreeram and T. Ramasami, *Resour. Conserv. Recycl.*, **38**, 185 (2003).
19. A.I. Hafez, M.S. El-Manharawy and M.A. Khedr, *Desalination*, **144**, 237 (2002).
20. K. Arun, T.I. Shankera, C. Carlos, L. Herminia and S. Avudainayagam, *Environ. Int.*, **31**, 739 (2005).
21. A. Maleki and M.A. Zarasvand, *Southeast Asian J. Trop. Med. Public Health*, **39**, 335 (2008).
22. M. Romic and D. Romic, *Environ. Geol.*, **43**, 795 (2003).
23. BIS, Indian Standard Drinking Water Specification, Manak Bhavan, New Delhi, p. 10500 (1991).
24. M.H. Assareh, A. Shariat and A. Ghamari-Zare, *Caspian J. Environ. Sci.*, **6**, 97 (2008).
25. M. Cheraghi, B. Lorestani and N. Yousefi, *Int. J. Bot.*, **5**, 190 (2009).