Soil Contamination from Toxic Elements Irrigated with Mixed Industrial Effluent and its Environmental Impact on the Urban Area of Karachi, Pakistan

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Abstract: The present research was designed to determine the chemical sources and mobilization of nine trace elements in soil samples, a potential hazard to inhabitant of Karachi was revealed due to accumulation trend of these trace metals. For productive utilization of effluent-contaminated agricultural land, mobilization and statistical analysis of potentially toxic elements in soil irrigated with mixed industrial effluent, surface and underground water have been undertaken. Samples collected from agriculture farms soils with sewage irrigation, located in the basin of and around Malir River were considered contaminated because, industrial and municipal effluents used for irrigation and different (poultry, industrial and municipal) wastes used as a fertilizer and conditioner, which results in trace heavy metals contamination and human exposure risk. Twenty four (24) contaminated four (4) non-contaminated soil and eight four (84) vegetable, fruit & fodder samples were collected from different agriculture farms included in this study. It is revealed that vegetable, fruit and fodder growing in effluent contaminated field show toxic metals transfer factor 0.11 to 1.5 for most of the PTE (Potentially Toxic Elements) like Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb and Zn. For 24 contaminated and non-contaminated soil samples, contamination factor (CF) and pollution load index (PLI) were estimated, showing> 2.5, 2.5×10^{-6}, 1.114 and 0.239 respectively.

Key words: Chemical source · Mobilization · PTEs · Enrichment · PLI · Effluent

INTRODUCTION

Metals exert a marked impact on the quality of soils and food production. Many investigations have been conducted on the health and ecological effects produced by contamination of terrestrial ecosystems with metals [1-2]. Plants growing on industrial effluent-contaminated soil accumulate potentially toxic elements (PTE) from the soil and to some extent from air. PTEs like iron (Fe), zinc (Zn), copper (Cu) and manganese (Mn) are essential trace elements to plant life while lead (Pb), chromium (Cr), nickel (Ni) and cadmium (Cd) are toxic even at a very low concentrations. However, all these metals are toxic beyond a certain threshold value that may vary with nature and species of element and plant. The accumulation of PTEs may vary from plant to plant and soil to soil. Epstein and Jefferies [3] reported that many varieties exhibited differential uptake of plant nutrients. Variation in nutrient absorption among crop varieties was most likely not caused by a single biological mechanism [4]. Metal variation in plants is due to the availability of metals to plants that depend on total concentrations in the soil and by the forms in which they occur [5]. The availability of soil metals to plants is also a function of soil properties like pH, organic carbon, cation exchange capacity [6-9] and microorganisms around the root zone. Most of the metals are retained in top soil and their concentration decreases with increase in depth. Folic acid and humic acid also play a major role in the migration of metals [1].

Main sources of PTEs in waste water originate from urban and industrial effluents as well as the deterioration of sewage pipes and plumbing fixtures. Waste water irrigation is known to contribute significantly to the heavy metal content of soils [11-14]. Traffic and industrial activities in the new urban area has been increasing and causing heavy metal contamination in urban and suburban soils. Urban soils were the recipients of large amounts of heavy metal from a variety of sources [15].

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Other sources of heavy metal contamination associated with agricultural soil are sewage sludge, fertilizer and pesticides [11, 16]. The contamination of soils directly influences public health, because soils exert a direct impact on human health due to the fact that individuals easily come into contact with them [17-18]. Industrial and domestic effluent are either used or disposed on land for irrigation purpose, which creates both opportunities and problems. The opportunities of wastewater irrigation are that it provides convenient disposal of products and has the beneficial aspects of adding valuable plant nutrients and organic matter to soil [19]. Irrigation is one of the best uses for sewage effluent because it does not require the high quality water that is of value to crops [20-22]. However, in suburban areas, the use of industrial or municipal waste water is common practice globally [22-23] including in Pakistan [11, 20]. Many investigations were conducted which showed heavy metal contamination levels in waste water irrigated soils [14-24, 12, 20]. To best of our knowledge no work has been done to study the rate of accumulation of PTE (mobilization, enrichment, contamination factors and pollution load index) in soil and plants growing on industrial effluent contaminated soil of Malir River basin. In this investigation, we studied the mobility ratio and enrichment factor to reveal the behavior of different vegetable fruit and fodder species to understand and identify the best adapted plants growing on contaminated soil for prospective utilization of agricultural farms.

MATERIALS AND METHODS

Soil contamination was assessed using various indices, including enrichment factors, contamination factors and degree of contamination. A further impact of heavy metal contamination and a resulting health risk were revealed through the transfer factor from soil to crop.

Sampling and Analytical Method: Sampling was carried out for 1 year from January 2009 to December 2010. In wastewater irrigated farms profiles were dug. Soil samples were taken at the following depths: 0 to 50 cm for topsoil. A total of twenty four (24) farms (n=96) samples were collected from sewage irrigated soil from site-A shown in Figure 1. A total of four (4) farms soil sample (n=16) were also collected from River, Canal and Tube well water-irrigated site-B shown in Figure 1. Vegetable, fruit & fodder sampling was made during mid-growing period (March-June 2009). Twenty two altogether sample were selected for this study which representing the major species cultivated in this area in the sampling season.
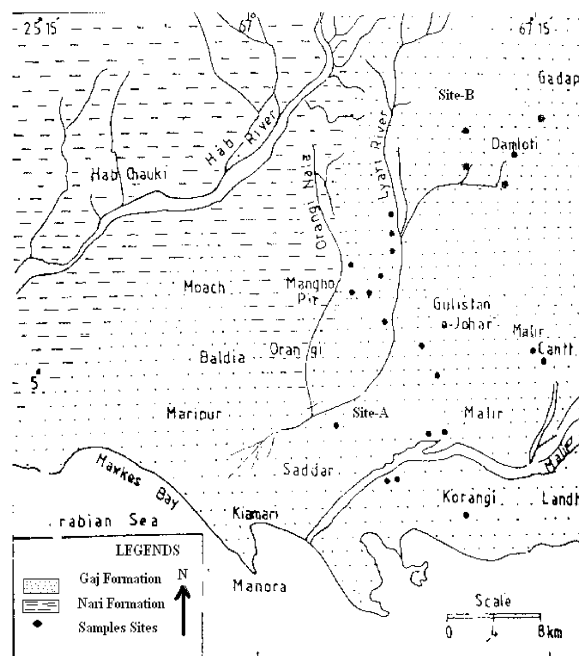

Fig. 1: Sampling Location

At each sampling site, twenty two (22) crops samples (n=88) were collected in the field by means of a random sampling method. In the laboratory, the soil samples after air drying at room temperature were sieved with nylon mesh (2 mm). The <2-mm fraction was ground in an agate mortar and pestle and passed through a 60 micron sieve. For heavy metal analysis, the soil samples were digested in aqua regia (1:3 HNO_3: HCl) and heated under reflux. After filtration, solutions were diluted with 2M HNO_3.The heavy metals in resulting solutions were determined using atomic absorption spectrometry Thermo iCE3500 [25-26].

Enrichment Factor: The enrichment factor (EF) was based on the standardization of a tested element against a reference one. A reference element is the one characterized by low occurrence variability. The most common reference elements are Sc, Mn, Ti, Al and Fe [27-30]. This study used Mn as a reference element. Eventually, the value of the enrichment factor was calculated using the modified formula based on the equation suggested by Buat and Chesselet [31].

$$EF = Cn_{(sample)}/Cref_{(sample)}/Bn_{(background)}/Bref_{(background)}$$

Where Cn (sample) is the content of the examined element in the sample environment, C_{ref} (sample) is the content of the reference element in the examined environment, Bn (background) is the content of the examined element in the reference environment and Bref (background)

is environment and Bref (background) is the content of the reference element in the reference environment. Five contamination categories are recognized on the basis of the enrichment factor [30].

EF < 2	Deficiency to mineral enrichment
EF = 2-5	Moderate enrichment
EF = 5-20	Significant enrichment
EF = 20-40	Very high enrichment
EF > 40	Extremely high enrichment

Contamination Factor (CF) and Pollution Load Index (PLI): The degree of extent of metal pollution in the affected soils was measured and compared using the pollution load index of Tomlison *et al.* [32]. The index is based on the values of the concentration factors CF of each metal in the soil. CF is the ratio obtained by dividing the mean concentration of each metal in the soil by baseline or background value [33-35].

$$SCF=\frac{C_{metal}}{C_{background}}$$

$$PLI = CF_1.CF_2.CF_3...........CF_n$$

Contamination factor is used to evaluate the pollution of the environment by single substance. The sum of contamination factors expresses the value of contamination degree which describes the contamination of the environment by all examined substances. The sum of the contamination factors for all the elements examined was represented as PLI. Values of PLI close to 1 indicate heavy metal loads near the background level; while values above 1 indicate soil pollution [36]. The degree of contamination defines the quality of the environment as follows:

F <1	Low contamination factor
1<CF < 3	Moderate contamination factor
3>CF < 6	Considerable contamination factor
CF > 6	Very high contamination factor

The value of contamination degree may be utilized in characterization the role of a given element in the global contamination of the reservoir by determining the proportion of a given element in the contamination [35, 37].

Transfer Factor: An approach based on soil-plant partition coefficients provides a simple and useful method for assessing uptake for the purpose of estimation and screening. To characterize quantitatively the transfer of an element from soil to plant, the soil-plant Partition Coefficient or Transfer Factor (TF) of Concentration Ratio or Biological Accumulation Coefficient (BAC) that expresses the ratio of contaminant concentration in plant parts to concentration in dry soil is used [32, 36, 38-40].

$$TF=\frac{C_{plant}}{C_{soil}}$$

Where C_{plant} & C_{soil} are the plant and soil concentrations, respectively. The parameter is zero if the element enters the plant only from the soil. A prerequisite of the soil-plant materials and methods transfer factor concept is the presence of a statistically significant relationship between the content of a given element in the soil and plant [41]. These values are needed for many assessment models to predict the concentration of an element for a given plant species at an anticipated contamination level in the soil [41]. TF describes the amount of an element expected to enter a plant from its substrate, under equilibrium conditions [42-43].

Site Description: The study area is located in basin of Malir River (Site-A) on E67°51´6.47½ N24°44´.52.34½ & E67°13´02.07½ N24°52´.01.27½ in east of Karachi Metropolitan city where the vegetable, fruit and fodder grown along and within the basin of the river are irrigated with domestic and industrial effluent from Korangi and Landhi Industrial zones, a suburban region, has a surface area of 9.3Km² (˜90% of total area) is occupied by vegetable and fodders crops. Agricultural lands in this area have been under wastewater irrigation for an unknown period of time. Site-B located on E66°59'46.83" N25° 7'5.57" north of Karachi Metropolitan irrigated with River/ Canal and Well water. A detail survey was done to identify the locations where waste water from industries and municipal/domestic sewage are currently used for irrigation of vegetables, fruit & fodders.

RESULTS AND DISCUSSIONS

Table 1 shows the soil (site A & B) physiochemical properties, variations in pH, OM and CEC with soil depth. At site A, soil pH decreases with depth. The mean pH in wastewater irrigated soils is 8.21 in topsoil and 7.09 in subsoil. At site B where river and well water are used, soil pH values of control soil is nearly neutral. Higher pH in the upper layers of soils of sites-A is attributed to alkalization effect of basic cat-ions (especially Ca) contained in wastewater [44]. Beside pH soil organic matter (OM) is the most important indicator of soil quality and plays a major role in nutrient cycling.

Table 1: Physiochemical properties

Site	Depth (cm)	pH (1:10)	OM (%)	CEC (1:10)(mol/kg)	Cat Ions-Exch. rate (mg/kg)	Clay (%)
A	0-10	8.21	23.2	51.9	3,410	21.29
	>10-20	8.07	31.9	43.4	2,240	20.22
	>20-30	8.19	17.9	44.9	1,830	29.17
	>30-40	6.47	12.38	20.1	1,050	32.75
	>40-50	7.09	2.89	7.3	1,260	36.14
B	0-10	7.64	3.29	8.38	2,360	11.28
	>10-20	7.38	2.28	6.9	177	9.97
	>20-30	7.20	1.94	5.58	162	9.08
	>30-40	7.02	1.39	4.93	144	4.38
	>40-50	6.98	0.84	4.14	132	3.99

Table 2: Minimum, Maximum, Mean Concentrations and Standard Deviation of PTEs in Sewage Irrigated Farms Soil, mg kg^{-1} (Site-A)

Metals ($N = 96$)	Minimum	Maximum	Mean±SD
Cd	0.94	2.78	2.083±0.489
Cr	18.74	99.69	40.96±18.27
Cu	4.66	15.94	11.61±5.176
Fe	5836.0	12796.0	10134.0±2023.0
Hg	0.259	5.463	1.248±1.23
Mn	332.6	632.0	466.104±89.5807
Ni	17.44	100.82	38.67±21.63
Pb	14.88	61.36	30.87±13.42
Zn	19.78	177.6	59.09±32.58

Table 3: Minimum, Maximum, Mean Concentrations and Standard Deviation of PTEs in River and Well water Irrigated Farm Soil, mg kg^{-1} (Sit-B)

Metals ($N = 16$)	Minimum	Maximum	Mean±SD
Cd	0.47	1.89	1.435±0.356
Cr	1.72	39.76	21.385±13.509
Cu	2.56	10.74	7.635±2.765
Fe	598.3	1247.2	9521.0±2959
Hg	0.001	0.0058	0.00145±0.0004
Mn	3.72	6.82	4.703±1.437
Ni	4.16	46.88	30.915±15.78
Pb	3.36	28.47	26.017±2.274
Zn	4.72	45.38	31.005±11.785

In this study, addition of organic matter through wastewater irrigation is comparable to those of sewage sludge application. In wastewater irrigated soils (site-A), there is a decrease in organic matter content ranging from 32% for topsoil to 3% for subsoil as compared to tube well water-irrigated soil OM contents are 0.84 to 3.24%. OM content in soils is considered as NOM (natural organic matter). Thus the use of wastewater with high BOD has increased OM up to 20% to 30% as compared to river and well water-irrigated soils. Cation exchange capacity (CEC) ranges from 51.9 to 7.3 (for site-A) and 8.4 to 4.14 (for site-B). In wastewater irrigated soils, a significant variation in CEC values is observed. This can be attributed to the high organic matter content and high loading of Ex-Ca rather than variability in clay content of soil. The concentration of Ex-Ca for these soils decreases sharply with depth. This indicates that topsoil have received a large amount Ca during wastewater application. This trend is very similar to the decreasing trend of CEC in soil profile. Although the soil adsorption capacity of sandy soil is quite low, the wastewater irrigated soils (site-A) can accumulate > 3400 mg/kg exchangeable Ca in topsoil. Apparently, a great increase in soil adsorption capacity induced by wastewater prompts the accumulation of certain heavy metals in the soil. In addition to OM content and pH, the exchangeable Ca may be a useful parameter for predicting the heavy metal accumulation in soil as this kind of Ca is water soluble and rapidly reacts with other elements [45]. Generally, it may be said that direct use of wastewater for irrigation has increased soil adsorption capacity through increase in pH, OM and Ex-Ca which in turn leads to accumulation of heavy metals in affected soils. Organic complex molecules of Low Molecular Weight (LMW) serve as carriers of micronutrients. LMW was shown to increase Cd uptake [46-47], whereas the presence of organic matter was reported to enhance the uptake of Zn in wheat plants [48].

Table 2 and Table 3 summarize the range, mean and standard deviation of PTEs concentrations in soil samples collected from the investigated sites. The results show that concentrations of PTEs in wastewater-irrigated soils are higher than those in control site.

Table 4: PTEs concentration (mean±SD) in Vegetables, Fruits and Fodder grown in sewage irrigated farms soil, mg kg^{-1}

N = 88	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn
Brinjal (*Solanum melogena L.*)	0.855±0.129	3.39±1.57	10.58±4.08	46.32±9.11	0.99±0.135	13.68±2.65	3.94±1.573	10.65±3.112	34.98±13.88
Beet root (*Beta volgaris*)	1.02±0.101	5.23±0.24	10.59±0.7	318.34±4.2	2.78±0.28	92.07±7.05	1.15±0.12	0.94±0.217	78.46±5.06
Ridge gourd (*Luffa acutangula L.* roxb)	0.839±0.302	1.16±0.88	9.98±2.74	42.96±14.97	0.938±0.69	18.95±8.84	4.725±1.34	10.918±4.43	44.08±13.69
Bottle gourd (*Legionary sicerraria Molina standl L*)	0.846±0.243	1.352±0.984	9.036±1.86	52.14±18.57	0.625±0.237	21.24±7.73	5.103±1.432	6.035±1.85	29.98±4.58
Bitter gourd (*Momordica charantia L.*)	1.496±0.702	0.964±0.301	8.274±1.728	50.46±17.81	0.965±0.167	19.28±1.78	4.156±0.703	10.85±4.08	37.174±11.15
Capsicum (*Capsicum sp.*)	1.197±0.702	0.118±0.026	9.04±0.069	31.16±1.35	0.341±0.122	14.05±0.307	3.62±0.52	15.14±0.185	37.74±1.89
Fenugreek (*Trigonella foenum-graecum L.*)	1.95±0.835	0.04±0.001	11.43±0.672	166.49±55.79	0.785±0.457	69.59±14.46	16.35±8.175	37.016±18.5	106.7±53.35
Spinach (*Spinacea oleracea L.*)	2.668±0.45	3.06±0.0318	9.795±0.37	483.67±22.157	0.526±0.039	81.616±1.0374	6.78±0.144	17.92±0.149	35.75±1.086
Green Chili (*Capsicum frutesceus*)	1.16±0.075	0.499±0.367	10.16±1.586	29.26±6.178	1.087±0.202	14.126±7.78	3.367±1.128	9.436±2.45	34.027±6.248
Cluster Bean (*Cyamaoposis tetragonoloba L.*)	1.128±0.087	0.0705±0.04	6.435±0.775	52.218±1.487	1.388±0.415	34.485±1.129	5.006±0.103	15.66±0.268	33.865±2.003
Mint (*Mentha spicata L.*)	1.033±0.2045	5.495±2.376	11.367±1.878	320.45±168.02	1.1096±0.47	81.716±26.17	5.627±0.716	12.22±0.616	42.038±5.299
Hyacinth Bean (*Dolichos lablab L.*)	0.535±0.0735	0.0635±0.031	4.396±0.574	60.31±1.45	0.773±0.126	17.389±2.317	5.362±1.242	13.86±0.735	34.7±3.28
Red Broad Bean (*Vicia faba L.*)	1.537±0.595	1.1±0.848	5.698±0.823	34.218±2.91	1.615±0.657	16.92±0.878	5.136±0.352	9.315±1.084	43.57±3.95
Cauli flower (*Brasica oleracea L.*)	0.937±0.045	3.98±1.27	6.087±1.368	47.284±12.39	0.173±0.024	17.295±3.648	3.287±0.844	4.907±0.655	38.274±2.984
Green Cabbage (*Brasica Juncea L.*)	1.026±0.238	5.628±1.66	9.69±2.18	58.347±13.277	0.9325±0.07	21.298±6.274	5.337±2.168	3.287±1.044	53.824±12.73
Sweet potato (*Solanum tuberosum*)	1.765±0.869	0.0335±0.008	5.26±0.614	291.85±5.928	0.539±0.208	14.126±3.18	4.35±0.498	20.796±0.68	17.994±0.427
Okra (*Abelmoschus esculentus L.*) moench)	1.05±0.212	3.1±2.404	9.533±3.748	39.908±28.15	0.811±0.15	22.73±4.43	4.524±0.342	21.249±24.3	51.54±29.65
Papaya (*Carica papaya*)	0.0065±0.004	0.816±0.223	0.152±0.0268	10.19±3.476	0.4225±0.21	0.68±0.293	0596±0.249	0.616±0.169	1.523±0.172
Guava (*Psidium guajava L.*)	0.807±0.0127	0.0346±0.008	4.91±1.102	38.47±1.253	0.822±0.233	8.872±0.574	3.71±0.542	3.876±0.58	13.556±1.023
Chico (*Makilkara Zapota L.*)	0.649±0.318	5.049±3.664	0.933±0.167	73.33±41.898	1.427±1.105	11.75±1.65	5.627±2.685	8.873±2.006	11.35±1.784
Corn seed (*Zea mays*)	0.86±0.179	0.0335±0.009	2.78±0.697	15.94±1.325	0.644±0.478	13.35±1.242	3.862±0.205	6.073±0.292	25.57±1.158
Fodder	0.994±0.307	2.24±1.74	8.136±2.91	234.46±78.65	1.253±0.944	80.927±49.67	5.093±1.739	13.437±5.16	40.25±11.84

Table 5: PTEs Transfer Factor (TF) from Soil to Vegetables, Fruits and Fodder, mg kg^{-1}

	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn
Brinjal (*Solanum melogena L.*)	0.421	0.0825	0.9114	0.0046	0.8013	0.0314	0.1027	0.3467	0.683
Beet root (*Beta volgaris*)	0.573	0.1367	1.015	0.0314	2.2357	0.2865	0.03875	0.031	1.32707
Ridge gourd (*Luffa acutangula L.* roxb)	0.4057	0.0374	0.975	0.00424	0.8427	0.04154	0.12487	0.3537	0.7568
Bottle gourd (*Legionary sicerraria Molina standl L*)	0.4156	0.03479	0.8675	0.0142	0.5015	0.0456	0.13389	0.285	0.5164
Bitter gourd (*Momordica charantia L.*)	0.72624	0.01857	0.7126	0.0149	0.8633	0.0414	0.1075	0.441	0.6382
Capsicum (*Capsicum sp.*)	0.6657	0.00298	0.868	0.0035	0.274	0.0302	0.1836	0.579	0.657
Fenugreek (*Trigonella foenum-graecum L.*)	1.1406	0.00187	1.1841	0.0254	0.648	0.158	0.2114	0.6895	1.1028
Spinach (*Spinacea oleracea L.*)	1.3708	0.1635	0.845	0.0567	0.4215	0.175	0.184	0.672	0.6058
Green Chili (*Capsicum frutesceus*)	0.567	0.0122	0.965	0.0037	0.962	0.0303	0.1762	0.3064	0.6748
Cluster Bean (*Cyamaoposis tetragonoloba L.*)	0.5434	0.00262	0.6448	0.0142	1.112	0.0748	0.1385	0.5163	0.653
Mint (*Mentha spicata L.*)	0.5862	0.1342	1.069	0.0316	0.9782	0.2653	0.1464	0.486	0.7114
Hyacinth Bean (*Dolichos lablab L.*)	0.2659	0.0024	0.3854	0.01495	0.6284	0.0373	0.1476	0.4583	0.6763
Red Broad Bean (*Vicia faba L.*)	0.7468	0.02776	0.49087	0.00338	1.29447	0.03629	0.1327	0.3017	0.73746
Cauli flower (*Brasica oleracea L.*)	0.5488	0.1875	0.5243	0.0047	0.1386	0.0371	0.085	0.159	0.6477
Green Cabbage (*Brasica Juncea L.*)	0.4926	0.1374	0.8346	0.0058	0.7472	0.0457	0.138	0.106	0.9109
Sweet potato (*Solanum tuberosum*)	0.8564	0.0017	0.4535	0.0377	0.4324	0.1946	0.1125	0.6738	0.3046
Okra (*Abelmoschus esculentus L.*) moench)	0.5042	0.07568	0.8211	0.00484	0.6589	0.05768	0.1184	0.6975	0.9627
Papaya (*Carica papaya*)	0.00312	0.0289	0.0135	0.0011	0.3565	0.00154	0.0244	0.02	0.0346
Guava (*Psidium guajava L.*)	0.4783	0.0027	0.4225	0.00469	0.749	0.02803	0.1859	0.126	0.239
Chico (*Makilkara Zapota L.*)	0.3128	0.1245	0.1704	0.0163	1.1426	0.0252	0.1464	0.3786	0.2831
Corn seed (*Zea mays*)	0.41378	0.0017	0.2483	0.00247	0.5167	0.0376	0.1898	0.2867	0.4325
Average transfer factor	SS1.0891	0.1184	1.2680	0.0281	1.5060	0.1613	0.2574	0.7261	

Table 6: PTEs Mean Concentrations, Contamination Factor (CF) and Pollution Load index (PLI) in Soil, mg kg^{-1}

	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn	EF	CF	PLI
F1-24 (Fsi)*	2.083	40.96	11.61	10134.0	1.248	466.11	38.67	30.87	59.09	2.19	2.58891	1.114
F1-4 (Frcwi)**	1.435	21.385	7.635	9521.0	0.0015	4.703	30.92	26.02	31.005	0.37	0.00000251	0.239

*Fsi Farms Soil with Industrial mixed Sewage Irrigated, **Frcwi Farm Soil Irrigated with River, Canal & Well Water

The obtained results also indicate both the sites exhibited different concentrations of heavy metals. Greater concentrations after wastewater irrigation in site-A compared to site-B are probably due to greater amounts of wastewater used in site-A. Cu does not show any significant change in both soils. On average, wastewater irrigation results in 4.5%, 7% and 4% increase in the Ni, Pb and Cd concentrations, respectively, in the soils of site-A, concentration of heavy metals in well water- irrigated soils is generally very close to background level in non-polluted soils. Thus, taking into account the obtained data and concentration in non-polluted soils (site-B), application of wastewater has seemingly enriched the soils in heavy metals. The PTEs concentrations range in soil of the study sites-A are Cd 0.4-2.78, Cr 18.74-99.69, Cu 4.66-15.94, Fe 5836-12796, Hg 0.259-5.463, Mn 332.6-632, Ni

17.44-100.82, Pb 14.88-61.36, Zn 19.78-177.6 and Site-B are Cd 0.47-1.89, Cr 1.72-39.76, Cu 2.56-10.74, Fe 598-1247, Hg 0.001-0.0058, Mn 3.72-6.82, Ni 4.16-46.88, Pb 3.36-28.47, Zn 4.72-45.38. Although the concentrations of these metals measured in soils site-A were beneath the maximum permitted levels, the trend has been towards increasing concentrations for Fe at both sites followed by Zn, Mn, Ni, Cr, Pb, Hg and Cd and the minimum was observed for Hg and Cd. Fe, Mn, Zn, Ni and Pb concentration were in increasing order. The reason for the high PTE concentration due to industrial emissions and industrial effluent discharge without treatment and vehicular emission nearby passing roads. At site-B the concentration of each metal has the lowest value in soil because industrial sewage mixed effluent was not using for irrigation. Table 4 shows the concentration ranges of PTEs in vegetable fruits and fodders samples being grown in farms of Malir River basin site-A. The transfer factor of PTEs soil to vegetable, fruits and fodders shown in Table 5, the average transfer factor trend is as follow Hg>Zn>Cu>Cd>Pb>Ni>Mn>Cr>Fe. The Enrichment Factor of the PTEs is >2, belongs to the categories "deficiency mineral enrichment" and "moderate enrichment" in the classification of Sutherland 2000 defined five contamination categories. Contamination factor and pollution load index of PTEs is also >2 and >1 respectively, belong to moderate contamination factor and high pollution load index in soil. The calculated contamination factor and pollution load index showed that the metal pollution in soils increased over the past decades shown in Table 6. Absorption and accumulation of heavy metals in plant tissue depends upon various factors, which include temperature, moisture, organic matter, pH and nutrient availability shown in Table 1.

CONCLUSION

The concentration of PTEs increased in soil and plants where waste water irrigation is frequently practiced. The concentrations of some metals were higher in vegetables and soils irrigated with industrial and municipal mixed wastewater than those irrigated with ground or river water. This is the first study on the potential impacts of wastewater irrigation on soil properties and PTEs contents in soils, vegetables, fruit and fodder in Malir River Basin. The results obtained from this preliminary study show that use of wastewater for irrigation purposes in the study area lead to change in soil quality (pH, OM, Ex-Ca), increase in heavy metal

concentration in soil (notably Cd, Cr, Cu, Fe, Ni, Hg, Pb and Zn) and vegetables (Cd, Cr, Ni, Pb and Zn) and probably pose potential health risk through consumption of affected vegetables (HQ > 1). Although the present severity of this situation is moderate, long-term application of wastewater will maximize the rate and extent of future contamination problems. PTEs concentration was above what are considered as acceptable limits for food production in soil and vegetables at each site [49-50]. However, the metal transfer (TF for Cd 1.089, Cr 0.118, Cu 1.27, Fe 0.028, Hg 1.51, Mn 0.16, Ni 0.257, Pb 0.726 and Zn 1.24) and accumulation trend increased in comparison to background values. In this study, it was observed that rapid pace of industrialization and urbanization in Karachi Metropolitan occupied a large area of Malir and Lyari River Basin irrigated by sewage or industrial mixed effluent. However, Cd, Cr, Cu, Mn, Ni, Fe, Pb and Zn concentrations in vegetables exceeded levels considered as potentially dangerous >0.3 mg/Kg for leafy vegetables [49]. The presence of PTEs in the vegetables requires further analysis and evaluation, particularly because of long-term effects on human health. Each of these problems is a matter of concern and needed to alleviate. In order to minimize the negative impacts of wastewater irrigation in the study area, the following approaches are proposed:

Strict legislation and stringent standards must be enforced to prevent the use of sewage & industrial mixed effluent for irrigation purposes. An integrated system for the treatment and recycling of wastewater needs to be developed in the study area. For this purpose, governmental authorities should provide prompting or supporting mechanisms.

In order to terminate irrigation with wastewater, the farmers are obligated to remove all pumps installation along Malir River basin. It is also proposed that through a general education pro- gram, they become aware of the negative impacts of wastewater irrigation. With respect to long term application of wastewater in affected sites, operational monitoring should be conducted to verify the build up of heavy metals in view of their significant accumulation in phyto available fraction associated with changes in soil properties.

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