Determination of Heavy Metals in Vegetables and Soils at Sewerage farm in Sindh Industrial Trading Estate(SITE), Karachi

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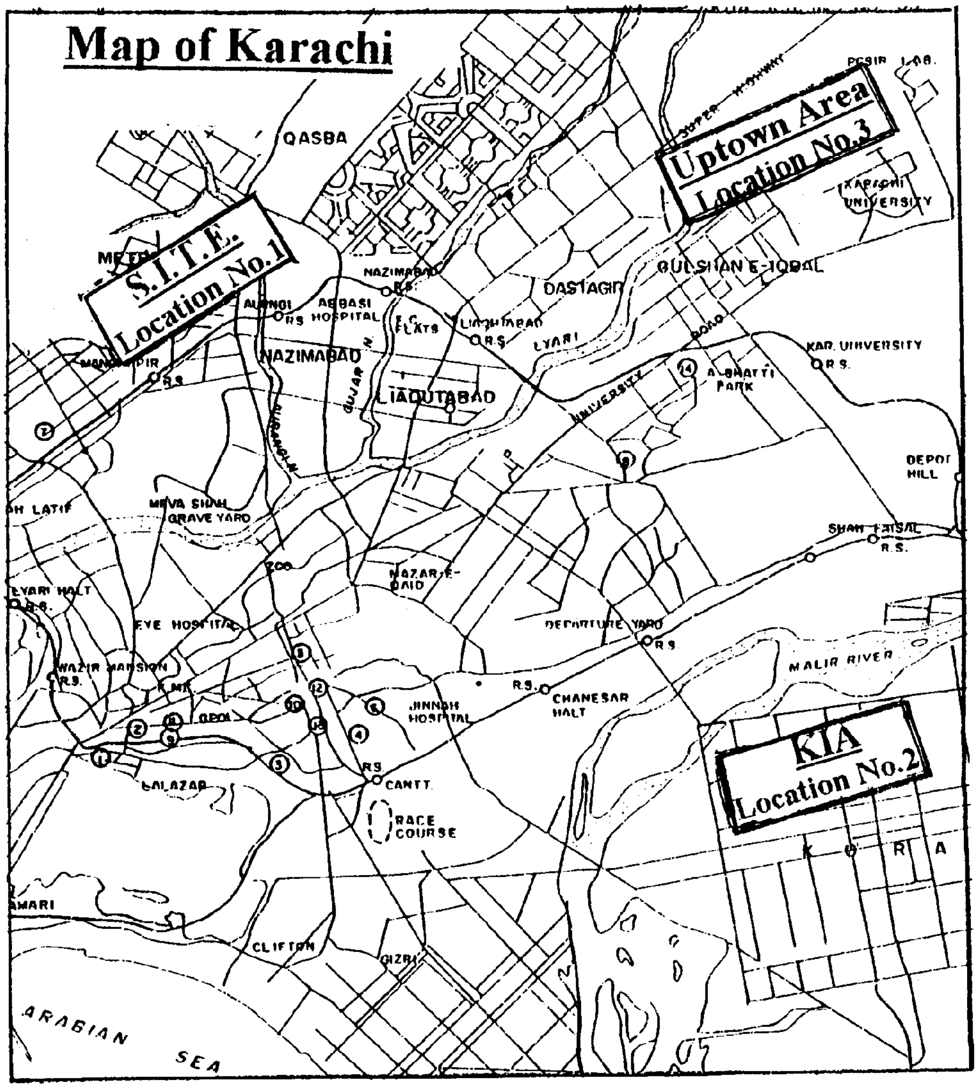
Summary: A study was conducted to determine the concentration of heavy metal accumulation, in soil and vegetables grown at Gutter Baghicha, where untreated mixture of industrial effluents and sewerage is being used. The maximum concentration of heavy metals determined in soil were found to be 12228 (Fe), 870 (Zn), 439 (Mn), 177 (Cu), 64 (Ni), 63 (Cr), 122(Pb), 0.98 (Cd) and 14 (Co) ppm. It is concluded that the high levels of heavy metals found in the vegetables grown in this area is due to continuous use of untreated industrial effluents The heavy metals accumulation in the vegetables grown on these soils were also determined. The matrix correlation for all these metals is reported. These correlations indicate that the metals came from the same source. The physical properties of soil and heavy metals concentration in particulate matter / water used for irrigation is also presented. This baseline data generated will help to establish any harmful effect on human with the use of vegetables grown with polluted waster.

Introduction

Heavy metals along with other pollutants are discharged to the environment through industrial activity, automobile exhaust, heavy-duty electric power generators, refuse burning and pesticides used in agriculture etc. Men, animals and plants through air, water and food take up these metals from the environment. Heavy metals have great significance due to their tendency to accumulate in the vital human organs over prolonged period of time. Injury to vegetation caused by heavy metals has been well recognised because of many botanical and chemical investigations during the past hundred years. Plants are more sensitive to pollution than animals or man. More than sixty elements in various parts of human body have been detected [1] among these at least 25 elements are essential to human out of which 14 are termed as trace elements.

Trace elements play a very important role in chemical, biological, biochemical and enzymatic reaction in the living cells of plants, animals and human bodies. The role of trace element in the body metabolism is of prime importance. Their deficiency causes diseases, whereas the presence of excess of trace elements causes toxicity to human life. Food contaminated by these elements causes several diseases affecting hundreds of million of peoples every year all over the world. Vegetables are widely used through out the world as part of food. In Pakistan also it is a major part of food and taken both in raw and cooked form. Untreated sewage and industrial wastewater is commonly used for the cultivation of vegetable around the urban area of Pakistan. Several studies have been carried out to estimate the heavy metals content in vegetables



grown in polluted and non-polluted areas of Pakistan [2-5]. Karachi is the largest and biggest industrialised city of Pakistan. Its present population is estimated to be more than ten million [6]. It is the centre of professional and commercial activities and only Port City of Pakistan.

The vegetable grown around Karachi City with sewerage and industrial wastewater is of great concern. The main aim of present study is conducted to investigate the presence of heavy metals in vegetable grown near the largest industrial area of Karachi and to identify their cause and source of contamination. The effect of local environment on the vegetables grown in this area becomes necessary to monitor vegetable sample and establish their heavy metal levels to avoid health hazards. Because low level of heavy metals present in food have the tendency to accumulate in human organs over prolong period of time.

Result and Discussion:

Present study was carried out to determine the concentration of heavy metals accumulation, in soil and vegetables grown at Gutter Baghicha, located in

S.I.T.E. where wastewater is being used from TP1. Different varieties of vegetables grown in the Gutter Baghicha, were analysed for Fe, Cu, Pb, Zn, Mn, Ni, Cd and Co contents. The precision and accuracy of the procedures used in these analysis were checked by analysing the NBS, standard reference material spinach (NBS-1570), for Zn, Cd, Pb, and Cu contents. Table I present the comparison of measured values with reference values, which are in good agreement.

Table I

Element	Measured Value (μg/g)	Reference Value (μg/g)
Zinc	48.92 ± 1.9	50 ± 2
Cadmium	1.41 ± 0.07	1.5± 0.02
Lead	1.34 ± 0.22	1.2 ± 0.2
Copper	10.62 ± 1.11	12 ± 2

The maximum concentration of Fe 319 mg/kg was found in spinach grown in plot no IV, Zinc 322 also in plot no IV, Mn 5.5 in pumpkin, Cu 21.62 in spinach grown in plot no V, Ni 4.6 in spinach grown in plot II. Cr 1.65, Pb 2.79 & Cd 5.77 mg/kg in spinach and Co 0.37 mg/kg in mustard grown in plot V. It can be seen here that spinach was the most contaminated vegetable grown in this area. Earlier observations suggested that leafy vegetables contain larger amount of heavy metals as they are relatively the most exposed food to environmental pollutants because of their larger surface area [7]. The minimum concentration of all the heavy metals determined were Fe 2.62 , Zn 34.20 , Mn 6.53 , Cu 8.34 , Ni 0.42, Cr 0.30, Pb 0.11, Cd 0.5, Co 0.02 mg/kg . The minimum concentration was found in Brinjil. The low concentration of heavy metals found in brinjil was because of the maximum rate of absorption of metals in roots, then stem, flower and fruits.

In Table II the matrix correlation for all the variables is reported. These correlations probably indicate that the metals come from similar sources and that their geographic distributions are also similar. Figures I to X show average variations of heavy metals accumulation in the vegetables grown in plot I to V. The maximum concentrations of majority of heavy metals determined were found in plot number IV and V. These plots are located near the lyari river and untreated wastewater is being pumped into these plots for irrigation. This may be the cause of relatively high concentration of the heavy metals in these plots. The concentration of

Table – II: Correlation of Heavy Metals in Vegetables Grown at Different Plots at Gutter Baghicha Site, Karachi

PLOT- I

	Fe	Zn	Mn	Cu	Ni	Cr	Pb	Cd	Co
Fe	1.000								
Zn	0.995								
Mn	-0.405	-0.462							
Cu	0.841	0.816	0.132						
Ni	0.950	0.904	-0.374	0.775					
Cr	0.911	0.806	-0.137	0.918	0.917				
Pb	0.815	0.806	0.072	0.952	0.805	0.972			
Cd	0.985	0.995	-0.545	0.755	0.934	0.876	0.758		
Co	-0.010	0.069	-0.340	-0.111	0.052	0.186	0.173	0.112	1.000

PLOT-II

	Fe	Zn	Mn	Cu	Ni	Cr	Pb	Cd	Co
Fe	1.000								
Zn	0.900								
Mn	0.975	0.860							
Cu	0.866	0.746	0.434						
Ni	0.733	-0.333	-0.427	0.434					
Cr	0.779	0.854	0.821	-0.502	0.014				
Pb	0.909	0.813	0.940	-0.205	-0.117	0.857			
Cd	0.744	-0.844	-0.632	0.794	0.651	-0.450	-0.483		
Co	0.773	0.477	0.425	-0.218	0.508	0.840	0.577	0.044	1.000

Table-II (continued)

PLOT-III

	Fe	Zn	Mn	Cu	Ni	Cr	Pb	Cd	Co
Fe	1.000								
Zn	0.944								
Mn	0.980	0.857							
Cu	0.152	-0.725	-0.375						
Ni	0.551	-0.333	-0.427	0.434					
Cr	0.590	0.854	0.821	-0.502	0.014				
Pb	0.689	0.813	0.940	-0.205	-0.117	0.857			
Cd	0.118	-0.844	-0.632	0.794	0.651	-0.450	-0.483		
Co	0.500	0.477	0.425	-0.218	0.508	0.840	0.044	0.044	1.000

PLOT - IV

	Fe	Zn	Mn	Cu	Ni	Cr	Pb	Cd	Co
Fe	1.000								
Zn	-0.375								
Mn	-0.427	0.434							
Cu	0.821	-0.502	0.014						
NI	0.940	-0.205	-0.117	0.857					
Cr	-0.632	-0.218	0.651	-0.450	-0.483				
Pb	0.425	-0.218	0.508	0.840	0.577	0.044			
Cd	0.118	-0.010	-0.042	0.956	-0.279	0.871	0.520		
Co	0.934	0.002	0.939	0.146	0.784	0.528	0.839	0.089	1.000

PLOT- V

	Fe	Zn	Mn	Cu	Ni	Cr	Pb	Cd	Co
Fe	1.000								
Zn	0.903								
Mn	0.959	0.865							
Cu	0.504	0.729	0.321						
Ni	0.707	0.740	0.851	0.125					
Cr	0.887	0.936	0.756	0.844	0.485				
Pb	0.885	0.606	0.814	0.224	0.459	0.683			
Cd	0.694	0.762	0.491	0.927	0.136	0.930	0.537		
Co	0.659	0.589	0.814	-0.092	0.959	0.347	0.531	-0.021	1.000

heavy metals determined in the water used in Gutter Baghicha is presented in Table III. It can be seen from the table that the highest concentration was found in untreated wastewater and lowest in the treated water from treatment plant effluent. It has been reported [8] that most of the metals gradually move down the soil profile. The rate of downward movement depends on the chemical characteristic of soil and the intrinsic properties of the element. The physical properties of soils form different plots were also determined and presented in Table IV. The analysis of all the soil samples showed that they belong to sandy clay loom class. There is not much difference in the quality of soils, only the pH of plot number IV and V was slightly high. The total organic carbon (TOC) in plot number V was found to be lowest (3.85%). The metals such as copper, zinc, manganese react in soils in presence of organic matter to form chelate at pH 6.5 or above and tend to become only slowly available to plants especially if they are present in high valent or oxidising form.[9]. The average concentration of heavy metals

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Table - III Heavy Metal Concentration in Water Samples at Gutter Baghicha.(mg/lit)

	Fe	Zn	Mn	Cu	Ni	Cr	Pb	Cd	Co
Sewage Water	0.312	0.048	0.076	0.025	0.015	0.032	0.015	0.004	0.004
Treated Water	0.153	0.035	0.066	0.016	0.011	0.015	0.005	0.003	0.003
Mixed Water	0.194	0.044	0.021	0.021	0.014	0.015	0.011	0.005	0.003

Table– IV: Physical Properties of Soils of Different Plots at Gutter Baghicha

Plot No	PH	Conductivity m/mohs	Moisture contents %	TOC %	Specific gravity	Bulk density	Pore space %	sand %	Texture clay %	Silt %	Soil class
1	7.5 ±0.11	0.85 ±0.02	13.7 ±0.09	6.18± 0.08	1.5 ±0.02	1.6 ±0.04	32.5 ±0.03	70.2 ±0.1	24.8 ±0.1	15.2 ±0.02	Sandy clay loom
2	7.12 ±0.9	0.75 ±0.01	56.5 ±1.2	5.22 ±0.06	2.5 ±0.06	1.8 ±0.02	27 ±0.01	59.3 ±0.8	24.8 ±0.09	13.5 ±0.06	Sandy loom
3	7.11 ±0.12	0.85 ±0.06	18.7 ±1.7	6.5 ±0.05	2.5 ±0.03	1.5 ±0.01	40 ±0.02	84.8 ±1.2	24.3 ±0.89	20.4 ±0.09	Sandy clay loom
4	7.6 ±0.14	0.95 ±0.03	13.6 ±1.1	6.77 ±0.03	2.5 ±0.01	1.7±0.01	32 ±0.09	66.1 ±1.7	20.4 ±0.1	13.6 ±0.05	Sandy clay loom
5	8.6 ±0.15	1.5 ±0.04	2.15 ±0.09	2.50. ±02	2.5 ±0.01	1.52 ±0.04	39 ±0.4	70 ±0.9	13.6 ±0.7	15.8 ±0.1	Sandy clay

Table - V: Average Heavy Metals Concentration in Soils at Gutter Baghicha (mg/kg)

Plot No	Fe	Zn	Mn	Cu	Ni	Cr	Pb	Cd	Co
1	11945± 5.3	729± 2.2	414± 1.7	151± 1.8	56±O.2	53± 0.9	94± 0.9	0.75± .01	13± .01
2	12027± 4.9	826± 3.4	339± 1.2	107± 1.5	64± 0.3	54± 0.8	67± 0.7	0.49± .01	13± 01
3	11514± 4.8	583± 1.9	309± 1.1	75± 0.4	38± 0.2	32± 0.7	120± 0.1	0.61± .02	10± .01
4	12118± 4.9	417± 1.7	370± 1.6	68± 0.2	39± 0.2	28±0.3	39± 0.2	0.49± .01	12± .01
5	12228± 5.2	870± 2.5	439± 2.1	177±1.1	64± 0.3	63± 0.6	122± 0.8	0.98± .02	14± .02

Table-VI :Heavy Metals Concentration in Particulate Matter (PM10) at Gutter Baghicha (Ug/m3)

Plot No	Fe	Zn	Mn	Cu	Ni	Cr	Pb	Cd	Co
1	341± 1.3	487± 1.1	5.7± 0.09	10.2± 0.13	0.78± 0.03	0.91± 0.04	11.2± 0.13	0.09± 0.01	0.6± 0.02
2	411± 1.4	505± 1.3	7.2± 0.08	14.3± 0.17	1.50± 0.07	1.0± 0.02	10.7± 0.11	0.04± 0.01	1.3± 0.03
3	412± 1.2	382± 1.1	6.9± 0.08	9.6± 0.09	0.73± 0.01	1.0± 0.03	19.5± 0.06	0.11± 0.00	0.5± 0.01
4	389± 1.2	376± 1.2	5.6± 0.07	8.2± 0.06	0.91± 0.01	0.89± 0.02	16.5± 0.13	0.23± 0.01	0.8± 0.02
5	448± 1.3	1260± 2.9	7.7± 0.09	12.2± 0.09	4± 0.09	2.4± 0.06	26.8± 0.17	0.33± 0.01	1.6± 0.01

determined in soils is presented in Table V. The absorption of Cd from the soil to vegetable is markedly observed in the Gutter Baghicha as the percentage intake of cadmium from the soil to vegetable specially in spinach was highest and as much as 1200 percent of cadmium was taken up from the soil by spinach. It was found that cadmium was more mobile in soils than other common trace metals [10] but there has been another report [11] that suggests the possibility of limiting the mobility and hence, presumably, the availability of cadmium to plants.

Tao Zhan 1986 [12], concluded in his study that precipitation and surface hydrolysis are likely to be the most important mechanism for cadmium immobilisation in soil. Carbonates, phosphates amorphous oxides and the edge-OH groups of clay minerals seriously influence cadmium mobility.

Liebig 1997 [13] emphasised the idea that maintenance of the natural cycle of element is required for the conservation of soil fertility. Many substances contained in wastewater effluents represent one of the available sources of fertiliser constituents apart from solid waste material such as garbage & artificial fertilisers. The nutrients may be returned to soil in admixture with the wastewater by irrigation or as sludge separated from the water by wastewater treatment. Over the past 20 years, there

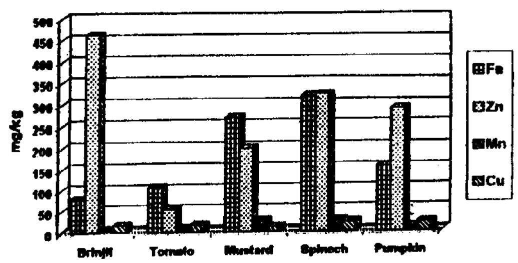

Fig. 1: Average Concentration of Heavey Metals in Gvegetables Grown in Plot-I.

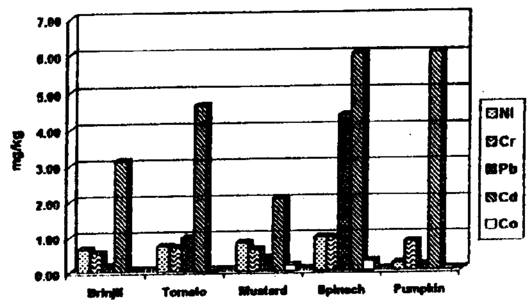

Fig. 2: Average Concentration of Heavey Metals in Gvegetables Grown in Plot-I.

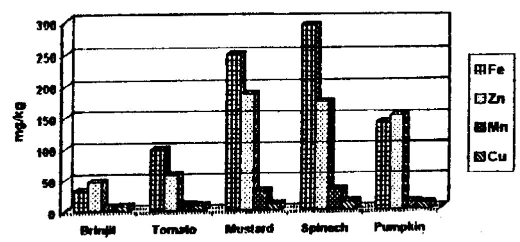

Fig. 3: Average Concentration of Heavey Metals in Gvegetables Grown in Plot-II.

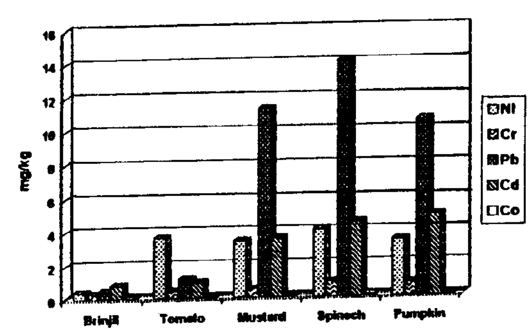

Fig. 4: Average Concentration of Heavey Metals in Gvegetables Grown in Plot-II.

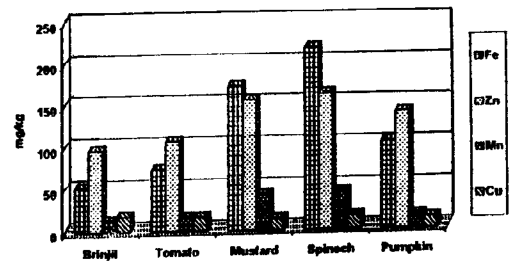

Fig. 5: Average Concentration of Heavey Metals in Gvegetables Grown in Plot-III.

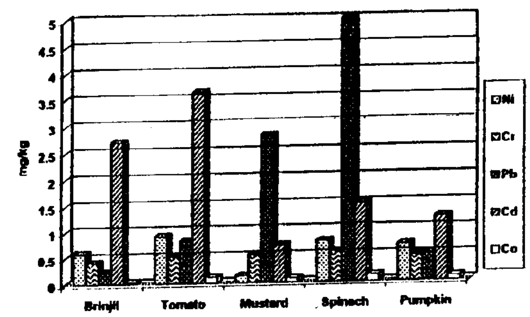

Fig. 6: Average Concentration of Heavey Metals in Gvegetables Grown in Plot-III.

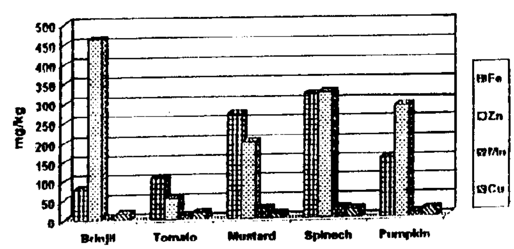

Fig. 7: Average Concentration of Heavey Metals in Gvegetables Grown in Plot-IV.

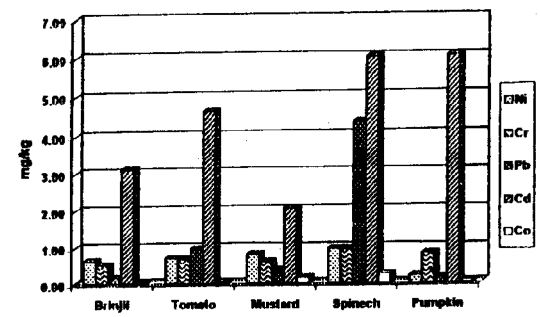

Fig. 8: Average Concentration of Heavey Metals in Gvegetables Grown in Plot-IV.

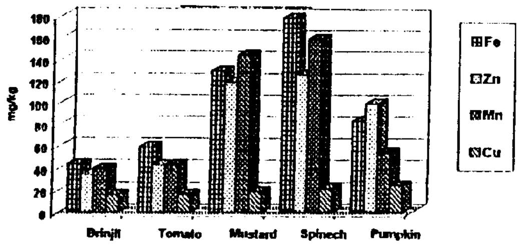

Fig. 9: Average Concentration of Heavey Metals in Gvegetables Grown in Plot-V.

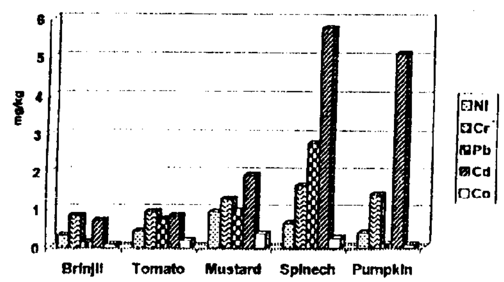

Fig. 10: Average Concentration of Heavey Metals in Gvegetables Grown in Plot-V.

has been a considerable revival of interest in the use of waste water for crop irrigation in arid and semiarid region as a result of scarcity of alternative water supplies and the need to increase local food production. Water resources planners have come to recognise the value of this practice in terms of both water conservation and nutrient recycling and as a method of preventing pollution of surface and ground water. In some countries, such as Israel, Jordan, Peru and Saudi Arabia, it is government policy to reuse all effluents from sewerage treatment plants, mainly for crop irrigation [14]. Karachi is located in a semiarid zone between Lat: $24^0.52'$ N, Long: 67^0 E on the coast of Arabian Sea. It is one of the megacity among 20 megacities of the world. The total gross unconstrained drinking water demand for Karachi in 1996-97 was estimated to be 595 mgd, but the Karachi Water and Sewerage Board (KWSB) was able to supply 404 mgd which is considerably less and represent a shortfall of about 200 mgd [15]. The water supply for the agriculture use around Karachi is negligible. Supplementation from ground water sources in Karachi is also not feasible for regular irrigation of crops, as they are generally insufficient or brackish. The use of wastewater for irrigation of crops and urban "green spaces" has expended significantly during the last fifty years throughout the world. It has becomes imperative to use treated wastewater for the cultivation of edible crops in and around Karachi due to scarcity of water.

Karachi generates over 230 mgd of sewerage from all sources. The sewerage system is divided up into a number of catchment and subcatchment. Karachi Municipal area sewerage is drained through the two rivers Malir and Lyari into the sea. These rivers are mainly rain water carrier and dry beyond Karachi.

Karachi Municipal Sewerage Farm, commonly known as Gutter Baghicha is located near the Sindh Industrial Trading Estate (SITE). Sindh Industrial Trading Estate (SITE) is one of the oldest and largest industrial estate of Pakistan [16]. It was established in 1953 and is located at Lat: 24^0 $54'$ N and Long: 67^0 $10'$ E in the district South of Karachi. It has a total area of 4400 acres and more than 2000 various types of industries are located in this area. Approximately 60 percent of these industries are textile mills while others deal with pharmaceuticals, chemicals, detergents, iron and steel, sulphur refining, vegetable oils, beverages and food products etc. Almost all the industries in the SITE discharge their untreated effluents into nearby nallas which ultimately join the Lyari river containing sewerage water discharged from main city. Municipal wastewater is likely to contain chemical pollutants whenever industrial discharges are allowed to enter the sewerage system. Studies were carried out earlier to determine the quantity of heavy metals in the wastewater flowing through Lyari river and the nallas flowing in SITE showed considerable quantity of heavy metals present in these effluents [17,18]. The mixture of industrial effluent and sewerage water is treated in treatment plant no.1 for Karachi. TP1 has been upgraded recently in 1998 to a capacity of 39 mgd. The existing sewerage treatment plant facilities are still undersized with a total theoretical capacity of 141 mgd for primary treatment and limited biological treatment of less than 60 percent of the flow [15].

Contribution of heavy metals from air was also determined. Table VI shows the heavy metals concentration in particulate matter (PM10). It has been observed that the highest concentration of heavy metals were determined in plot no.1 and 2, because both these plots are near to the main road. The Daily average traffic recorded near to this site was 39743 vehicles per day. It can be seen here that substantial amount of heavy metals are also added to the soil through air. An earlier study [19] showed that a mean concentration of 109 ppm (Pb), 82 ppm (Cu), 96 ppm (Mn) and 139 ppm of (Zn) were found in the soils of roadside spaces of SITE area. It was also concluded in the study that almost all heavy metals in soil of green spaces and gardens were contributed by automobile exhaust in the urban area of Karachi [20]. Metals may accumulate in rural and urban soils as a result a variety of human activities. Particles larger than 1μ are deposited due to impaction and gravitational settling [21]. The vegetables are considered as "protective supplementary food" as they contain large quantities of minerals, vitamins, carbohydrates, essential amino acids and dietary fibre, which are required for normal functioning of the human metabolic processes. They are also important to neutralise the acid produce during digestion, besides being useful "roughage" according to food experts. The required amount of vegetables in our daily diet must be 300 to 350g per person [22], whereas [23] estimated that only 80-90g per person is being used in Pakistan. The lack of knowledge of the health risks and wide adoption of unforeseeable standards have tended to encourage the belief in poorer countries that reuse of effluents for irrigation is a costly process requiring sophisticated treatment technology. This has resulted both in failure to plan for wastewater reuse where sewerage schemes have been installed and uncontrolled use by farmers of raw sewage or treated effluent after discharge to surface water channels. In arid and semiarid regions, it is imperative that reuse is taken into account as feasible option for the disposal of collected wastewater rather than as something that is possible only under exceptional conditions.

Experimental

Fresh vegetable samples were collected from Karachi Municipal Corporation (KMC) sewerage farm near Sindh Industrial Trading Estate (SITE). The Gutter Baghicha was divided into five plots for the determination of heavy metals concentration in the soils. Five samples were collected from each plot, four from all corners and one from centre. Samples of Spinach (Spinacea Oleracea), Tomato (Lycopercium), Brinjal (Solanum Melongena), Pumpkin (Cucurbita Pepo) and Mustard (Brassica) were collected from five different sectors of Karachi Municipal Sewerage farm near SITE. Figure 1 shows the location diagram. These vegetables were commonly grown on all the five sectors. Three samples of each vegetable were collected from each plot.

All vegetable samples were washed with distilled/deionized water and air-dried. The dried samples cut into the pieces with teflon knife, and the pieces of vegetables further dried at 80 ± 1^0C.

a)Five grams of the dried samples were wet ashed with 40 ml (1:1) $HNO_3 - HClO_4$ and heated to near dryness in a platinum dish, few drops of hydrofluoric acid were added and heating was continued to dryness. The residue was treated with 10 ml concentrated HCl and boiled for 30 minutes, then 20 ml distilled water was added and solution was heated for further 15 minutes and made up to 50 ml. [24]. Heavy metal analysis were carried out by Hitachi Z-8000 Atomic Absorption Spectrophotometer with Zeeman correction using air acetylene flame with standard addition methods. All reagents used for the preparation of sample for analysis were of Ultra high purity grade. BDH, Spectrosol standard stock solutions were used for calibrations. The purity of distilled water used for the preparation of all reagents and calibration standards was equivalent to ASTM specification type II reagent water [25].

b)Soil samples were prepared according to the methods specified by USEPA [26], and analysed by AAS. The results are presented in table IV. Physical properties of soil of different plots at Gutter Baghicha was determined according to the procedures given in Encyclopaedia of Soil & Marine Pollution [27].

c)The measurement of aerial burden of heavy metals were carried out by high volume air sampler Model No. HVPPM 10 25A manufactured by General Metal Works Inc: 8368 Bridgetown, Ohio, USA, particulate matter (PM10) were collected by Placing HVS at three different locations near the Gutter Baghicha. The heavy metals in particulate matter were analysed by standard method using flame AAS stated above in (a).

d)Wastewater samples used for the irrigation of these crops were collected and analysed according to the methods for chemical analysis of municipal and industrial effluents. National Environmental Quality Standards, [28].

Conclusion

The high levels of heavy metals found in the vegetables grown in the Gutter Baghicha is due to the continuous use of untreated industrial effluents. The information gained on heavy metal accumulation in vegetables are of valuable nutritional interest. This data will help in establishing baseline levels on the use of untreated sewerage. Further study on other crops grown at Karachi Municipal Corporation sewerage farm (Gutter Baghicha) with the use of treated sewerage & industrial effluent after renovated treatment plant. Further study will help to establish any harmful effect on human with the use of vegetables grown with treated effluent/untreated wastewater. and will compare heavy metal load on the soils of this area over several years.

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