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Soils and Vegetables Enrichment with Heavy Metals from Application of Sewage Water

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Abstract
Application of waste water for irrigation purposes has increased over the past years due to the shortage of water. This waste water contains high amounts of heavy metals which are very toxic. The objectives of this study were To analyze the heavy metals in selected area of Lahore, To determine the concentration of metals in soil and different parts of plants (Leaves and fruit) and To determine the distribution of heavy metals into different soil strata The present study revealed that heavy metal content was above the toxicity level in leafy vegetables grown in the area of Lahore. This study showed that among the different tested plant species, the amount of heavy metals was more in leaves than fruits. Plants whose fruits grow below the soil showed higher concentration of heavy metals while other showed less concentration whose edible portion was above the ground level. The concentration of heavy metals in upper layer of soil (0 -15 cm) is higher than the lower layer (15-30 cm). The reason behind is that the upper layer was receiving sewage water permanently while the penetration of sewage water below 15 cm was less. That's why the heavy metals accumulated more in the upper layer of the soil than the lower layer.
Keywords: heavy metals, plants, soil strata, toxic, waste water

INTRODUCTION

Water contamination with heavy metals is great environmental issue (VASUDERAN *et al*., 2003).Heavy metals are metallic chemical element that has a relatively high density and toxic at low concentration. Examples of heavy metals are Mercury (Hg), Cadmium (Cd), Arsenic (As), Chromium (Cr), Thallium (Tl) and Lead (Pb), heavy metals are natural components of earth crust that cannot be degraded. They enter our body via food, drinking water and air and cause many adverse effects even at very low concentration. The reason of its toxicity is that heavy metals are noncompetitive inhibitors for several enzymes (ESPOSITO *et al*., 2001).

Water is an essential molecule needed by all living things for their survival and subsistence on the surface of earth. About (6%) water is used for domestic, (3%) for industrial and (90%) of available water is used for irrigation purposes. Instead of having the biggest canal irrigation system networks, still there is shortage of surface water supplies in Pakistan. Net deliveries of surface water supplies are 1.80 acre feet per cropped area which is insufficient to meet the crop requisite and it is also less than optimum water requirements which are likely to be 4-5 acre feet (TARAR, 1997). This shortage is being compensated by the conjunctive use of ground water for irrigation to grow cereals and use of urban waste water (sewage and industrial effluents) for growing vegetables especially in areas around cities (LONE, 1995).

Use of waste water for irrigation give very good crop yields because it contains large amount of organic material and inorganic elements necessary for proper growth and development of crops (MITRA AND GUPTA, 1999). Waste water contains heavy metals also which are phytotoxic if they are present in large amounts or transferred to animal and human beings through food chain and harmful for them (GHAFOOR *et al.,*1995).

Effluents discharged from different industries contained chemicals which pollute the water (ASLAM,1998). The industrial effluents contain higher values of physico-chemical parameters like temperature, pH, conductivity, hardness, alkalinity, chemical oxygen demand, total soluble salts, nitrates, nitrites and cations (Na, K, Ca and Mg). Sewage water contains considerable amount of heavy metals such as Zn, Fe, Cu, Mn, Pb, Cd, Cr, Ni, Co etc. Some of the heavy metals are essential for proper plant growth but the other are unnecessary so after accumulating in the soil they could be transferred to food chain and caused several adverse effects. Fe, Mn, Co, Cu and Ni are important nutrients and their permissible limits are quite low but they are present in concentration higher than their permissible limits, they show toxic effects on biological system. The elements, which have been identified from different industrial effluents, are heavy metals and trace metals including Cr, Cd, Cu, Pb, Ni, Zn, Co, Mg, Fe and As.

Two main sources of heavy metals in the soil are natural and anthropogenic contamination. anthropogenic sources are more part of heavy metals than natural sources(NRIAGU & PACYNA,1988). Heavy metals are considered to be one of the main sources of the environmental pollution, since they have a significant effect on soil quality. They may beare toxic at very low concentration and their toxicity increases with the accumulation of water in the soils. (BRADL.,2004; LI *et al*.,2001; SASTRE *et al*.,2002).

These heavy metals can directly damage human beings by disturbing mental and neurological function, impairing neurotransmitter production and utilization, and changing numerous metabolic body processes. Heavy metals have adverse effect on blood and cardiovascular, detoxification pathways (colon, liver, kidneys, skin), endocrine (hormonal), energy production pathways, enzymatic, gastrointestinal, immune, nervous (central and peripheral), reproductive, and urinary systems (GREENWOOD AND EARNSHAW,1986).

Toxic effect of Heavy metals is the result of complex interaction of major toxic ions with other essential or non-essential ions. These metals reduce the activity of hydrolysis viz., a amylase, phosphatase, RNAse and proteins. They interfere in the enzyme action by replacing metal ions from the metaloenzymes. Cadmium has severe effect on seedling length, dry weight, reduces photosystem II activity, causes structural change in chloroplast and reduces photosynthesis, availability of carbon dioxide, lowers stomatal conductance, interfere with membrane permeability and reduces leaves respiration (AGARWAL,2002).

Toxic effect of lead are inhibits germination, reduces photosynthesis, reduces transpiration, causes reduction in chlorophyll production, and reduces gaseous exchange in leaves. Similarly, toxic levels of nickel and chromium has severe effect on dry matter production and yield (AGARWAL,2002).

The objectives of my study were;

- To analyze the heavy metals in selected area of Lahore
- To determine the concentration of metals in soils and different parts of plants (leaves and fruit).
- To determine the distribution of heavy metals into different soil strata

MATERIAL AND METHODS

An experiment was conducted for the analysis of heavy metals in plants and soil samples irrigated with sewage water permanently in the Institute of soil chemistry and environmental sciences, AARI, Faisalabad. Following procedure was followed:

Collection of Samples

There are a large number of effluents water channels spreading around the Lahore city. Mostly these channels are covered but at some places they are opened. To determine the metal contamination in the effluent irrigated vegetables and soils, a number of farmers' fields were selected. These fields were irrigated with the city effluent. The selected fields were located adjacent to the Taj Company drain, Band road drain (double sarak wala nala), Bakar Mandi drain, Ravi Sewage water areas were (1). Shadra River Area, (2). Ravi River Area, (3). Chota Sandha Kalan, (4). Akram Park, (5). Darogha Wala, (6). Ghosia Colony and (7). Faryad Colony near T-5 Ravi River, Bombay Jhogian Wala Ganda Nala , Babu Sabu Area, Thokar Niaz Baig Area. Samples of soil and plants (leaves and fruits) were collected from these sites.

Sewage water analysis

Equipments

EC meter**,** pH meter**,** Atomic Absorption Spectrophotometer**,** Collection bottles**,** FunnelsFilter paper**,** Storage bottlesand volumetric flasks

Electrical Conductivity (EC)

EC is actually a measure of the ionic activity of a solution in term of its capacity to transmit current.

Determination of pH

The pH value determines whether water is hard or soft. In general, water with a low pH (< 6.5) could be acidic, soft, and corrosive. Therefore, the water could contain metal ions such as iron, manganese, copper, lead, and zinc...or, on other words, elevated levels of toxic metals. Water with a pH > 8.5 could indicate that the water is hard. Hard water does not pose a health risk, but can cause aesthetic problems. While the ideal pH level of drinking water should be between 6- 8.5, the human body maintains pH equilibrium on a constant basis and will not be affected by water consumption. For example our stomachs have a naturally low pH level of 2 which is beneficial acid that helps us with food digestion.

Method

Samples of sewage water were collected randomly from collection sites. The pH and EC of samples was determined by pH meter and EC meter. Then filter the samples with Whatman 42 filter paper and store the samples in storage bottles. Read the Pb concentration by Atomic Absorption spectrophotometer (AAS). Five standards using distilled water were prepared as matrix for each element with a range as following for

Pb = 0.5, 1.0, 1.5, 2.0, 2.5 ppm
Ni = 0.5, 1.0, 1.5, 2.0, 2.5 ppm
Cd = 0.5, 1.0, 1.5, 2.0, 2.5 ppm

Standardization of Instrument

Atomic absorption spectrophotometer was standardized with standard solutions of each element. Standards were prepared from 1000ppm stock solution of each element.

Standards preparation

10 mL of stock solution was taken in 100 ml volumetric flask and make volume with distilled water up to the mark. Again 25 ml of 100 ppm solution was taken in 100 ml volumetric flask to make 25 ppm solution. Five standards (0.5, 1.0, 1.5, 2.0, 2.5 ppm) for the detection of each through (AAS) were prepared from 25 ppm solution. Took 1, 2, 3, 4 and 5 ml of 25 ppm solution in 50 ml volumetric flasks and make the volume up to the mark with distilled water.

Standard was prepared using formula

$\mathbf{C_1V_1 = C_2V_2}$

$C_{1=}$ concentration of stock solution

$V_{1=}$ volume to be determined

$C_{2=}$ concentration to be made

$V_{2=}$ known volume

Soil Sampling

Material

Soil auger, Spade, Bucket and Plastic Bags

Sampling method

After considering average field conditions i.e. extreme high and low value, for example, slope, appearance of crop and a grid line was established at regular intervals (15-30 m) and each intersection 1 m diameter area was sampled by taking 8-10 course. The depth of sampling was chosen according to land use.

Handling of Sample

Contamination was prevented at all stages. As crushing is easier at right moisture level. The soil was passed through 2- 3 mm sieve and air dried. The samples were stored and used in soil analysis according to requirements.

Soil analysis

Equipments

Atomic absorption spectrophotometer (AAS)**,** Glass beakers**,** Mechanical shaker**,** Filter papers**,** Funnels**,** Storage bottles**,**Volumatric flasksand Cylinders.

Chemicals Reagents

1-0.005M DTPA

2-0.01M $CaCl_2$ (anhydrous)

3-0.1M TEA (tri-ethanol amine, adjusted to pH 7.3 with dilute HCl).

DTPA Preparation

1.97g of DTPA, 1.1g of anhydrous $CaCl_2$ and 14.92 g of TEA were dissolved in approx. 800 ml of distilled water. After sufficient time for DTPA to dissolve on magnetic stirrer hot plate, volume was made. Adjusted the pH 7.3 with 1:1 HCl or 1:1 NH_4OH while stirring (Lindsay and Norvell 1978)

Method for Soil Analysis

25 g soil sample was taken and 50 ml of DTPA solution added to it. Then it was shaken continuously for 2 hours on horizontal shaker and was filtered. A blank solution (containing all reagents except soil) was run with samples as blank. Read each element concentration on concentration mode by Atomic Absorption Spectrophotometer. At least 5 standards were prepared for each element with a range as following

For Pb = 0.5, 1.0, 1.5, 2.0, 2.5 ppm

Ni = 0.5, 1.0, 1.5, 2.0, 2.5 ppm

Cd = 0.5, 1.0, 1.5, 2.0, 2.5 ppm

Calculations required

Heavy Metal (ppm) =AAS reading x dilution factor

Plant Sampling

Material

1-Paper bags

2-Cutter

Sampling method

Sampling was carried out from a vegetable farms located along drain where vegetables were grown by untreated sewage water.

For Plant sampling, leaves and fruits (edible portion) were taken randomly from different vegetable crops. No young leaves and old leaves were taken. Leaves of moderate size and age were collected. Same method was applied for edible part of vegetables sampling. Plant samples were washed and cut into pieces, air dried in Fluidized Bed Dryer at 80°C for 4 hrs. The dried material was then powdered in a hammer mill. The samples of plants were homogenized before air-drying and stored in clean, sample bottles which were used in plant analysis according to requirements.

Dry digestion for Plant analysis

Apparatus

Furnace, Hot Plate, Atomic Absorption Spectrophotometer, Electrical balance, Pyrex digestion tubes, Tube's rack/stand, Flask, Filter paper (Watman-42), Funnels and Sampling bottle

Reagents/medium required

1- 2 M HCl
2-distilled water

Method

1g of dried and grinded sample of plant (leaves and fruit) was weighed in crucibles and then the crucibles were placed in furnace for 2-3 hours at 550 C^0. After letting the crucibles to cool down they were taken out from the furnace. Then 5 ml of 2 M HCl was added to each crucible to dissolve the ash. The crucibles were placed on hot plate at low temperature to dissolve ash completely. If ash remained un-dissolve add more HCl and heat on hot plate until complete mixing. Then these plant samples were diluted up to 50 ml with distilled water. After dilution each solution was filtered using Watman-42 filter paper and stored in sampling bottles.

A blank solution (containing all reagents except plant sample) was also digested with samples as blank. Read on concentration mode by Atomic Absorption spectrophotometer. At least 4 standards using Distilled water was prepared as matrix for each element with a range as following.

For
Pb = 0.5, 1.0, 1.5, 2.0, 2.5 ppm
Ni = 0.5, 1.0, 1.5, 2.0, 2.5 ppm
Cd = 0.5, 1.0, 1.5, 2.0, 2.5 ppm

Calculations required

Heavy metal (ppm) = AAS reading x dilution factor

Results

pH of sewage water

The pH of sewage water is ranging from 7.1 to 8 which is shown in graph below.

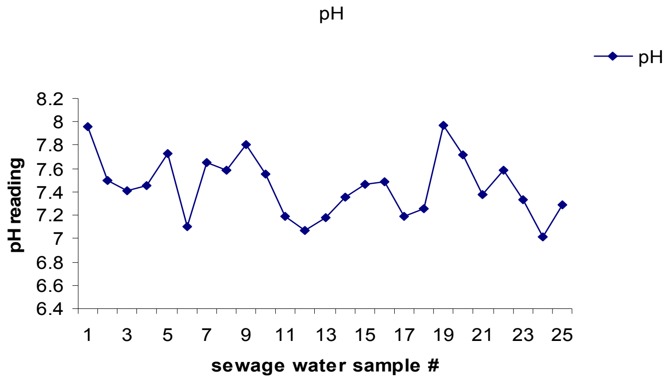

Fig A: pH of sewage water used for irrigating vegetable growing soils

EC of sewage water

EC of sewage water is ranging from 0.5 to 3 which is shown in graph below.

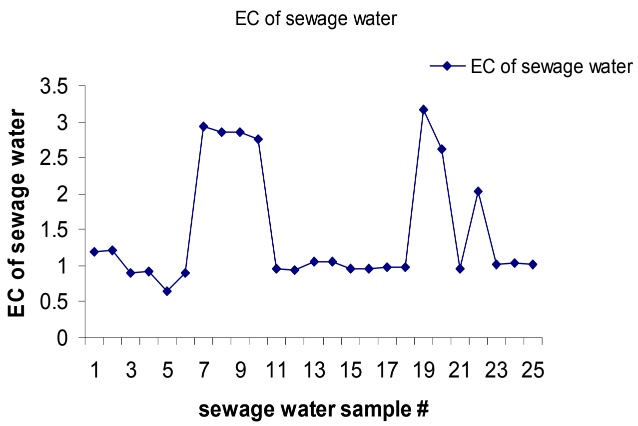

Fig B: EC of sewage water used for irrigating vegetable growing soils

Heavy metal concentration in Sewage water and soil samples taken from 0-15cm depth

Data about heavy metals concentration in sewage water and soil samples is given in Figers below.The results in the tables show statistical parameters of the data presented in the figers. Tables indicate that there is negative correlation between the samples of sewage water and soil samples from the depth of 0-15cm which means it would not be necessary that if lead concentration in soil sample increase or decrease as result of increase or decrease in sewage water.

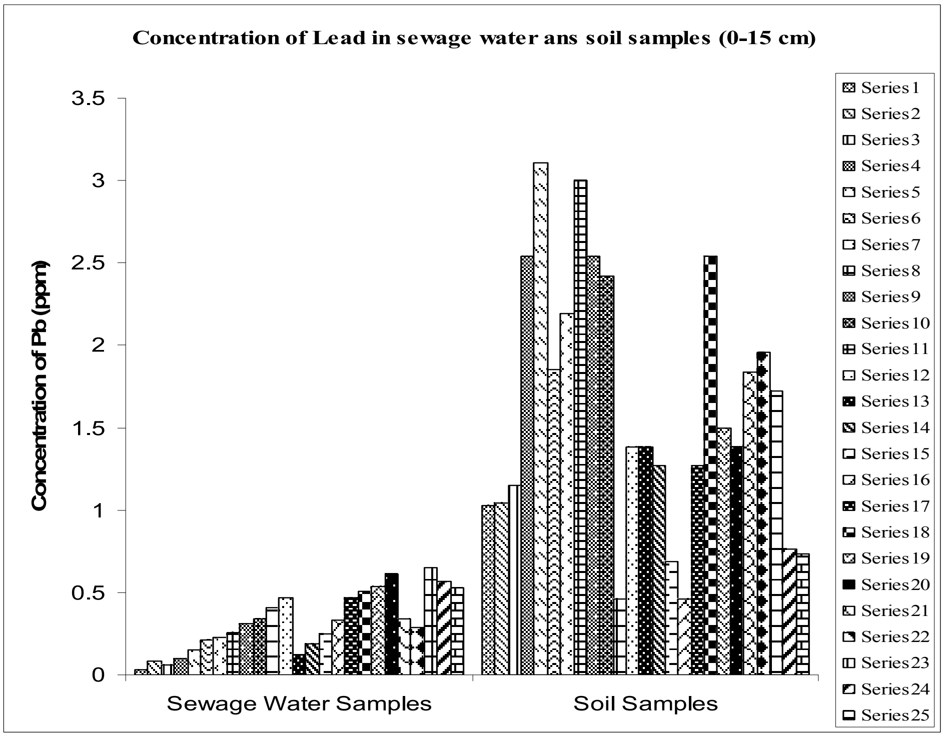

Fig 1: Pb concentration in Sewage water and soil taken from 0-15 cm depth

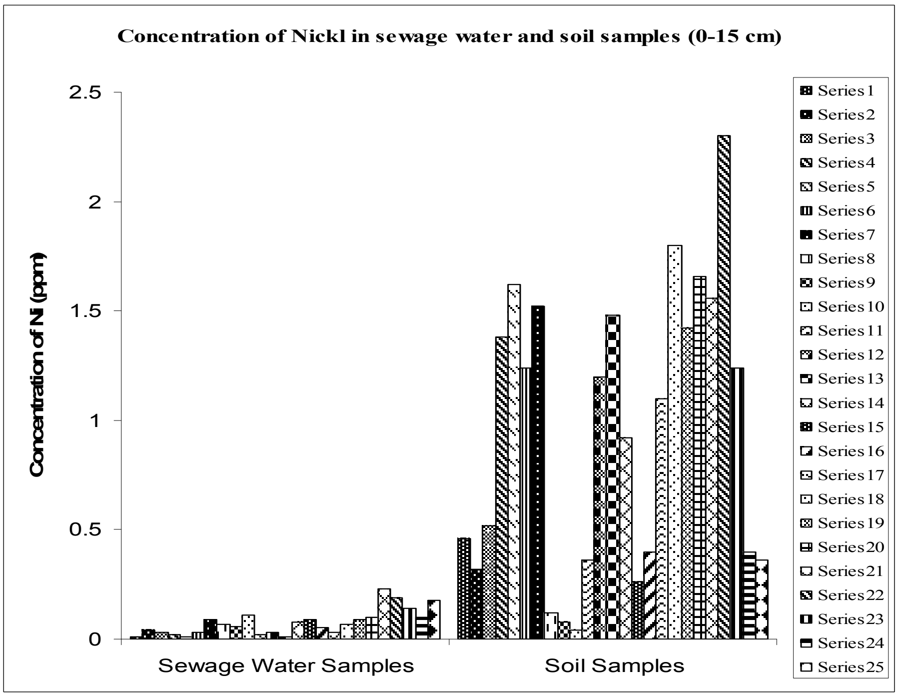

Fig 2: Ni concentration in Sewage water and soil taken from 0-15 cm depth

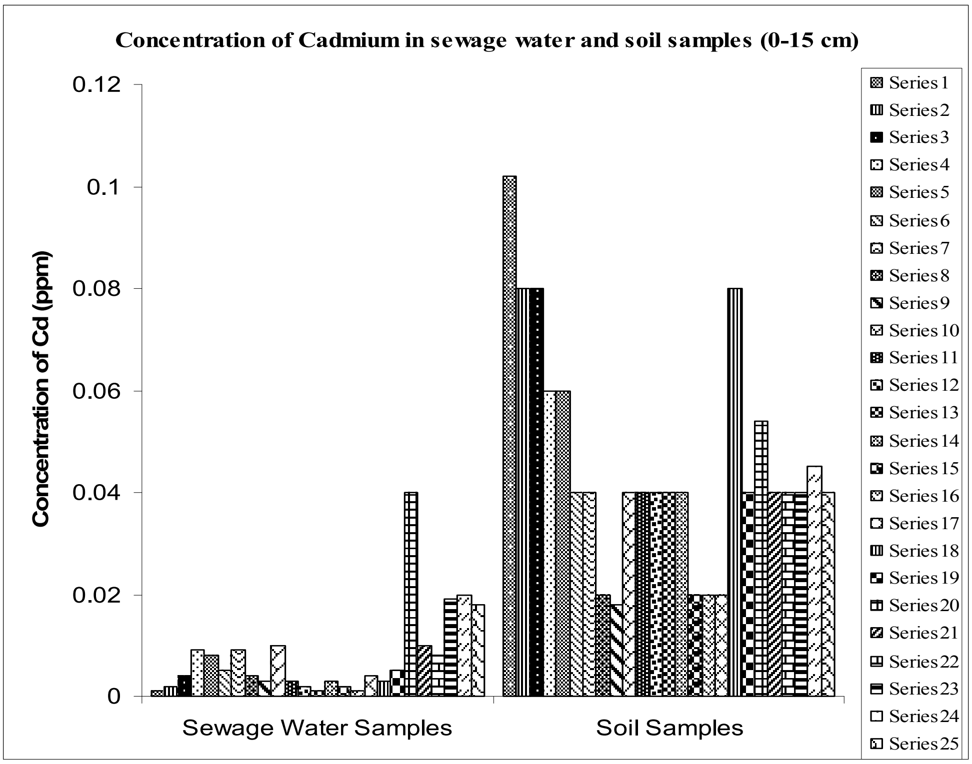

Fig 3: Cd concentration in Sewage water and soil taken from 0-15 cm Depth

Table 1: Statistical analysis Data of sewage water and soil samples 0-15cm(for Pb)

Statistical Values	Sewage water samples	Soil samples (0-15cm)
Min	0.03	1.44
Max	0.65	45
Average	0.32	10.73
STDEV	0.18	10.93
Median	0.31	7.92
Mode	0.34	2.74

Table 2: Statistical analysis Data of sewage water and soil samples 0-15cm(for Ni)

Statistical Values	Sewage water samples	Soil samples (0-15cm)
Min	0.01	0.24
Max	0.23	0.75
Average	0.08	0.39
STDEV	0.06	0.14
Median	0.07	0.35
Mode	0.03	0.24

Table 3: Statistical analysis Data of sewage water and soil samples 0-15cm (for Cd)
Heavy metal concentration in Sewage water and soil samples taken from 15-30cm depth

Statistical Values	Sewage water samples	Soil samples (0-15cm)
Min	0.001	0.02
Max	0.04	1.46
Average	0.008	0.16
STDEV	0.0087	0.30
Median	0.004	0.06
Mode	0.003	0.02

Data about heavy metals concentration in sewage water and soil samples is given in Figures below.
The results in the tables show statistical parameters of the data presented in the figures. Tables indicated that there is negative correlation between the samples of sewage water and soil samples from the depth of 15-30 cm which means it would not be necessary that if lead concentration in soil sample increase or decrease as result of

increase or decrease in sewage water.

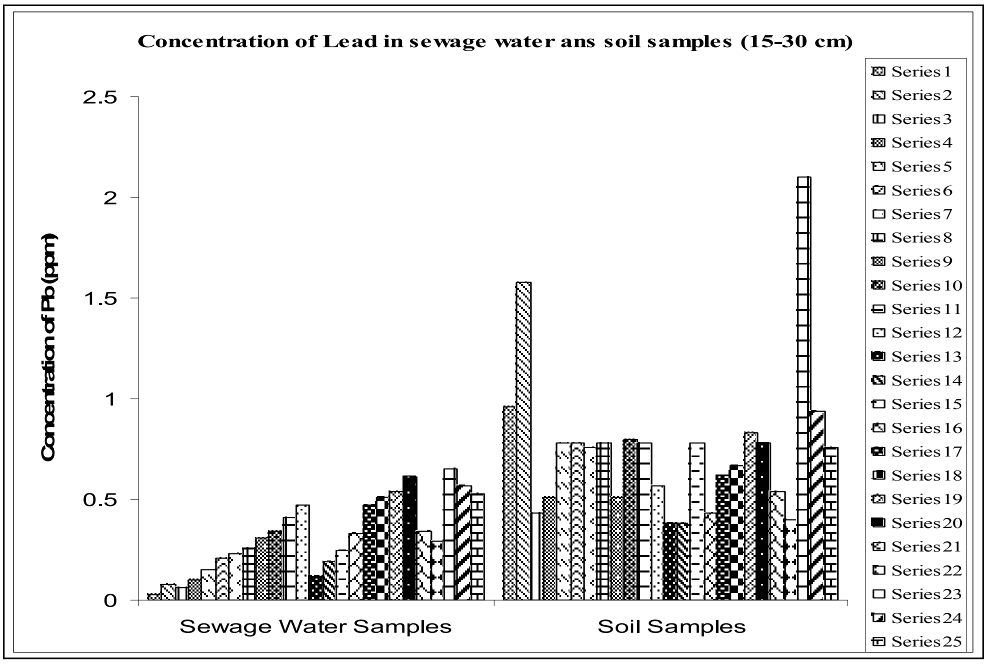

Fig 4: Pb concentration in Sewage water and soil taken from 15-30 cm depth

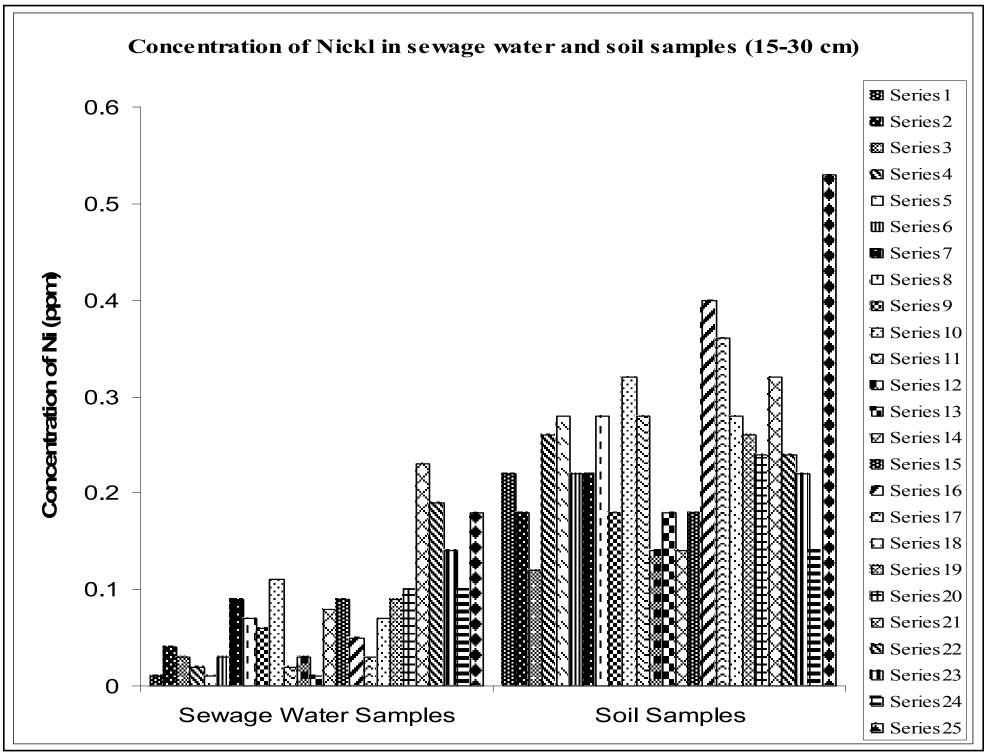

Fig 5: Ni concentration in Sewage water and soil taken from 15-30 cm depth

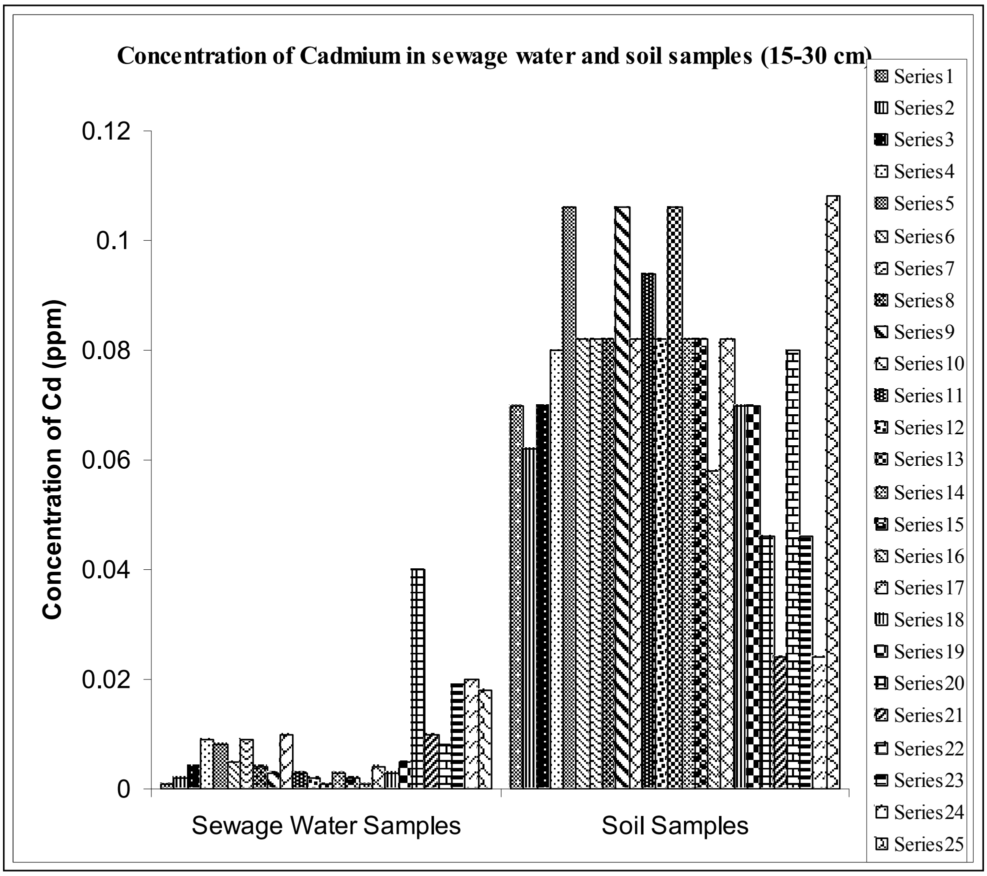

Fig 6: Cd concentration in Sewage water and soil taken from 15-30 cm depth

Table 4: Statistical analysis Data of sewage water and soil samples 0-15cm(for Pb)

Statistical Values	Sewage water samples	Soil samples (15-30cm)
Min	0.03	0.32
Max	0.65	2.1
Average	0.32	0.75
STDEV	0.18	0.39
Median	0.31	0.76
Mode	0.34	0.78

Table 5: Statistical analysis Data of sewage water and soil samples 15-30 cm(for Ni)

Statistical Values	Sewage water samples	Soil samples (15-30cm)
Min	0.01	0.12
Max	0.23	0.54
Average	0.08	0.25
STDEV	0.06	0.09
Median	0.07	0.24
Mode	0.03	0.22

Table 6: Statistical analysis Data of sewage water and soil samples 15-30 cm (for Cd)

Statistical Values	Sewage water samples	Soil samples (15-30cm)
Min	0.001	0.024
Max	0.04	0.11
Average	0.008	0.075
STDEV	0.0087	0.023
Median	0.004	0.082
Mode	0.003	0.082

Heavy metal concentration in Sewage water and vegetable leaf samples

Data about heavy metals concentration in sewage water and vegetable leaf samples is given in Figures.

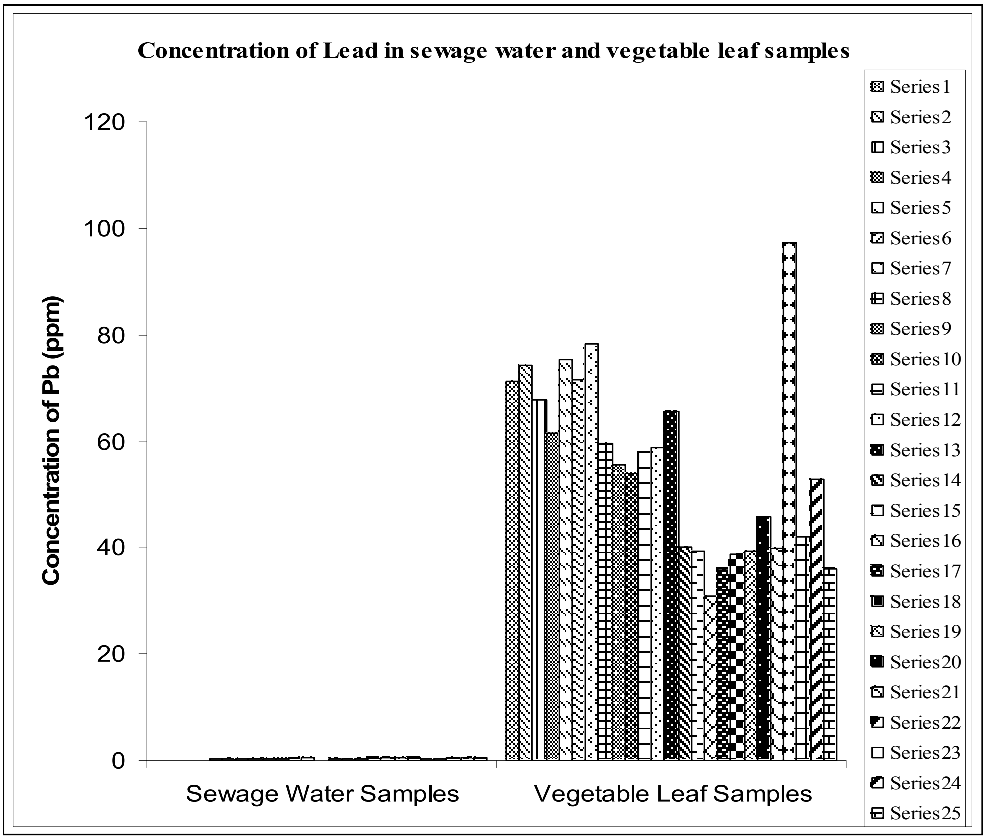

Fig 7: Pb concentration in Sewage water and vegetable leaf samples

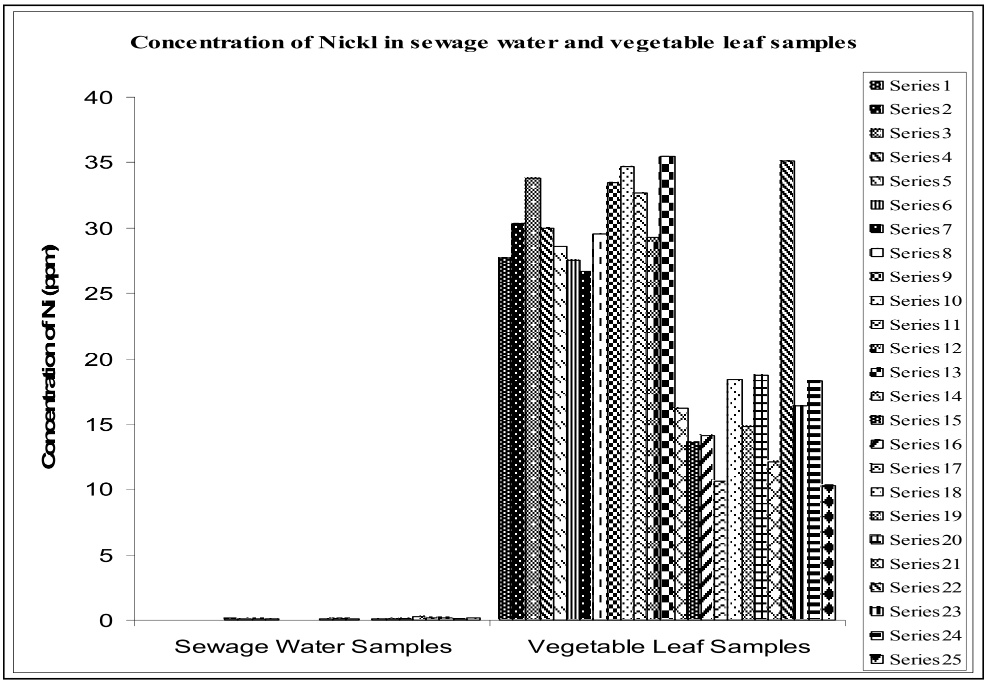

Fig 1.8: Ni concentration in Sewage water and vegetable leaf samples

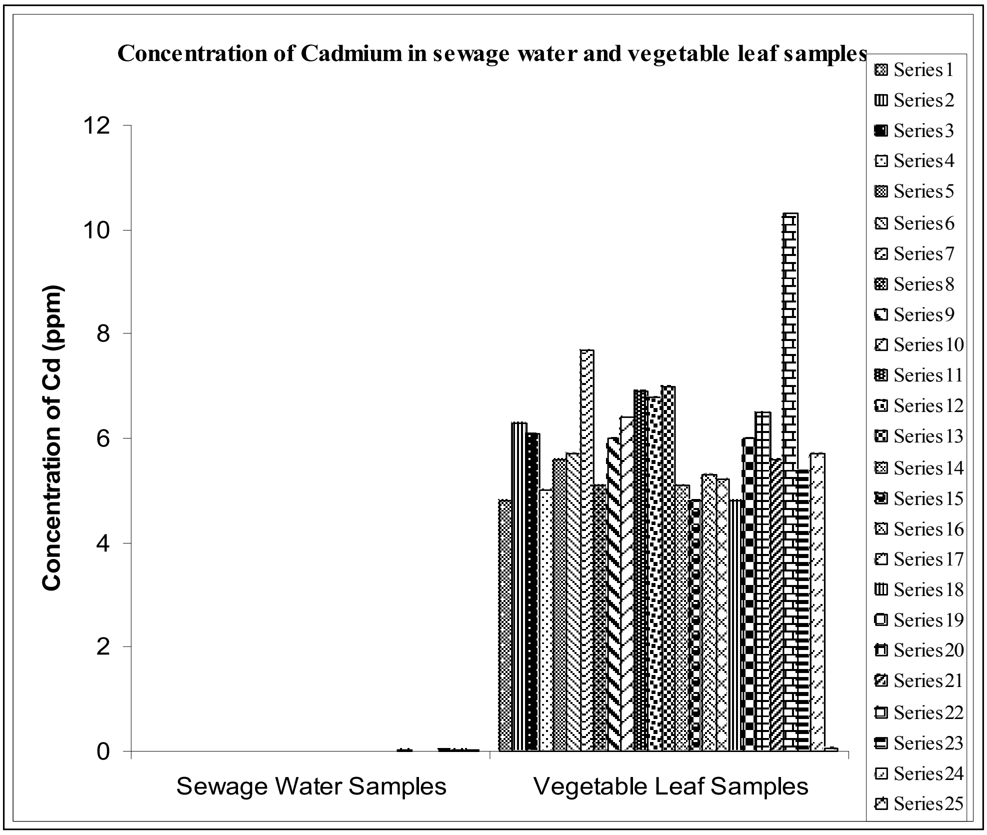

Fig 9: Cd concentration in Sewage water and vegetable leaf samples

Heavy metal concentration in Sewage water and vegetable fruit samples
Data about lead concentration in sewage water and vegetable fruit samples is given in Figures.

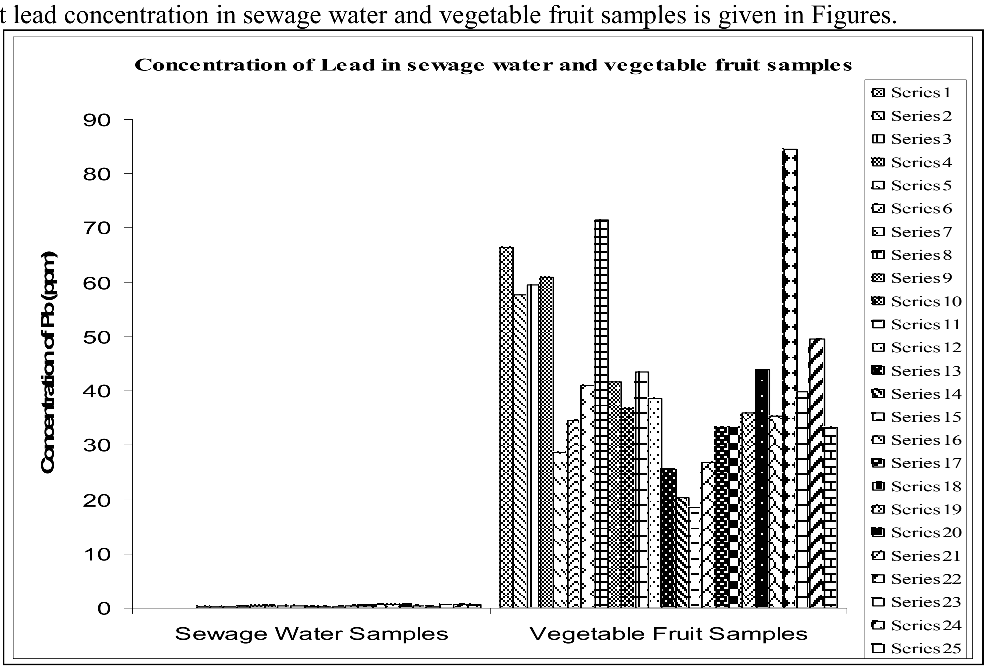

Fig 10: Pb concentration in Sewage water and vegetable fruit samples

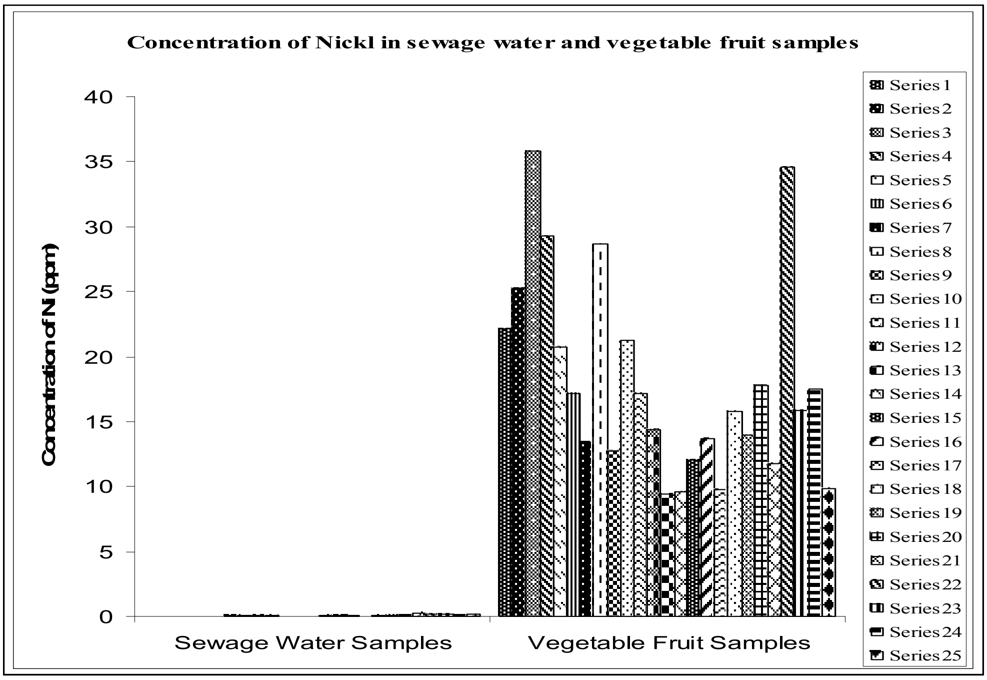

Fig 11: Ni concentration in Sewage water and vegetable fruit samples

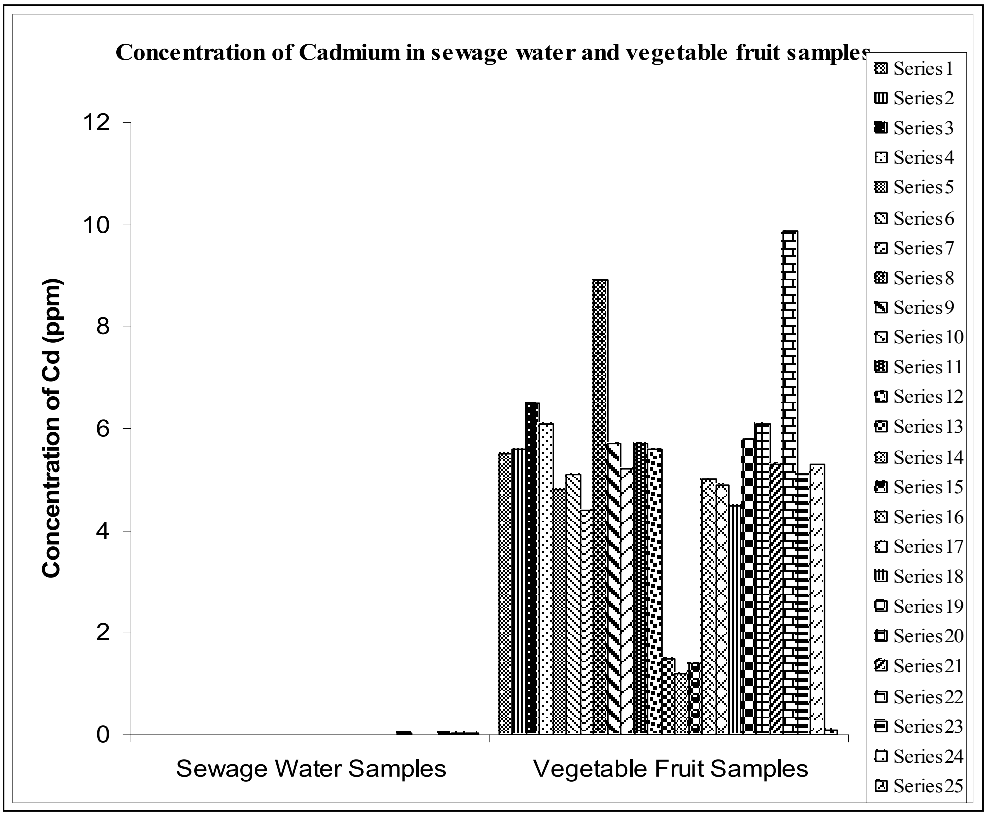

Fig 12: Cd concentration in Sewage water and vegetable fruit samples

DISCUSSION

Concentration of heavy metals in soil is increased by the application of sewage water because it contain heavy metals as shown in fig number 1, 2, 3, 4, 5 and 6 in the result section.these figers shows the concentration of heavy metals in those soil samples in which sewage water was applied is increased by the application of sewage water.similar results was shown by Kabala *et al* (2011).they analyzed irrigation with municipal wastewater lead to an accumulation of organic matter, nutrient elements, and trace metals in soils. Copper (Cu), zinc (Zn), and lead (Pb) forms in soils under long-term irrigation (for 100–120 years) with treated wastewater. These results also presented by Hani and Pazira(2011) who investigated heavy metal sources and their spatial distribution in agricultural fields in the south of Tehran .The concentration of Cd, Cu, Co, Pb, Zn, Cr, and Ni were determined in 106 samples. The results show that Cd, Cu, Ni, and Zn exhibit pollution risk in the study area. The sources of the high pollution levels evaluated were related to the use of urban and industrial wastewater.

Results indicated that the concentration of heavy metals in upper layer of soil (0 -15 cm) is higher than the lower layer (15-30 cm). The reason behind is that the upper layer was receiving sewage water permanently while the penetration of sewage water below 15 cm was less. That's why the heavy metals accumulated more in the upper layer of the soil than the lower layer. Same results was reprsented by Jaradat *et al* (2011).The overall trend of heavy metal variations with particle size was that as sizes increase, concentrations decrease. The Pb, Zn, Cd and Cu profiles in soil demonstrated high concentrations in the top layer, 0-4 cm, but fall rapidly with increasing soil depth.similar results also shown by Akan *et al*(2010).

This study also showed that the increase in heavy metal accumulation in different species and their different parts is not constant and is not in proportion to the increase in heavy metal concentration in soils.these results are match with the results of Arora *et al* (2008). Who carried out a study to assess levels of different heavy metals like iron, manganese, copper and zinc, in vegetables irrigated with water from different sources. The results indicated a substantial build-up of heavy metals in vegetables irrigated with wastewater. The range of various metals in wastewater- irrigated plants was 116–378, 12–69, 5.2–16.8 and 22–46 mg/kg for iron (Fe), manganese (Mn), copper (Cu) and zinc (Zn), respectively. The highest mean levels of Fe and Mn were detected in mint and spinach, whereas the levels of Cu and Zn were highest in carrot.

The present study revealed that heavy metal content was above the toxicity level in leafy vegetables grown in the area of Lahore. This study showed that among the different tested plant species, the amount of heavy metals was more in leaves than fruits. Plants whose fruits grow below the soil showed higher concentration of heavy metals while other showed less concentration whose edible portion was above the ground level. While leafy vegetables (Spinach, Cabbage, Coriander etc) showed higher concentration in leaves than in fruits. Similar research results are shown by Dikinya and Areola (2010).they analyzed and compared heavy metal concentration in secondary wastewater irrigated soils being cultivated to different crops: olive, maize, spinach Results showed that the wastewater irrigated soils in the Glen Valley have higher cadmium, nickel and copper than desirable levels, while the levels of mercury, lead and zinc are lower than the maximum threshold values recommended for crop production. The control sites showed that the soils are naturally high in some of these heavy metals (e.g copper, zinc, nickel) and that crop cultivation under wastewater irrigation has actually lowered the heavy metal content. Comparing between the crops, mercury and cadmium levels are highest in soils under maize and decline linearly from maize to spinach to olive to tomato and control site. By contrast, concentrations of the other metals are at their lowest in maize and then increase from maize to spinach to olive to tomato and to control site.

Same results were pointed by Varalakshmi and Ganeshamurthy (2010).Among all the vegetables, Amaranthus and palak, accumulated higher concentrations of heavy metals followed by carrot and radish. The Cd concentration of all the vegetables grown near Varthur and Bellandur tanks exceeded the PFA safe limit. Pb and Ni concentrations exceeded the safe limits in all the vegetables in all the tank areas.

The results in the table7, 8 and 9 showed statistical parameters indicated that there is negative correlation between the samples of sewage water and vegetable leaves samples which means it would not be necessary that if heavy metal concentration in soil sample increase or decrease as result of increase or decrease in sewage water.in result section table9, 10 and 11 showed negative correlation between the samples of sewage water and vegetable fruit samples.similar trend was analsed by Singh *et al.* (2010).They quantified the concentrations of heavy metals, viz. Cd, Cr, Cu, Ni, Pb and Zn in soil, vegetables and the waste water used for irrigation.

CONCLUSION

It is concluded from this study that Sewage water contain high concentration of heavy metals, when this water is used for irrigation purposes it not only increase heavy metals in soil but also increase their concentration in the plants that grown in that soil.Continuose use of sewage water increase heavy metal ions concentration in plants to phytotoxic level. It is therefore recommended that sewage water should be used for irrigation after proper treatment or at least dilution with canal irrigation system.

The concentration of heavy metals in upper layer of soil (0 -15 cm) is higher than the lower layer (15-30 cm). The reason behind is that the upper layer was receiving sewage water permanently while the penetration of sewage water below 15 cm was less. That's why the heavy metals accumulated more in the upper layer of the soil than the lower layer.

Heavy metal content was above the toxicity level in leafy vegetables grown in the area of Lahore. To prevent the heavy metal pollution standards should be settled so that their concentration remain in the permissible level of WHO.

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