



**EVALUATION OF HEAVY METALS DISTRIBUTION AND ROLE IN
PHYSICAL PROPERTIES OF SOIL IN SEWAGE IRRIGATED SITES
OF ALLAHABAD, INDIA**

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ABSTRACT

In present investigation, the depth-wise distribution of four heavy metals viz. Cd, Cr, Pb and Zn was observed. Continuous use of sewage irrigation on agricultural land increased the DTPA-extractable Cd, Cr, Pb and Zn from 0.081 ± 0.01 - 0.270 ± 0.01 mg kg⁻¹, 0.084 ± 0.005 - 0.46 ± 0.02 mg kg⁻¹, 0.082 ± 0.002 - 0.80 ± 0.033 mg kg⁻¹ and 8.40 ± 0.16 - 16.40 ± 0.432 mg kg⁻¹ in surface soil (0-15cm), respectively. A very low amount of heavy metals (Cd, Cr, Pb and Zn) was observed in (45-60 cm) depth in comparison to surface soil (0-15 cm) in all the soil

examined. Similarly accumulation of total heavy metals (Cd, Cr, Pb and Zn) observed from 1.30 ± 0.10 - 4.60 ± 0.20 mg kg⁻¹, 1.23 ± 0.05 - 4.40 ± 0.53 mg kg⁻¹, 1.78 ± 0.36 - 6.8 ± 0.20 mg kg⁻¹ and 57.93 ± 1.72 - 95.30 ± 5.03 mg kg⁻¹ in surface soil (0-15cm) respectively. A low amount of total heavy metals (Cd, Cr, Pb and Zn) was observed in 45-60 cm depth in comparison to surface soil (0-15 cm) in all the soil examined indicating low mobility of these metals down the depth. The soil organic carbon content in soils were positively and significantly correlated with DTPA-extractable Cd ($r=0.81^{**}$), Cr ($r=0.75^*$), Pb ($r=0.61^*$) and Zn ($r=0.96^{**}$), while clay contents showed negative impact on the extractability of these metals. Similarly correlations of total heavy metals with physical properties were observed positively, while pH and clay content showed negative impact.

KEYWORDS: Heavy metals, accumulation, physical properties of soils.

INTERODUCTION

Due to rapid industrial development and urbanization during the last two decades in India, disposal of industrial effluents has become a serious problem. The application of industrial and city effluents to land has also been becoming popular during recent years as an alternative means of treatment and disposal. Besides being a useful source of plant nutrients, these effluents often contain high amount of various organic and inorganic materials as well as heavy metals, depending upon the industry from which these are originating. In the recent decades, concentration of heavy metals in soil attracted considerable attention because they are non-degradable. In certain concentration they are essential to plants but in higher concentration can become toxic. The waste contains some very serious contaminants such as lead, cadmium, beryllium and brominates flame retardants (Dogbevi, 2007; Pinto 2009). Liquid waste, wastewater, fats, oils or grease or used oil have various contaminants including soil particles and other sediment, heavy metals, organic compounds, animal waste. It may be originated from various sites and by different uses (Massoud and Ahmad 2005). Industrial wastes will be as varied as the industries that generate the wastes. Municipal waste-water also contains a variety of inorganic substances from domestic and industrial sources, including a number of potentially toxic elements such as arsenic, cadmium, chromium, copper, lead, mercury, zinc etc (Ferrari et al., 1999). The fate of a heavy metal added to a soil will be controlled by a complex set of chemical reactions and by a number of physical and biological processes acting within the soil. Metal ions will enter the solution from these various forms of combination at greatly different rates. They may then either :(i) remain in solution and pass in to the drainage water; (ii) be taken up by plants growing on the soil or (iii) be retained by the soil in sparingly soluble or insoluble forms. A fourth possibility should also be listed, namely loss in the gaseous phase. Colloidal organic matter has a strong affinity for heavy metal cations, and the retention of added metals is often well correlated with the amount of soil organic matter. Organic matter may provide sites for cation exchange reaction, but its strong affinity for heavy metal cations is due to ligands or groups that form chelates and/or complexes with the metals. The functional groups include COOH, phenolic, alcoholic, and enolic OH, and carbonyl ($>C=O$) structures of various, types.

The proposed study was, therefore, carried out to achieve the following objectives:

1. To find out the effect of sewage irrigated soil characteristics such as pH, CEC, organic C, clay contents etc. on the metal bioavailability in soils.
2. To find out the concentration level (DTPA and Total heavy metal) in sewage irrigated sites.

METHOD AND MATERIAL

Soil sampling from the experimental site

Representative soil samples from alluvium soils which had been receiving sewage effluents for fifteen years were collected from different. Soil samples from different depths (0-15, 15-30, 30-45 and 45-60 cm) were collected from four experimental sites and these samples has three location in particularly areas.

Table 1: Location of representative soil samples.

SI. No	Site No.	Location of sites
1.	A ₁	Karela Bag sewage site, Allahabad
2.	A ₂	Daraganj sewage irrigated site, Allahabad
3.	A ₃	Phaphamau sewage irrigated site, Allahabad
4.	A ₄	SDI farm, Allahabad

METHODS OF SOIL ANALYSIS

Mechanical analysis of soil

For the determination of the percentage of different sizes (Sand, silt and clay) soil was dispersed in water with sodium hydroxide. Sieving separated coarse sand particles. Silt and Clay were separated by the pipette method and fine by decantation (Chopra and Kanwar, 2002).

Method of collecting sewage samples

Composite individual samples were collected in one liter plastic bottles from different selected places and all such samples were thoroughly mixed to get representative samples were thoroughly mixed to get representative sample for analysis of metals and soluble salts. One liter of such representative sample is sufficient for all determinations. The sampled bottles were tightly stopped to prevent any CO₂ being absorbed from the atmosphere to decrease the pH value of the same.

Preservation of samples

In glass sample containers, some of the element like Cd, Cr, Pb and Zn may be adsorbed on walls of the containers. Such losses due to adsorption are higher particularly at a pH around '7'. However, by lowering the pH of water samples to 2 or less by HNO₃ the losses can be reduced considerably.

Method for heavy metals detection in sewage

Metals have the tendency to form complexes readily with the organic constituents; hence it is necessary to destroy them by digestion with strong acids. This preliminary acid digestion not destroys organic matter but also brings all suspended metallic in to the solution.

Extraction for total heavy metals content in soil

One gram of soil in 5 ml conc. HNO_3 and 5 ml HClO_4 (Perchloric acid 60%) were added and the contents were heated up to dryness. Then hot distilled water was added. The contents were heated up to dryness. Then hot distilled water was added. The contents filtrated and volume was made up to 50 ml.

Preparation of DTPA solution

DTPA solution was prepared by a method developed by Lindsay and Norvel (1978) used to extract the available heavy metals in soil samples. 1.97g (0.05M) DTPA powder, 13.3 ml (0.1M) Tri-ethanol amine and 1.47g (0.01M) Calcium Chloride (CaCl_2) were dissolved in distilled water and the volume was made up to 1 liter after adjusting the pH to 7.3.

Extraction of soil with DTPA solution

Five gram soil and 20 ml DTPA solution was added and the contents were shaken for two hours and then filtrate through What man filter paper No.42. The clean filtrate was used for the estimation of heavy metals by Atomic Absorption Spectrophotometer.

Soil pH

Soil pH was measured using ELICO pH meter (Model LI 127) at 1:2:5 soil water ratio.

Organic carbon

Organic carbon was determined by rapid titration method of Walkley and Black (1934), and the values were converted to organic matter by multiplying with Bemlen factor, i.e. 1.724.

Cation Exchange capacity

Cation exchange capacity was determined by using neutral normal ammonium acetate solution (Singh, 1987).

Statistical Analysis

Pearson's Coefficient of Correlation

This measure of correlation obtained by Prof. Karl Pearson is based on arithmetical description. Pearson's coefficient of correlation or the product moment coefficient of correlation is measured by the formula:

$$r = \frac{\text{cov}(x, y)}{\sigma_x \sigma_y}, \text{ where } \text{cov}(x, y) = \frac{\sum (x - \bar{x})(y - \bar{y})}{n}$$

stands for the sample co-variance of x and y , $\sigma_x = \sqrt{\frac{\sum (x - \bar{x})^2}{n}}$ and $\sigma_y = \sqrt{\frac{\sum (y - \bar{y})^2}{n}}$ stand for sample standard deviations of x and y , respectively. Thus, using the direct method, 'r' is calculated as:-

$$r = \frac{\sum (x - \bar{x})(y - \bar{y})}{\sqrt{[\sum (x - \bar{x})^2 (\sum (y - \bar{y})^2)]}}$$

Here, the hypothesis (H_0) is tested that the sample has been taken from a bivariate normal population with zero correlation coefficient, i.e. $\rho = 0$. If the hypothesis is true, the statistic is computed.

$$t = \frac{r}{\sqrt{(1 - r^2)/(n - 2)}}$$

Which follows a 't' distribution with $(n - 2)$ df. Here, the quantity $\sqrt{[(1 - r^2)/(n - 2)]}$ is the S.E. of 'r' in a random sample of n . If the absolute value of this statistic i.e. $|t| \geq t_{0.05}(n - 2)$, the hypothesis is rejected at 5% level, otherwise the sample is said to be consistent with hypothesis.

RESULT AND DISCUSSION

Accumulation and distribution of heavy metals in sewage irrigated soils

The study of accumulation and distribution of heavy metals in different soil profiles is very important as these heavy metals influence both the soil and crops grown in contaminated soils. Long-term application of wastewater to agricultural lands often causes the build-up of the toxic metals in soils, the extent of which depends on the period of application. Detailed studies regarding the movement of heavy metals in soil profiles especially those irrigated with sewage water are lacking. The present study was undertaken with a view to analyze the soils from various sites, receiving sewage irrigation or sludge addition in order to determine heavy metal pollutions. Depth-wise movement of Cd, Cr, Pb and Zn was investigated in sewage irrigated soils.

Profile-wise distribution of heavy metals in sewage irrigated soils was studied at four locations sites and established several correlations among available and total heavy metals (Cd, Cr, Pb and Zn) in surface soils with physico-chemical properties (soil pH, electrical conductivity, organic carbon, cation exchange capacity, clay, DTPA-extractable heavy metals and Total heavy metals (Cd, Cr, Pb and Zn) in soils.

Table-2: Physico-chemical properties of soil.

Site	pH	EC (dsm ⁻¹)	Organic C (g kg ⁻¹)	CEC [Cmol (p ⁺) kg ⁻¹]	Sand (%)	Silt (%)	Clay (%)
A ₁	7.85±0.17	1.20±0.04	4.82±0.06	22.4±1.30	40.20±1.16	34.53±0.33	24.80±0.86
A ₂	7.95±0.04	1.16±0.05	4.60±0.08	18.6±0.43	47.60±1.13	32.20±1.39	17.40±1.17
A ₃	7.75±0.18	1.12±0.04	4.4±0.32	19.46±0.61	48.00±0.50	32.00±1.63	18.00±0.32
A ₄	7.96±0.17	1.10±0.02	4.42±0.04	18.6±0.43	48.20±1.39	26.40±1.01	22.40±1.23
Mean	7.88±0.09	1.15±0.04	4.56±0.19	19.76±1.80	46.00±3.87	31.28±3.45	21.90±2.83

DTPA extractable metals (mg kg⁻¹)

Site	Cd	Cr	Pb	Zn
A ₁	0.270±0.01	0.46±0.02	0.80±0.033	16.40±0.432
A ₂	0.24±0.01	0.40±0.032	0.68±0.016	12.40±0.53
A ₃	0.18±0.02	0.32±0.043	0.62±0.43	10.46±0.50
A ₄	0.081±0.01	0.084±0.005	0.082±0.002	8.40±0.163
Mean	0.192±0.083	0.32±0.16	0.55±0.317	11.92±3.40

Total metals (mg kg⁻¹)

Site	Cd	Cr	Pb	Zn
A ₁	4.60±0.20	4.40±0.53	6.80±0.20	95.30±5.03
A ₂	3.93±0.30	3.53±0.40	5.40±0.20	85.00±4.42
A ₃	2.26±0.032	2.40±0.20	3.80±0.20	77.60±2.62
A ₄	1.30±0.016	1.23±0.052	1.78±0.36	57.93±1.72
Mean	3.02±1.51	2.99±1.38	4.44±2.16	78.95±15.78

Note: Data are mean value of three replications (mean ± SD) from each experimental location obtained from surface soils (0-15): The four experimental sites are namely Karela Bag (A₁), Daraganj (A₂), Phaphamau (A₃), SDI (A₄).

Table-3: Variation in pH in soils.

Depth (in cm)	Sites				
	Sewage irrigated soil			Non-sewage irrigated soil	Mean
	A ₁	A ₂	A ₃	A ₄	
0-15	7.85±0.17	7.95±0.40	7.75±0.19	7.96±0.17	7.88±0.09
15-30	7.34±0.04	7.20±0.16	7.00±0.40	6.85±0.06	7.09±0.23
30-45	7.00±0.81	6.90±0.04	6.85±0.15	6.81±0.4	6.98±0.07
45-60	6.98±0.14	6.50±0.40	6.62±0.01	6.78±0.13	6.72±0.20
Mean	7.29±0.40	7.13±0.61	7.05±0.48	7.01±0.57	

Note: Data are mean values of three replications (mean ± SD) collected from soil profiles of four locations are Karela Bag Sewage sites (A₁), Daraganj (A₂), Phaphamau (A₃), SDI (A₄).

Table-4: Variation in Electrical conductivity (dSm⁻¹) in soils.

Depth (in cm)	Sites				
	Sewage irrigated soil			Non-sewage irrigated soil	Mean
	A ₁	A ₂	A ₃	A ₄	
0-15	1.20±0.02	1.16±0.04	1.12±0.02	1.10±0.02	1.13±0.44
15-30	1.10±0.03	1.00±0.02	1.08±0.02	0.66±0.01	0.96±0.20
30-45	0.78±0.02	0.72±0.02	0.68±0.02	0.70±0.02	0.72±0.04
45-60	0.67±0.02	0.64±0.04	0.56±0.02	0.58±0.02	0.61±0.05
Mean	0.92±0.25	0.88±0.24	0.86±0.28	0.76±0.23	

Foot Notes are same as Table 3

Soil pH and Electrical Conductivity

Soil pH almost decreases with increasing depth of soil profile (Table 3 & 4). Soil pH (7.75±0.19 to 7.98±0.04) and EC (1.12±0.02 to 1.20±0.02) in surface soils have wide variation from one to another site. Such change in pH may be attributed to downward movement of sewage-effluents containing organic acids and humic acid in the soil. Higher EC was observed in sewage irrigated soils. Such changes in pH and EC were also reported by Malla and Totawat (2006). Soil pH is a major factor influencing the availability of elements in the soil for plant uptake (Marschner, 1995). In contrast to the heavy metal content of water, the content of heavy metal in soil may be due to the insolubility of the metals due to high pH as these metal ions generally accumulate in the surface soil layers (Ghafoor et al., 1995) as a result adsorption on the soil particles factors like soil pH, amount of organic matter redox potential of soil and rate of addition of metals mainly effect their adsorption and retention in soil (Bride 1994). The correlation between EC with DTPA-Zn (r=0.35), DTPA-Cd (r=0.66*), DTPA-Pb (r=0.59*) and DTPA-Cr (r=0.64*) were observed positive (Table 16). However,

the correlation between pH with DTPA-Cd, Cr, Pb and Zn were observed negative significant ($r=-0.26$), ($r=-0.36$), ($r=-55^*$) and ($r=-0.19$) respectively. The correlation between EC with DTPA-Cd, Cr and Pb were strongly positive as well as highly significant. Perveen (2011) Kumar et al., (2010a) Rattan et al.(2005), Ajad (1981) have found almost similar findings.

Table-5: Variation in Organic carbon (g kg^{-1}) in soils.

Depth (in cm)	Sites				
	Sewage irrigated soil			Non-sewage irrigated soil	Mean
	A ₁	A ₂	A ₃	A ₄	
0-15	4.82±0.06	4.60±0.81	4.40±0.32	4.42±0.04	4.56±0.19
15-30	3.64±0.03	3.42±0.06	4.00±0.32	3.94±0.02	3.75±0.27
30-45	2.95±0.04	2.80±0.16	3.82±0.14	3.45±0.04	3.25±0.47
45-60	2.50±0.07	2.36±0.04	3.54±0.04	3.24±0.03	2.91±0.57
Mean	3.48±0.1.01	3.29±0.97	3.94±0.36	3.76±0.52	

Foot Notes are same as Table 3

Organic Carbon

Organic carbon (mean $4.56\pm 0.19 \text{ g kg}^{-1}$) was maximum in surface soil (Table 5), which varied among different sites (A₁ to A₄); and their contents at all the investigated sites decreases with increase in depth of soil profile from 4.56 ± 0.19 to $2.91\pm 0.57 \text{ g kg}^{-1}$ soil. Since organic matter plays an important role in metal binding, some researchers have tested whether organic carbon (OC) compounds influence metal leaching. Fotovat et al. (1996) reported that metals such as Cd, Ni and Zn may be influenced in their solubility characteristics from the presence of OC. The correlation coefficients between organic carbon and DTPA- extractable Cd ($r=0.81^{**}$), Cr ($r=0.75^*$), Pb ($r=0.61^*$) and Zn (0.96^{**}) were observed positive (Table 16). However, the correlation coefficients between organic carbon and DTPA-extractable Cd and DTPA-Zn were strongly positive as well as highly significant. Organic carbon in sewage irrigated soil was higher than that of non sewage irrigated soil. The effect of soil depth and soils and their interaction on soil organic carbon were significant. The dumps were physically observed to have large masses of completely decayed organic materials on the soil. The retention of metals to soil organic matter is also weaker at low pH, resulting in more available metal in the soil solution for root absorption. Many metal cations are more soluble and available in the soil solution at low pH (below 5.5) including Cd, Cu, Hg, Ni, Pb, and Zn (McBride, 1994; Blaylock and Huang, 2000). Organic matter improves soil structure and increases the soil's ability to hold water (PEIC, 2003). These differences are due to higher concentration of these metal ions and organic carbon in sewage effluents (Banin

et al.1981; Sakal et al., 1992, Rattan et al.(2005), Kumar et al., 2010a), (Perveen et al., 2011).

Table-6: Variation in Cation Exchange Capacity (Cmol (p⁺) kg⁻¹) in soils.

Depth (in cm)	Sites				
	Sewage irrigated soil			Non-sewage irrigated soil	Mean
	A ₁	A ₂	A ₃	A ₄	
0-15	22.40±1.30	18.60±0.43	19.46±0.61	18.60±0.43	19.76±1.80
15-30	21.20±0.28	17.80±0.65	18.40±0.32	17.40±0.43	18.70±1.71
30-45	20.40±1.39	16.60±0.49	17.20±0.65	16.60±0.43	17.70±1.82
45-60	18.60±0.59	15.40±0.32	16.60±0.48	15.60±0.25	16.55±1.46
Mean	20.65±1.59	17.10±1.04	17.91±1.27	17.05±1.26	

Foot Notes are same as Table 3

Cation Exchange Capacity

CEC (mean 19.76±1.80 Cmol (p⁺) kg⁻¹) are maximum in surface soil (Table 6), which varied among different sites (A₁ to A₄); and their contents at all the investigated sites decreases with increase in depth of profile from 19.76±1.80 to 16.55±1.46 (Cmol (p⁺) kg⁻¹) soil. The correlation coefficients between CEC and DTPA-extractable Cd (r=0.63*), Cr (r=0.62*), Pb (r=0.58*) and Zn (r=0.86**) were observed positive and significant (Table 16). Under acidic conditions, H⁺ ions displace metal cations from the cation exchange complex (CEC) of soil components and cause metals to be released from sesquioxides and variable-charged clays to which they have been chemisorbed (*i.e.* specific adsorption (McBride, 1994). These differences are due to higher concentration of these metal ions and CEC in sewage effluents (Banin et al., 1981; Sakal et al., 1992; Rattan et al. (2005); Kumar et al., 2010 a).

Table-7: Variation in clay (%) in soils.

Depth (in cm)	Sites				
	Sewage irrigated soil			Non-sewage irrigated soil	Mean
	A ₁	A ₂	A ₃	A ₄	
0-15	18.60±0.71	22.20±0.59	32.60±1.46	20.80±0.16	23.55±6.21
15-30	22.40±1.92	30.40±0.43	34.76±0.20	22.40±0.32	27.98±5.65
30-45	28.40±0.32	34.80±0.50	38.40±0.43	26.40±0.43	32.00±5.57
45-60	29.20±0.58	36.96±0.12	42.20±0.16	34.60±0.43	35.74±5.39
Mean	25.15±4.84	31.09±6.52	36.98±4.21	26.05±6.91	

Foot Notes are same as Table 3

Clay

Clay (mean 23.55 ± 6.21) are maximum in surface soil (Table 7), which varied among different sites (A_1 to A_4); and their contents at all the investigated sites decreases with increase in depth of profile (mean 23.55 ± 6.21 to 35.74 ± 5.39). However, the correlation coefficients between Clay and DTPA-extractable Cd ($r=-0.09$), Cr ($r=-0.05$) and Pb ($r=-0.16$) were observed negative correlation but Zn ($r=0.41^*$) were observed positive correlation (Table 16), similar findings has also been reported by (Esteban *et al.*, 2000), Rattan *et al.* (2005).

Table-8: Distribution of DTPA-extractable Cd (mg kg^{-1}) in soils.

Depth (in cm)	Sites				
	Sewage irrigated soil			Non-sewage irrigated soil	Mean
	A_1	A_2	A_3	A_4	
0-15	0.270 ± 0.01	0.240 ± 0.01	0.18 ± 0.02	0.081 ± 0.01	0.192 ± 0.29
15-30	0.230 ± 0.01	0.200 ± 0.02	0.100 ± 0.073	0.050 ± 0.008	0.145 ± 0.08
30-45	0.160 ± 0.01	0.120 ± 0.01	0.080 ± 0.010	0.037 ± 0.006	0.099 ± 0.052
45-60	0.114 ± 0.01	0.065 ± 0.005	0.033 ± 0.003	0.033 ± 0.003	0.061 ± 0.038
Mean	0.194 ± 0.077	0.156 ± 0.625	0.098 ± 0.39	0.050 ± 0.02	

Foot Notes are same as Table 3

DTPA-extractable Cadmium in soils

The data presented in the table 8 & fig.1 indicates that DTPA-extractable Cd in surface soil was minimum (0.081 ± 0.01) at SDI Allahabad (A_4), which has not been receiving sewage irrigation as compared to those receiving sewage irrigation as compared to those receiving sewage irrigation in different amounts. The DTPA-extractable Cd in sewage irrigated surface soils at various depths varied from 0.033 ± 0.003 to $0.270 \pm 0.01 \text{ mg kg}^{-1}$. The DTPA-extractable Cd decreases with increased depth of soil profiles; and the correlation between DTPA-Cd with clay ($r=-0.01$) and pH ($r=-0.26$) were observed negative, while the correlation between DTPA-Cd with organic carbon ($r=0.81^{**}$), EC ($r=0.66^{**}$) and CEC ($r=0.63^*$) were positive and significant (Table 16). This study indicates that these soil properties significant affect the availability of DTPA-Cd, especially organic carbon and EC play dominant role in the mobility of Cd in the sewage irrigated soils (Lund *et al.*, 1976; Kumar *et al.*, 2010 b; Udon *et al.*, 2004; Rattan *et al.*, 2005).

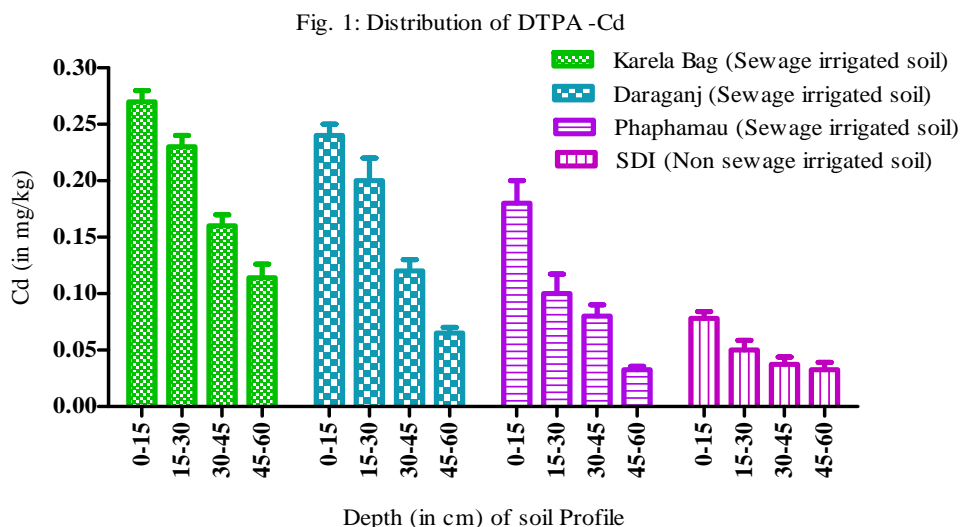


Table-9: Distribution of DTPA-extractable Cr (mg kg^{-1}) in soils.

Depth (in cm)	Sites				Mean
	Sewage irrigated soil			Non-sewage irrigated soil	
	A ₁	A ₂	A ₃	A ₄	
0-15	0.46±0.02	0.40±0.032	0.32±0.043	0.084±0.005	0.31±0.16
15-30	0.36±0.02	0.32±0.043	0.26±0.032	0.046±0.004	0.25±0.14
30-45	0.18±0.02	0.19±0.020	0.15±0.041	0.034±0.004	0.14±0.07
45-60	0.14±0.016	0.15±0.016	0.14±0.015	0.018±0.002	0.11±0.062
Mean	0.29±0.015	0.27±0.11	0.22±0.087	0.045±0.028	

Foot Notes are same as Table 3

DTPA-extractable Chromium in soils

The data presented in the table 9 & fig.2 indicates that DTPA- extractable Cr in surface soil was observed lowest ($0.084\pm 0.005 \text{ mg kg}^{-1}$) at SDI Allahabad (A₄), which has not been receiving has sewage irrigated as compared to those receiving sewage irrigation in different amounts. The DTPA-extractable Cr in sewage irrigated surface soils at various depths varied from 0.14 ± 0.015 to $0.46\pm 0.02 \text{ mg kg}^{-1}$. The DTPA-extractable Cr decrease with increased depth of soil profiles; and correlation between DTPA-Cr with clay ($r=-0.05$) and DTPA- Cr with pH ($r=-0.36$) were observed negative correlation, whereas, correlation between DTPA-Cr with organic carbon ($r=0.75^{**}$), EC ($r=0.64^*$), CEC ($r=0.62^*$) were positive correlation (Table 16). This study indicates that these soil properties highly significantly affect the availability of DTPA- Cr, especially EC and organic carbon play dominant role in the mobility of Cr in the sewage irrigated soils. The high concentration of Cr in surface soil layer (0-15 cm) than that in the lower soil depths indicates their tendency to accumulate in the surface layer by Ghafoor et al.,(2005), Adhikari et al., (2004) and Uwash et al.(2011). Soon

and Abboud (1993) reported the solubility of heavy metals in the following order: Cd >Pb> Ni > Cu. Soil pH significantly influences the solubility, availability and toxicity of metal elements in soil (Nwucheet al., 2008). Pereira *et al.* (2006), AciegoPietri and Brookes (2008) found that low pH values and high metal contents negatively affected the biomass C and the activity of soil microorganisms.

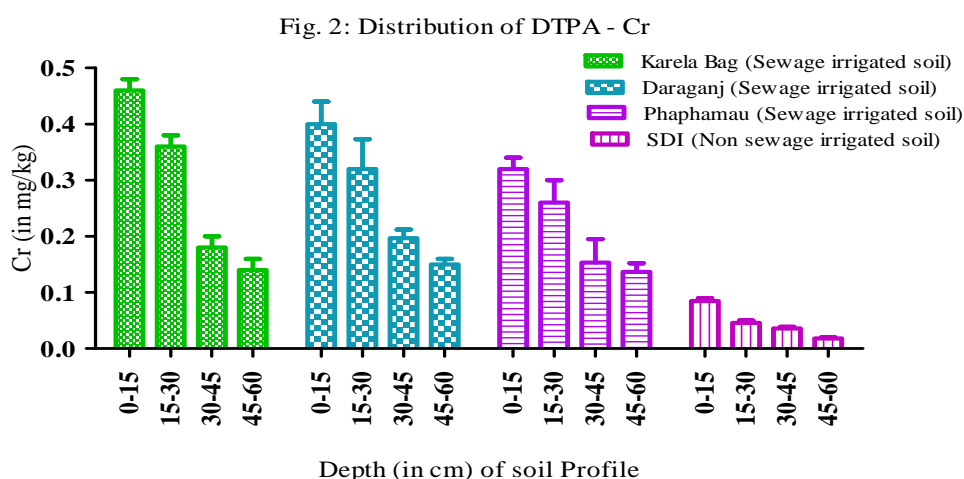


Table-10: Distribution of DTPA-extractable Pb (mg kg^{-1}) in soils.

Depth (in cm)	Sites				Mean
	Sewage irrigated soil			Non-sewage irrigated soil	
	A ₁	A ₂	A ₃	A ₄	
0-15	0.80±0.033	0.68±0.016	0.62±0.043	0.082±0.002	0.54±0.31
15-30	0.68±0.021	0.60±0.016	0.50±0.013	0.064±0.003	0.46±0.27
30-45	0.52±0.016	0.52±0.043	0.46±0.043	0.040±0.003	0.38±0.23
45-60	0.40±0.032	0.44±0.032	0.38±0.016	0.032±0.032	0.31±0.19
Mean	0.60±0.175	0.56±0.103	0.49±0.100	0.054±0.022	

Foot Notes are same as Table 3

DTPA-extractable Lead in soils

The data presented in table 10 & fig. 3 indicates that DTPA-extractable Pb in surface soil was observed lowest (0.082 mg kg^{-1}) at SDI Allahabad (A₄), which has not been receiving in different amounts. The DTPA-extractable Pb in sewage irrigated surface soils at various depths varied from 0.38 ± 0.016 to $0.80 \pm 0.033 \text{ mg kg}^{-1}$. The DTPA-extractable Pb decrease with increase depth of soil profiles also reported similar findings by Ghafoor *et al.*, (2005) and MacLean *et al.*, (1987). The correlation between DTPA-Pb with clay ($r = -0.16$) and between DTPA-Pb with pH ($r = -0.55^*$) were observed negative, whereas, the correlation

between DTPA-Pb with organic carbon ($r=0.61^*$), EC ($r=0.59^*$) and CEC ($r=0.58^*$) were observed positive (Table 16). However, the correlation between DTPA-Pb with organic carbon and EC were strongly positive as well as highly significant. This study indicates that these properties significantly affect the availability of DTPA-Pb, especially organic carbon and EC play dominant role in the mobility of Pb in the sewage irrigated soils. Comparatively less amount of available lead in lower horizons was due to the reduced by Aubert and Pinta (1977). Adsorption of lead by organic matter, clay etc. possibly restricted their mobility to the deeper horizons, by way of forming insoluble complex with organic matter (Garg and Totawat 2005; Jaybaskaran and Sri Ramulu ; Sakal *et al.*, 1992; Udom *et al.*, 2004).

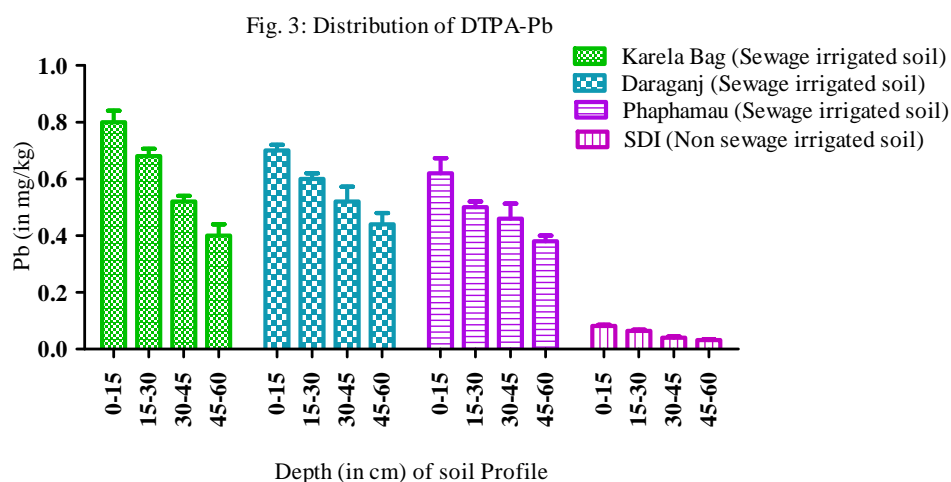


Table-11: Distribution of DTPA-extractable Zn (mg kg^{-1}) in soils

Depth (in cm)	Sites				
	Sewage irrigated soil			Non-sewage irrigated soil	Mean
	A ₁	A ₂	A ₃	A ₄	
0-15	16.40±0.432	12.4±0.53	10.46±0.50	8.40±0.163	11.91±3.40
15-30	13.00±0.91	10.12±0.42	8.40±0.432	6.20±0.432	9.43±2.87
30-45	8.4±0.40	8.20±0.53	6.50±0.50	5.40±0.432	7.12±1.43
45-60	6.4±0.41	4.70±0.30	4.60±0.40	3.20±0.432	4.73±1.30
Mean	11.05±4.51	8.85±3.26	7.49±2.51	5.80±2.14	

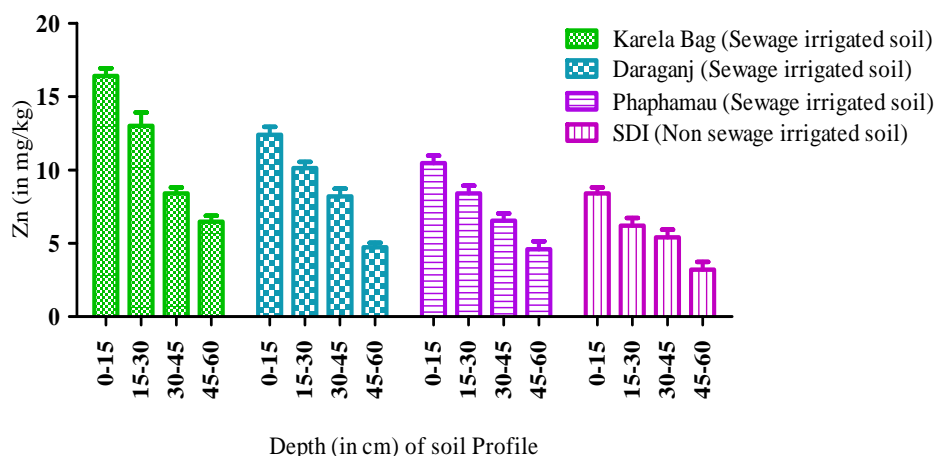
Foot Notes are same as Table 3

DTPA-extractable Zinc in soils

The DTPA-Zn differs significantly with the sites and depth of sampling under soil profiles; and the concentration of DTPA- Zn ranged from 3.2 ± 0.43 to 16.40 mg kg^{-1} (Fig.4). Data in the table 11 showed that at (A₁-A₃) sites receiving sewage irrigated, Zn accumulated more in the surface soil and content decrease with soil depth indicating low mobility of Zn through soil profiles. In non-sewage irrigated soil, low content of Zn was found in comparison to sewage

irrigated soil. Zn content remains more or less constant throughout the depth of soils. In light textured soils (A_1 and A_2), decline in the DTPA-extractable Zn was higher than that in heavy textured type of soils (A_3 and A_4). This may be due to high infiltration and percolation rates of sewage in light textured soils than in the heavy textured soil. Continuous and successive sewage irrigation results in the build-up of heavy metals in the surface soil due higher adsorption and low permeability of these soils. DTPA-Zn in surface soil is correlated with pH ($r=0.19$) and were observed negative correlation whereas, the correlation between DTPA-Zn with EC, ($r=0.35$), CEC ($r=0.86^{**}$) organic carbon ($r=0.96^{**}$) and clay ($r=0.41^*$) were observed positive c. These correlation studies suggest that different soil properties significantly influence DTPA-Zn in sewage irrigated soils (Table 16). Maximum correlation between DTPA-Zn and organic carbon indicates that Zn- organic matter complex augments the availability of Zn in the soil system. Udom *et al.*, (2004) also reported similar findings.

Fig. 4: Distribution of DTPA -Zn

Table-12: Distribution of total Cd (mg kg^{-1}) in soils

Depth (in cm)	Sites				Mean
	Sewage irrigated soil			Non-sewage irrigated soil	
	A_1	A_2	A_3	A_4	
0-15	4.60±0.20	3.93±0.30	2.26±0.30	1.30±0.10	3.02±1.55
15-30	4.00±0.20	3.53±0.30	2.00±0.20	1.10±0.10	2.66±1.48
30-45	3.53±0.30	3.13±0.41	1.60±0.20	0.79±0.09	2.15±1.29
45-60	1.80±0.20	1.53±0.23	1.20±0.20	0.65±0.01	1.30±0.49
Mean	3.48±1.37	3.03±1.05	1.77±0.46	0.96±0.29	

Foot Notes are same as Table 3

Total Cadmium in soils

The data presented in table 12 & fig. 5 indicates that total Cd in surface soil is minimum is ($1.30 \pm 0.10 \text{ mg kg}^{-1}$) at SDI Allahabad (A_4) which has not been receiving sewage irrigation in different amounts. The total Cd in sewage irrigated surface soils at various depths varied from 1.20 ± 0.20 to $4.6 \pm 0.20 \text{ mg kg}^{-1}$. The total Cd decrease with increase depth of soil profile; and the correlation between total Cd with pH ($r = -0.05$) were observed negative whereas, the correlation between total-Cd with organic carbon ($r = 0.91^{**}$), EC ($r = 0.62^*$), CEC ($r = 0.65^*$), clay ($r = 0.16$) were positive and significant (Table 17). Lund *et al.*, (1976), Singh, (2000) and Kumar *et al.*, (2010 b) also reported almost similar findings.

Fig. 5: Distribution of Total -Cd

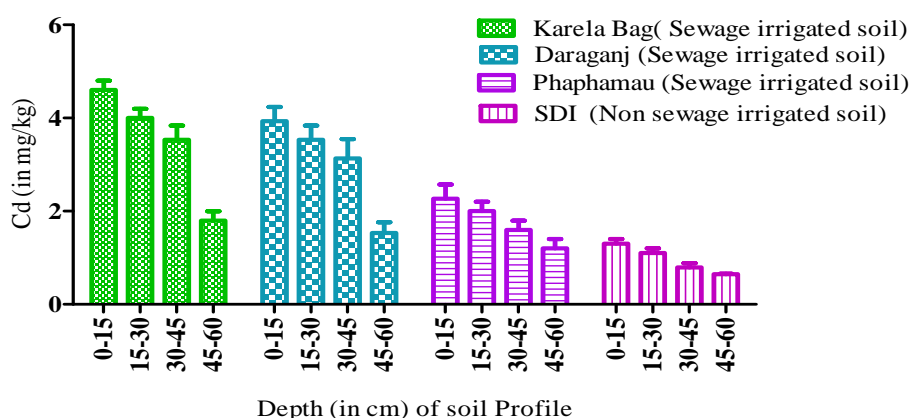


Table -13: Distribution of total Cr (mg kg^{-1}) in soils

Depth (in cm)	Sites				Mean
	Sewage irrigated soil			Non-sewage irrigated soil	
	A ₁	A ₂	A ₃	A ₄	
0-15	4.40 ± 0.53	3.53 ± 0.41	2.40 ± 0.20	1.23 ± 0.052	2.89 ± 1.38
15-30	3.80 ± 0.20	3.00 ± 0.20	1.93 ± 0.30	1.03 ± 0.065	2.47 ± 1.23
30-45	3.40 ± 0.20	2.66 ± 0.30	1.80 ± 0.20	0.85 ± 0.016	2.18 ± 1.10
45-60	2.20 ± 0.40	1.80 ± 0.20	1.60 ± 0.20	0.70 ± 0.043	1.58 ± 0.63
Mean	3.45 ± 0.93	2.77 ± 0.74	1.93 ± 0.34	0.95 ± 0.150	

Foot Notes are same as Table 3

Total chromium in soils

The data presented in the table 13 and fig.6 indicates that total Cr in surface soil is was observed lowest ($1.23 \pm 0.052 \text{ mg kg}^{-1}$) at SDI Allahabad (A_4), which has not been receiving sewage irrigation as compared to those receiving sewage irrigation in different amounts. The total-Cr in sewage irrigated surface soils at various depths varied from 1.60 ± 0.163 - $4.40 \pm 0.20 \text{ mg kg}^{-1}$. The total Cr decrease with increase depth of soil profiles; and the correlation

between total- Cr with pH ($r=-0.17$) were observed negative whereas, the correlation between total-Cr with organic carbon ($r=0.91^{**}$), EC ($r=0.56^*$), CEC ($r=0.72^*$), clay ($r=0.18$) were observed positive (Table-17). However, correlation between total-Cr with organic carbon was strongly positive as well as highly significant. Mitsimbonas *et al.*, (1998) has also reported similar findings.

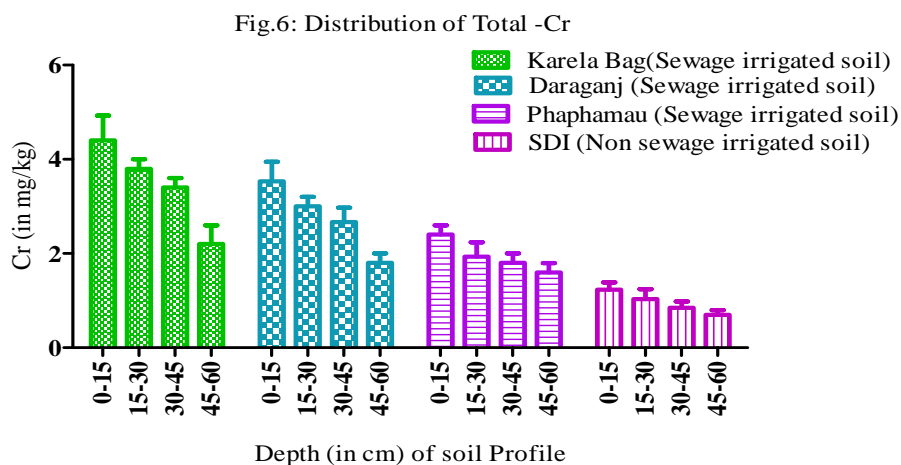


Table-14: Distribution of total Pb (mg kg^{-1}) in soils

Depth (in cm)	Sites				Mean
	Sewage irrigated soil			Non-sewage irrigated soil	
	A ₁	A ₂	A ₃	A ₄	
0-15	6.80±0.20	5.40±0.20	3.80±0.20	1.78±0.36	4.40±2.13
15-30	6.00±0.40	4.80±0.20	3.20±0.40	1.48±0.28	3.81±1.93
30-45	5.20±0.20	4.00±0.42	2.60±0.20	1.00±0.20	3.11±1.77
45-60	3.40±0.20	3.00±0.53	2.00±0.20	0.55±0.05	2.23±1.27
Mean	5.35±1.45	4.10±0.97	2.90±0.77	1.20±0.54	

Foot Notes are same as Table 3

Total Lead in soils

The data presented in the table 14 and fig.7 indicates that total Pb in surface soil is was observed lowest ($1.78\pm0.36 \text{ mg kg}^{-1}$) at SDI Allahabad (A₄), which has not been receiving sewage irrigation as compared to those receiving sewage irrigation in different amounts. The total-Pb in sewage irrigated surface soils at various depths varied from 2.00 ± 0.20 - $6.8\pm0.20 \text{ mg kg}^{-1}$. The total-Pb decrease with increase depth of soil profiles; and the correlation between total- Pb with pH ($r=-0.29$) were observed negative correlation, whereas, the correlation between total-Pb with organic carbon ($r=0.89^{**}$), EC ($r=0.56^*$), CEC ($r=0.72^{**}$), clay ($r=0.16$) were observed positive (Table17). Soil pH had significant negative correlation with total content of lead ($r=-.29$), whereas, relationship between total lead content and EC

($r=0.56^*$) positive and significant. These results are in conformity with the findings of Roy *et al.*, (1987) and Mitsimbonas *et al.*, (1998).

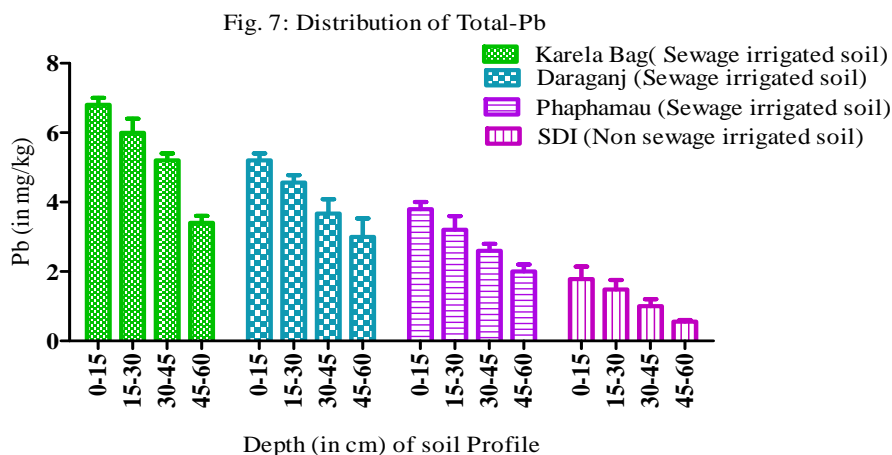


Table-15: Distribution of total Zn (mg kg^{-1}) in soils

Depth (in cm)	Sites				
	Sewage irrigated soil			Non-sewage irrigated soil	Mean
	A ₁	A ₂	A ₃	A ₄	
0-15	95.30±5.03	85.00±4.42	77.60±2.62	57.93±1.72	79.16±13.82
15-30	88.60±2.60	73.33±3.05	66.86±4.27	51.53±1.39	74.30±14.33
30-45	72.60±3.05	63.33±3.05	60.93±3.00	39.16±1.59	62.90±15.80
45-60	43.00±2.69	40.93±4.67	34.00±360	24.93±0.49	35.71±8.05
Mean	74.88±23.29	65.64±18.70	59.84±18.56	43.38±14.56	

Foot Notes are same as Table 3

Total Zinc in soils

The DTPA-Zn differs significantly with the sites and depth of sampling under soil profiles; and the concentration of total- Zn ranged from 24.93 ± 0.49 to $95.30\pm 0.30 \text{ mg kg}^{-1}$ (Fig. 8) Data in the table 15 showed that at A₁-A₃ sites receiving sewage irrigated, Zn accumulated more in the surface soil and content decreases with soil depth indicating low mobility of Zn through soil profiles. In non-sewage irrigated soil, low content of Zn was found in comparison to sewage irrigated soil. Zn content remains more or less constant throughout the depth of soils. In light textured soils (A₁ and A₂) decline in the total-Zn was higher than that in heavy textured type of soils (A₁ and A₂). This may be due to high infiltration and percolation rates of sewage –in light textured soils than in the heavy textured soil. Continuous and successive sewage irrigation result in the build-up of heavy metals in the surface soil due to higher adsorption and low permeability of these soils. Total-Zn in surface soil is correlated with pH ($r=-0.34$) were observed negative whereas, the correlation between total-Zn with EC

($r=0.56^*$), CEC ($r=0.71^*$), clay ($r=0.09$) and organic carbon ($r=0.83^{**}$) were positive. These correlation studies suggest that different soil properties significantly influence total-Zn in sewage irrigated soils (Table 17). Maximum correlation between total-Zn and augments the availability of Zn in the soil system. Udom *et al.*, (2004) and Sharma *et al.*, (2007) also reported similar findings.

Fig. 8: Distribution of Total-Zn

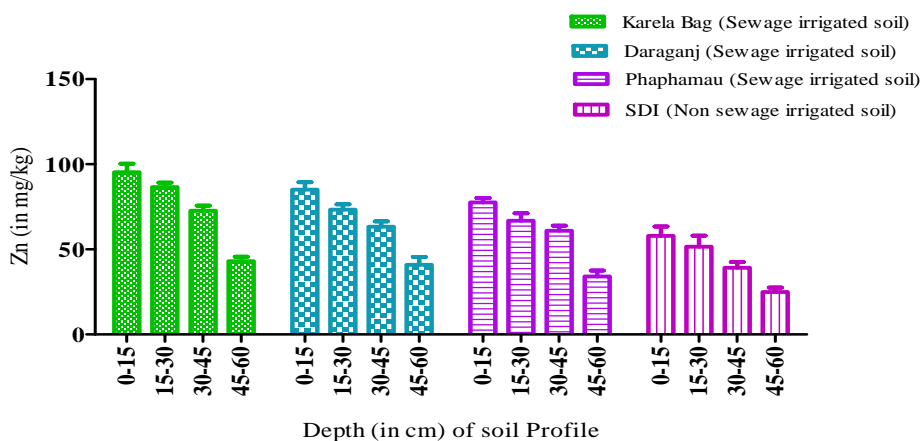


Table-16: Correlation coefficients (r values) of heavy metals with soil properties

Parameters	DTPA-Cd	DTPA-Cr	DTPA-Pb	DTPA-Zn
pH	-0.26	-0.36	-0.55*	-0.19
EC	0.66*	0.64*	0.59*	0.35
CEC	0.63*	0.62*	0.58*	0.86**
Organic carbon	0.81**	0.75*	0.61*	0.96**
Clay	-0.09	-0.05	-0.16	0.41*

*Significant at 5%, **Significant at 1%

Table-17: Correlation coefficients (r- values) of heavy metals with soil properties

Parameters	Total-Cd	Total-Cr	Total-Pb	Total-Zn
pH	-0.05	-0.17	-0.29	-0.34
EC	0.62*	0.56*	0.56*	0.56*
CEC	0.65*	0.72*	0.72*	0.71*
Organic carbon	0.91**	0.91**	0.89**	0.83**
Clay	0.16	0.18	0.15	0.09

*Significant at 5%, **Significant at 1%

The sub soil can remove a large proportion of any heavy metal that remains in solution in the downwards moving water. As the content of organic matter generally decrease with depth in the profile, the removal is attributable to the increasing content and/or activity of the inorganic colloids. Any downwards movement of heavy metals leaching will also be

influenced by soil physical properties, including texture and permeability as well as by climate and seasonal variation in rainfall and evaporation (Hodgson *et al.*, 1963). The significant factors influencing the availability of heavy metals are soil Ph and the quality of soil organic matter (Barancikova and Makovnikova, 2003; Puschenreiter *et al.*, 2005). The movement of heavy metals down the soil profile is often evident in high applications of heavy metals, usually in sewage sludge, in soils with low organic matter and clay contents, acidic conditions, and when high rainfall or irrigation water rates have been applied. The movement occurs through soil macropores or cracks which is also referred to as preferential flow. The effect of pH on heavy metal availability to plants has been reported by many researchers and it is accepted that as pH decreases, the solubility of cationic forms of metals in the soil solution increases and, therefore, they become more readily available to plants (Gray *et al.*, 1998; Singh *et al.*, 1995; Evans *et al.*, 1995; Filius *et al.*, 1998; Mann and Ritchie, 1995; Chlopecka *et al.*, 1996. Evans (1989) explained that pH has a major effect on metal dynamics because it controls adsorption and precipitation, which are the main mechanisms of metal retention to soils. Metal solubility in the solution depends on the solubility product of the solid phase (precipitate) containing the metal. Soil pH was significantly greater and decreased with depth. pH is one of the factors which influence the bioavailability and the transport of heavy metals in the soil and according to Smith and Giller (1992) heavy metal mobility decreases with increasing soil pH due to precipitation of hydroxides, carbonates or formation of insoluble organic complexes. The amount of heavy metals mobilized in soil environment is a function of pH, properties of metals, redox conditions, soil chemistry, organic matter content, clay content, cation exchange capacity and other soil properties (Arun and Mukherjee, 1998; Kimberly and William, 1999; Sauvee *et al.*, 2000).

CONCLUSION

Frequent sewage irrigation on agriculture land increases the DTPA-extractable and total heavy metals (Cd, Cr, Pb and Zn) in soils. Sewage irrigated soil increases the heavy metals concentration in soil, leading to increased plant uptake of heavy metals, which injurious to human and animal health. In present investigation, the depth-wise distribution of four heavy metals viz. Cd, Cr, Pb and Zn were observed in following pattern. From the foregoing results, it concluded that the higher accumulation of heavy metals (Cd, Cr, Pb and Zn) in the surface soil (0-15 cm) decreased with increased depth of soil profile. But clay contents increased with decreased depth of soil. Continuous use of sewage irrigation on agricultural land increased

the DTPA-extractable Cd, Cr, Pb and Zn from 0.081 ± 0.01 - 0.270 ± 0.01 mg kg⁻¹, 0.084 ± 0.005 - 0.46 ± 0.02 mg kg⁻¹, 0.082 ± 0.002 - 0.80 ± 0.033 mg kg⁻¹ and 8.40 ± 0.16 - 16.40 ± 0.432 mg kg⁻¹ in surface soil (0-15cm), respectively. A very low amount of heavy metals (Cd, Cr, Pb and Zn) were observed in (45-60 cm) depth in comparison to surface soil (0-15 cm) in all the soil examined. Similarly accumulation of total heavy metals (Cd, Cr, Pb and Zn) from 1.30 ± 0.10 - 4.60 ± 0.20 mg kg⁻¹, 1.23 ± 0.05 - 4.40 ± 0.53 mg kg⁻¹, 1.78 ± 0.36 - 6.8 ± 0.20 mg kg⁻¹ and 57.93 ± 1.72 - 95.30 ± 5.03 mg kg⁻¹ in surface soil (0-15cm) respectively. A low amount of total heavy metals (Cd, Cr, Pb and Zn) were observed in 45-60 cm depth in comparison to surface soil (0-15 cm) in all the soil examined indicating low mobility of these metals down the depth. The DTPA-extractable heavy metals (Cd, Cr, Pb and Zn) and total heavy metals content of sewage irrigated and non-sewage irrigated soils decreased with increasing soil depth. The soil organic carbon content in soils were positively and significantly correlated with DTPA-extractable Cd ($r=0.81^{**}$), Cr ($r=0.75^*$), Pb ($r=0.61^*$) and Zn ($r=0.96^{**}$), while clay contents showed negative impact on the extractability of these metals. Similarly correlations of total heavy metals with physical property were observed positively, while pH and clay content showed negatively impact.

In non-sewage irrigated soil, low content of heavy metals were found in comparison to sewage irrigated soil. Under risk assessment, profile-wise study indicated accumulation of Cd, Cr, Pb and Zn below up to 0.7m. Karela bag sewage irrigated soil was highly polluted than other three sites.

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