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Depth wise accumulation of heavy metals in sewage contaminated and uncontaminated soils

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ABSTRACT

Continuous use of sewage irrigation on agricultural land increased the total Cd, Pb, Cr and Zn from 2.21±0.24-5.21±0.41 mg kg^{-1}, 3.62±0.31-4.56±0.42 mg kg^{-1}, 2.72±0.19-4.24±0.33 mg kg^{-1} and 67.58±2.34-88.47±3.89 mg kg^{-1} in surface soil (0-10 cm), respectively. A very low amount of heavy metals (Cd, Pb, Cr and Zn) were observed in (30-50 cm) depth in comparison to surface soil (0-10 cm) in all the soil examined. Similarly increased the accumulation of DTPA-extractable Cd, Pb, Cr and Zn from 0.216±0.032-0.256±0.033 mg kg^{-1}, 0.64±0.22-0.82±0.22 mg kg^{-1}, 0.38±0.17-0.54±0.22 mg kg^{-1} and 12.57±0.53-15.28±1.09 mg kg^{-1} in surface soil (0-10cm) respectively. A low amount of total heavy metals (Cd, Pb, Cr and Zn) were observed in 30-50 cm depth in comparison to surface soil (0-10 cm) in all the soil examined indicating low mobility of these metals down the depth. The total heavy metals (Cd, Pb, Cr and Zn) and DTPA-extractable heavy metals content of sewage contaminated and uncontaminated soils decreased with increasing soil depth. The soil organic carbon content in soils were positively and significantly correlated with DTPA-extractable Cd (r=0.98**), Pb (r=0.93**), Cr (r=95**) and Zn (r=1.00**), 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 uncontaminated soil, low content of heavy metals were found in comparison to contaminated soil. Under risk assessment, profile-wise study indicated accumulation of Cd, Pb, Cr and Zn below up to 50 cm. Naini contaminated soil was highly contaminated than other three sites.Thus, it may be concluded that a high concentration of extractable heavy metals in surface soils (0-10 cm) will not only reduce the plant growth but will also affect the availability of other essential elements to plants.

Key words: Accumulation, heavy metals mobility, soil profile, contaminated soil

I. INTRODUCTION

Soil pollution by heavy metals, such as cadmium, lead, chromium and zinc etc. is a great problem of concern. Although heavy metals are naturally present in soil but it gets contaminated to an alarming level which comes from local sources: mostly industries and vehicular exhaust supplemented by local activities.

In India, urban population especially in city areas is increasing rapidly. This rapid increase in urban population causes a significant pressure on urban services like municipal solid waste (MSW) management. MSW management systems in all cities in India are very much traditional and labor based and most of the solid wastes are disposed in the open dumping spaces due to lack of regulatory systems and effective management. Open dumping of municipal solid waste without source segregation is the usual practice in developing countries like India. Co-disposal of household hazardous waste including batteries, paint residues, ash, treated woods and electronic wastes increases the heavy metal content in MSW dumping sites (Ahsan et al., 2013; Karim et al., 2014).

The mining activities are among the main sources of soil contamination by heavy metals This risk may arise during operation and after mine closure duto tailings which are often stored in the absence of any environmental management plan (Laghlimi et al., 2015).

II. MATERIALS AND METHODS

A. Soil sampling from the experimental site

The experimental sites are located between latitudes 25º20’-20º57’ N and longitudes 81º52’-81º86’ E and belong to the Indian tropical sub-humid region of Indo-Gangetic plain

Allahabad, Uttar Pradesh, India. The soils of Gangetic plain are Alluvial Entisols having some recent origin. The mean texture of the experimental soil was silty clay loam (sand 49.06 ± 5.65 %, silt 28.36 ± 6.53 % and clay 22.45 ± 4.39 %).Representative soil samples from alluvial soils which had been receiving sewage effluents for fifteen years were collected from different depths (0-10, 10-20, 20-30 and 30-50 cm) from four experimental sites given the table-1.

Table 1: Location of representative soil samples

SI. No	Site No.	Location of sites
1.	S_1	SDI farm uncontaminated soil, Allahabad
2.	S_2	Jhunsi contaminated soil, Allahabad
3.	S_3	Mumfordganj contaminated soil, Allahabad
4.	S_4	Naini contaminated soil, Allahabad

The larger fields were divided into suitable and uniform parts, and each of these uniform parts was considered a separate sampling unit. In each sampling unit, soil samples were drawn from several spots in a zigzag pattern, leaving about 2 m area along the field margins.

III. METHODS OF SOIL ANALYSIS

a. 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 sand by decantation (Chopra and Kanwar, 2002).

b. Soil pH

Soil pH was measured with 1:2.5 soil water ratio using Elico digital pH meter (Model LI 127, Elico Ltd., Hyderabad, India) at the Laboratory of Sheila Dhar Institute of Soil Science, University of Allahabad, Allahabad-211002, Uttar Pradesh, India. Double distilled water was used for the preparation of all solutions.

c. Organic carbon

One gram soil was digested with 10 ml of 1 N potassium dichromate ($K_2Cr_2O_7$) solution and 20 ml of concentrated sulphuric acid (18M, 96%). The solution was shaken well for two minutes and kept for half an hour and then diluted with 200 ml of distilled water. Then 10 ml of ortho-phosphoric acid (15M, 85%) and 1 ml of diphenylamine indicator were added in solution. The solution became deep violet in colour and further it was titrated against N/2 ferrous ammonium sulphate solution, till the violet colour changed to purple and finally to green (Chopra and Kanwar, 2002).

d. Cation Exchange Capacity

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

C. Extraction for total heavy metals content in soil

One gram of soil was mixed in 5 ml of HNO_3 (16M, 71%) and 5 ml of $HClO_4$ (Perchloric acid 11 M, 71%). The composite was heated up to dryness. The hot distilled water was added. The contents were filtrated and volume was made up to 50 ml. The clean filtrate was used for the estimation of heavy metals (Cd, Pb, Cr and Zn) by Atomic Absorption Spectrophotometer (AAS) (AAnalyst600, Perkin Elmer Inc., MA, USA).

D. Preparation of DTPA solution

DTPA solution was prepared by a method developed by Lindsay and Norvell (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.

E. Extraction for available heavy metals (Cd, Pb, Cr and Zn) Content in Soil

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

F. Statistical Analysis

Graph Pad Prism (version 5.04) and MS-Excel 2010 software were used for drawing figures.

G. 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:

$$r = \frac{\text{cov}(x,y)}{\sigma_x \sigma_y}$$

, where $\text{cov}(x,y) = \sum (x - \bar{x})(y - \bar{y})/n$ stands for the sample co-varianc

$\sigma_x = \left[\sum (x - \bar{x})^2 / n\right]$ $\sigma_y = \left[\sum (y - \bar{y})^2 / n\right]$

a $\sqrt{\quad}$ and $\sqrt{\quad}$ stand for sample standard deviati

x and y, respectively. Thus, using the direct method, 'r' is calculated as:-

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

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

$$t = \frac{r}{\sqrt{(1 - r^2)/9(n-1)}}$$ 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. $|t| \quad t_{0.05}$ (n-2), the hypothesis is rejected at 5% level, otherwise the sample is said to be consistent with hypothesis.

IV. RESULTS AND DISCUSSION

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

A. Physico-chemical properties of soil

Soil pH and Electrical Conductivity

Soil pH and electrical conductivity (EC) almost decreases with increasing depth of soil profile (Table-2 & 3). Soil pH (7.62±0.11 to 8.02±0.23) and EC (0.76±0.11 to 1.24±0.21) 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. EC was observed maximum in the soil profiles of Naini contaminated soil (S_4) to the extent of 0.71±0.05 d S m^{-1} in the lowest horizon (of 30–50 cm depth) to 1.24±0.21 dS m^{-1} in the surface horizon (of 0–10 cm depth), which was followed by the soil profiles of Mumfordganj contaminated soil (S_3) to the extent of 0.63±0.06 dS m^{-1} in the lowest horizon (of 30–50 cm depth) to 1.21±0.16 dS m^{-1} in the surface horizon (of 0–10 cm depth).It is evident from the data that frequent sewage-irrigation contributes to the build-up of soil fertility to some extent and can mitigate the scarcity of water in the dry and tropical regions (Annu et al., 2015; Mani et al., 2013a). Such changes in pH and EC were also reported by Kumar et al. (2010). The correlation between EC with DTPA-Cd (r=1.00**), DTPA-Pb (r=0.97**), DTPA-Cr (r=0.97**) and DTPA-Zn (r=0.97**) were observed positive (Table -8). However, the correlation between pH with DTPA-Cd, Pb, Cr and Zn were observed negative significant (r= -0.004), (r= -0.07), (r= -0.19) and (r= -0.06) respectively. The correlation between EC with DTPA-Cd, Pb, Cr and Zn were strongly positive as well as highly significant. Annu et al. (2015);Bansal and Singh, 2014; Mani et al. (2013a); Abii (2012); Perveen (2011); Kumar et al. (2010) have found almost similar findings.

TABLE-2: Variation in pH in soils

Depth (in cm	Sites				
	SDI farm uncontaminated soi	Contaminated soil			
	S_1	S_2	S_3	S_4	Mean
0-10	7.81±0.11	7.92 ± 0.13	8.02±0.2	7.62±0.1	7.8±0.1
10-20	7.14±0.13	7.20±0.14	7.8 ± 0.1	7.1 ± 0.1	7.3±0.3
20-30	6.9±0.05	7.10±0.15	7.6 ± 0.1	6.8 ± 0.1	7.1±0.3
30-50	6.7±0.09	6.90±0.21	7.2 ± 0.1	6.6 ± 0.1	6.9±0.2
Mean	7.1±0.48	7.3±0.44	7.7±0.3	7.0±0.4	

Note: Data are mean values of three replications (mean ± SD) collected from soil profiles of four locations are SDI farm uncontaminated soil (S_1), Jhunsi contaminated soil (S_2), Mumfordganj contaminated soil (S_3), Naini contaminated soil (S_4).

TABLE-3: Variation in Electrical *Conductivity (d S m^{-1}) in soils*

Dept (in cm	Sites				
	SDI farm uncontaminate soil	Contaminated soil			
	S_1	S_2	S_3	S_4	Mean
0-10	0.76±0.11	1.16±0.1	1.21±0.1	1.24±0.21	1.09±0.2
10-20	0.64±0.04	1.12 ± 0.	1.00 ± 0.1	1.11 ± 0.09	0.97±0.2
20-30	0.380±0.07	0.75 ± 0.	0.70 ± 0.0	0.86 ± 0.13	0.67±0.2
30-50	0.42±0.07	0.58 ± 0.	0.63 ± 0.0	0.71 ± 0.05	0.59±0.1
Mean	0.55±0.18	0.89±0.2	0.90±0.2	0.93±0.24	

Foot Notes are same as Table-2

B. Organic Carbon

Organic carbon (mean 4.25±0.58 g kg^{-1}) was maximum in surface soil (TABLE-4), which varied among different sites (S_1 to S_4); and their contents at all the investigated sites decreases with increase in depth of soil profile from 4.25± 0.58 to 2.34±0.16 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. Mani et al. (2013a) and Esteban et al. (2000) reported

the similar finding. The correlation coefficients between organic carbon and DTPA- extractable Cd (r=0.98**), Pb (r=0.93**), Cr (r=0.95**) and Zn (r=1.00**) were observed positive (Table-8). However, the correlation coefficients between organic carbon and DTPA-extractable Cd and DTPA-extractable Zn were strongly positive as well as highly significant. Organic carbon in sewage contaminated soil was higher than that of non-sewage contaminated soil. The effect of soil depth and soils and their interaction on soil organic carbon were significant. The metal content and organic carbon in the soils of sewage-effluent-contaminated sites were substantially higher than uncontaminated site.

Organic matter improves soil structure and increases the soil's ability to hold water (PEIC, 2003).These differences may be due to relatively higher concentration of these metal ions and organic carbon in sewage contaminated soils (Akan et al., 2010; Kumar et al., 2010; Perveen et al., 2011; Mani et al., 2013a; Bansal and Singh, 2014).

TABLE-4: Variation in Organic carbon (g kg^{-1}) in soils

Dept (in cn	Sites				
	SDI farm uncontaminate soil	Contaminated soil			
	S_1	S_2	S_3	S_4	Mean
0-10	3.45 ± 0.24	4.24 ± 0.1	4.56 ± 0.1	4.76±0.23	4.25±0.5
10-2	2.58 ± 0.22	3.78 ± 0.2	3.42 ± 0.1	3.62 ± 0.2	3.35±0.5
20-3	2.21 ± 0.21	3.24 ± 0.1	2.67 ± 0.2	2.86 ± 0.1	2.75±0.4
30-5	2.15 ± 0.23	2.28 ± 0.1	2.38 ± 0.1	2.54 ± 0.2	2.34±0.1
Mea	2.60±0.60	3.39±0.84	3.26±0.97	3.45±0.99	

Foot Notes are same as Table-2

C. Cation Exchange Capacity

CEC (mean 20.3±1.7 C mol (p^+) kg^{-1}) are maximum in surface soil (TABLE-5), which varied among different sites (S_1 to S_4); and their contents at all the investigated sites decreases with increase in depth of profile from 20.3±1.7 to 16.8±1.3 (Cmol (p^+) kg^{-1}) soil. CEC [18.2–22.1 Cmol (p^+) kg^{-1}] in surface soils had wide variation from one to the other site due to sewage-irrigation commonly practiced by the vegetable producers (Mani et al., 2013a). The correlation coefficients between CEC and DTPA-extractable Cd (r=0.29), Pb (r=0.46*), Cr (r=0.50*) and Zn (r=0.21) were observed positive and significant (Table-8). These differences are due to higher concentration of these metal ions and CEC in sewage contaminated soils. Almost similar findings also reported by Rattan et al., 2005; Akan et al., 2010; Mani et al., 2013a; Bansal and Singh, 2014).

TABLE-5: Variation in Cation Exchange Capacity (Cmol (p^+) kg^{-1}) in soils

Depth (in cm	Sites				
	SDI farm uncontaminated soil	Contaminated soil			
	S_1	S_2	S_3	S_4	Mean
0-10	19.6 ± 1.2	21.3 ± 1.6	18.2 ± 1.7	22.1 ± 1.9	20.3±1.7
10-20	18.1 ± 1.3	20.2 ± 1.2	17.4 ± 1.5	21.4 ± 1.4	19.3±1.9
20-30	17.3 ± 1.5	18.1 ± 1.1	16.1 ± 1.4	20.2 ± 1.5	17.9±1.7
30-50	16.2 ± 1.4	17.4 ± 1.3	15.3 ± 1.6	18.2 ± 1.7	16.8±1.3
Mean	17.8 ± 1.4	19.3 ± 1.8	16.8 ± 1.3	20.5 ± 1.7	

Foot Notes are same as Table-2

D. Clay

Clay (mean 21.65±3.87) are minimum in surface soil (TABLE-6), which varied among

different sites (S_1 to S_4); and their contents at all the investigated sites increase with increasing depth of profile (mean 21.65±3.87 to 34.65±4.53). However, the correlation coefficients between Clay and DTPA-extractable Cd (r= -0.48*), Pb (r= -0.64*), Cr (r= - 0.67*) and Zn (r= -0.40) were observed negative correlation (Table-8). Esteban et al. (2000); Rattan et al. (2005) and Mani et al. (2013a) has also reported similar findings.

TABLE-6: Variation in clay (%) in soils

Dept (in cm)	Sites				
	SDI farm uncontaminate soil	Contaminated soil			
	S_1	S_2	S_3	S_4	Mean
0-10	24.34 ± 1.22	19.25 ± 1.4	25.5 ± 1.30	17.5 ± 1.3	21.65 ± 3.8
10-2	26.2 ± 1.45	21.6 ± 1.1	31.4 ± 1.16	24.2 ± 1.8	25.85 ± 4.1
20-3	28.4 ± 1.24	25.8 ± 1.4	36.1 ± 1.64	27.6 ± 1.4	29.48 ± 4.5
30-5	32.1 ± 1.48	36.9 ± 1.5	39.8 ± 1.10	29.8 ± 1.5	34.65 ± 4.5
Mea	27.76 ± 3.34	25.89 ± 7.8	33.2 ± 6.18	24.78±5.3	

Foot Notes are same as Table-2

B. HEAVY METALS ACCUMULATION AND CONTENT IN CONTAMINATED SOILS

Total Cadmium in soils

The data presented in Fig.-1 indicates that total Cd in surface soil is minimum is (0.16±0.08 mg kg^{-1}) at SDI farm uncontaminated soil Allahabad (S_1) which has not been receiving sewage water contaminated as compared to receiving sewage water contaminated in different amounts. The total Cd in sewage contaminated surface soils at various depths varied from 0.86±0.22 to 5.21±0.41 mg kg^{-1}. The total Cd decrease with increase depth of soil profile; and the correlation between total Cd with pH (r= -0.17) and clay (r= -0.35) were observed negative whereas, the correlation between total-Cd with organic carbon (r= 0.98**), EC (r=0.90**) and CEC (r= 0.18) were positive and significant (Table-7). Singh, (2000); Kumar et al., (2010 b) and Mani et al., (2013b) Annu et al., (2015) also reported almost similar findings.

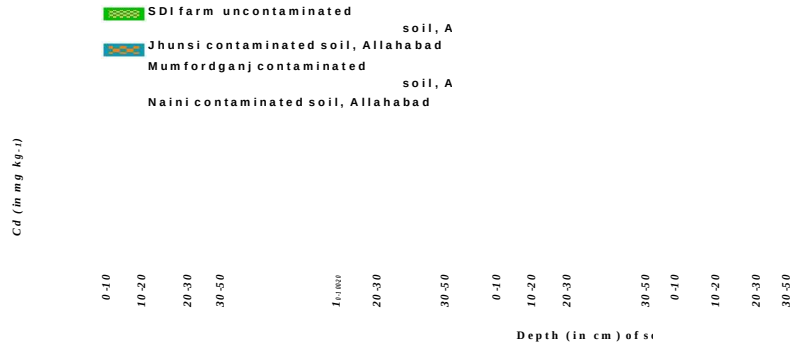

Fig. -1: Accumulation of Total -Cd

Total Lead in soils

The data presented in the Fig.-2 indicates that total Pb in surface soil is was observed lowest (1.15±0.22 mg kg^{-1}) at SDI farm uncontaminated soil Allahabad (S_1), which has not been receiving sewage irrigation as compared to those receiving sewage irrigation in different amounts. The total-Pb in sewage water contaminated surface soils at various depths varied from 1.36±0.24-4.56±0.42 mg kg^{-1}. The total-Pb decrease with increase depth of soil profiles; and the correlation between

total- Pb with clay (r= -0.58*) were observed negative correlation, whereas, the correlation between total-Pb with pH (r=0.11), EC (r=0.92**), CEC (r=0.41*), organic carbon (r=0.82**) were observed positive (Table-7). Soil clay had significant negative correlation with total content of lead (r= -.58*), whereas, relationship between total lead content and EC (r=0.92**) and organic carbon (r=0.82**) positive and highly significant. These results are in conformity with the findings of Annu et al. (2015) and Mani et al. (2013b).

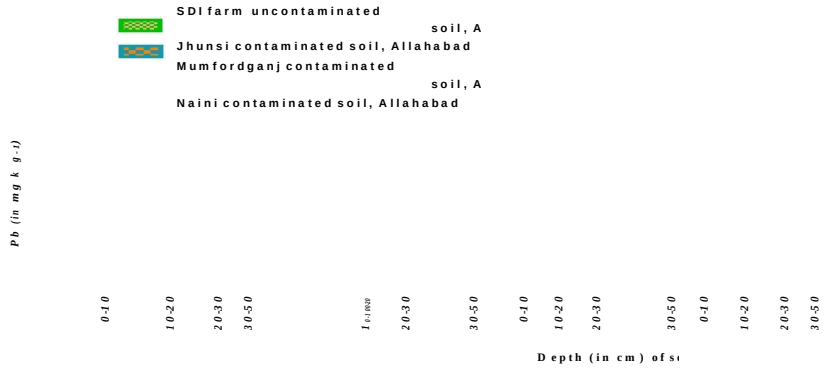

Fig. -2: Accumulation of Total -Pb

Total chromium in soils

The data presented in the Fig. -3 indicates that total Cr in surface soil is was observed lowest (1.12±0.21 mg kg^{-1}) at SDI farm uncontaminated soil Allahabad (S_1), which has not been receiving sewage water contaminated as compared to those receiving sewage water contaminated in different amounts. The total-Cr in sewage contaminated surface soils at various depths varied from 1.32±0.21-4.24±0.33 mg kg^{-1}. The total-Cr decrease with increase depth of soil profiles; and the correlation between total- Cr with pH (r= -0.18) and clay (r= - 0.46*) were observed negative, whereas, the correlation between total-Cr with EC (r=0.95**), CEC (r= 0.28), organic carbon (r= 1.00**) were observed positive (Table-7). However, correlation between total-Cr with organic carbon was strongly positive as well as highly significant. Mitsimbonas et al., (1998);Kumar et al., (2012);Bansal and Singh, (2014) has also reported similar findings.

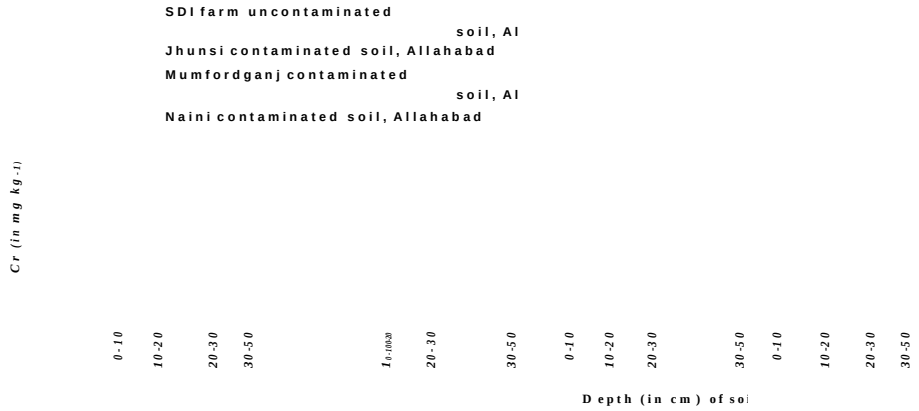

Fig. -3: Accumulation of Total -Cr

Total Zinc in soils

The total-Zn differs significantly with the sites and depth of sampling under soil profiles; and the concentration of total- Zn ranged from 24.36±1.22-88.47±3.89 mg kg-^{1}. Data in the Fig.-4 showed that at S_2 – S_4 sites receiving sewage water contaminated, Zn accumulated more in the surface soil and content decreases with soil depth indicating low mobility of Zn through soil profiles. In uncontaminated soil, low content of Zn was found in comparison to sewage water contaminated soil. Zn content remains more or less constant throughout the depth of soils. In light

textured soils (S_3 and S_4) decline in the total-Zn was higher than that in heavy textured type of soils (S_3 and S_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 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= -0.64*) and clay (r= -0.85**) were observed negative, whereas, the correlation between total-Zn with EC (r=0.74*), CEC (r= 0.76*), organic carbon (r= 0.80**) were positive. These correlation studies suggest that different soil properties significantly influence total-Zn in sewage contaminated soils (Table-7). Maximum correlation between total-Zn and augments the availability of Zn in the soil system. Udom et al., (2004); Sharma et al., (2007);Kumar et al., (2012); Annu et al., (2015) also reported similar findings.

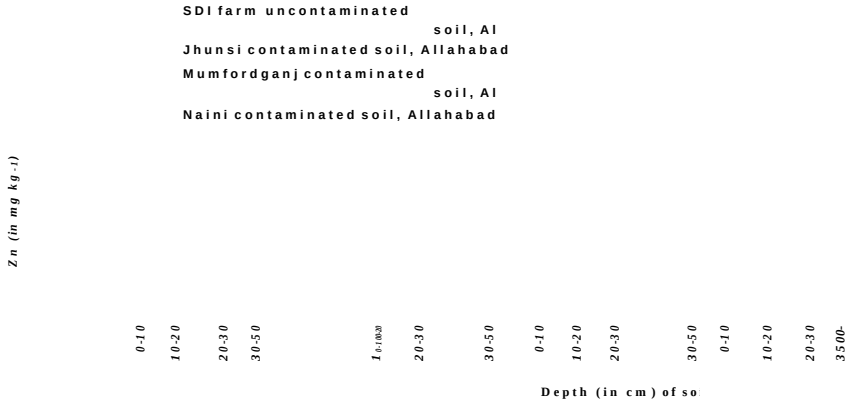

Fig. -4: Accumulation of Total -Zn

DTPA-extractable Cadmium in soils

The data presented in the Fig.-5 indicates that DTPA-extractable Cd in surface soil was minimum (0.068±0.023) at SDI farm uncontaminated soil Allahabad (S_1), which has not been receiving sewage water contaminated as compared to those receiving sewage water contaminated in different amounts. The DTPA-extractable Cd in sewage water contaminated surface soils at various depths varied from 0.087±0.023 to 0.256±0.033 mg kg^{-1}. The DTPA-extractable Cd decreases with increased depth of soil profiles; and the correlation between DTPA-Cd with clay (r= -0.48*) and pH (r= -0.004) were observed negative, while the correlation between DTPA-Cd with EC (r=1.00**), CEC (r=0.29) and organic carbon (r=0.98**) were positive and significant (Table-8). 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. The mobility seemed to be governed by high complexing nature of organic matter in sewage contaminated with Cd. Formation of highly stable and soluble metal fulvate complexes facilitates the movement of Cd and its complexes through soil. Almost similar findings also reported by Kumar et al., 2010a; Mani et al., 2013a; Bansal and Singh, 2014; Annu et al., 2015.

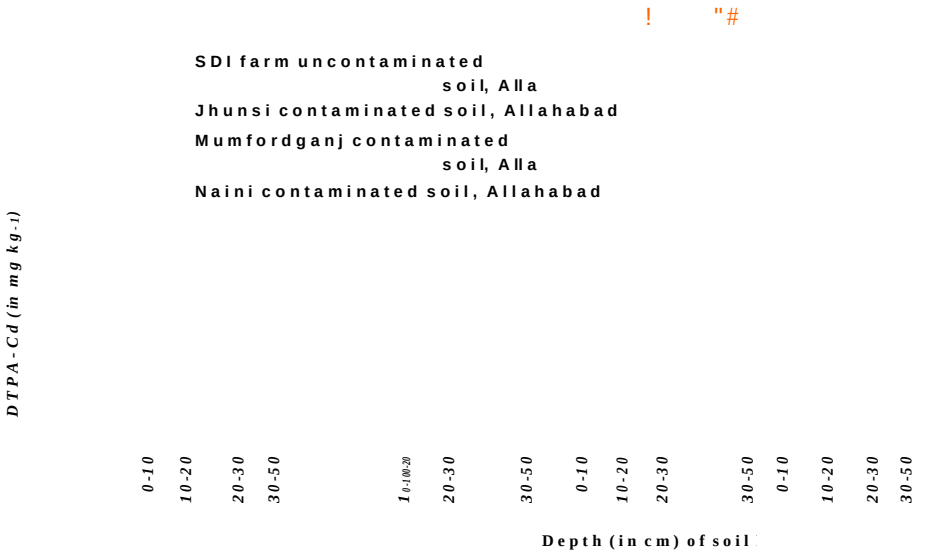

Fig. -5: Accumulation of DTPA-Cd

DTPA-extractable Lead in soils

The data presented in Fig. -6 indicates that DTPA-extractable Pb in surface soil was observed lowest (0.056 ± 0.014 mg kg^{-1}) at SDI farm uncontaminated soil Allahabad (S_1), which has not been receiving in sewage water contaminated as compared to those receiving sewage water contaminated in different amounts. The DTPA-extractable Pb in sewage contaminated surface soils at various depths varied from 0.44±0.13 to 0.82±0.22 mg kg^{-1}. The DTPA-extractable Pb decrease with increase depth of soil profiles also reported similar findings by Ghafoor et al., (2005); Mani et al., (2013b) and Annu et al. (2015). The correlation between DTPA-Pb with clay (r= -0.64*) and pH (r= -0.07) were observed negative, whereas, the correlation between DTPA-Pb with EC (r=0.97**), CEC (r=0.46*) and organic carbon (r=0.93**) were observed positive (Table-8). 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 contaminated 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; Udom et al., 2004).

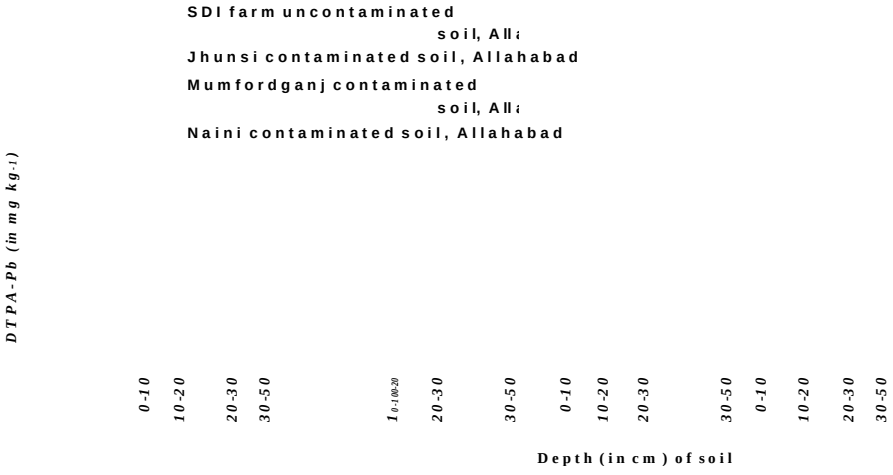

Fig. -6: Accumulation of DTPA-Pb

DTPA-extractable Chromium in soils

The data presented in the Fig.-7 indicates that DTPA-extractable Cr in surface soil was

observed lowest (0.032±0.012 mg kg^{-1}) at SDI farm uncontaminated soil Allahabad (S_1), which has not been receiving in sewage water contaminated as compared to those receiving sewage water contaminated in different amounts. The DTPA-extractable Cr in sewage contaminated surface soils at various depths varied from 0.12±0.06 to 0.54±0.22 mg kg^{-1}. The DTPA-extractable Cr decrease with increased depth of soil profiles; and correlation between DTPA-Cr with clay (r= -0.67*) and DTPA- Cr with pH (r= -0.19) were observed negative correlation, whereas, correlation between DTPA-Cr with EC (r=0.97**), CEC (r=0.50*) and organic carbon (r=0.95**) were positive correlation (Table-8). Almost similar findings also reported byBansal and Singh, 2014. 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 contaminated soils. The higher concentration of Cr in surface soil layer (0-10 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 (Nwuche and Ugoji, 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**.**

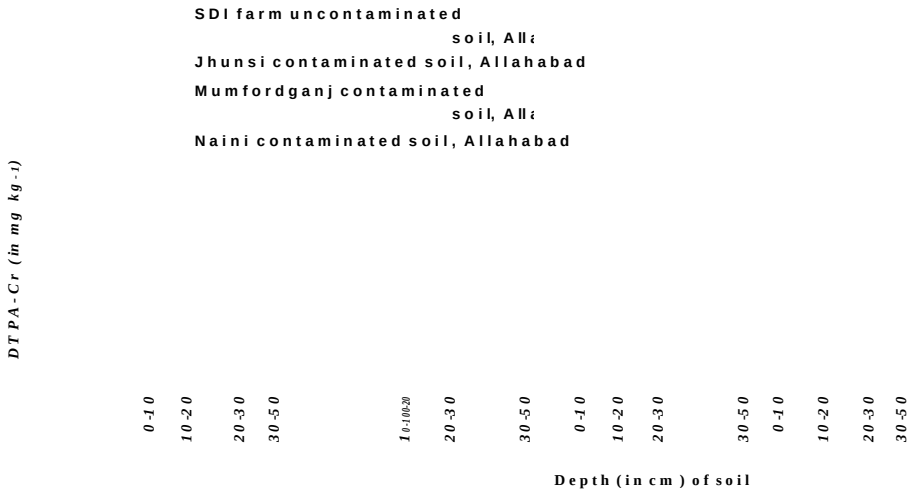

Fig. -7: Accumulation of DTPA-Cr

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 3.69±0.33 to 15.28 ± 1.09 mg kg^{-1}. Data in the Fig.-8 showed that at (S_3 and S_4) sites receiving sewage water contaminated, Zn accumulated more in the surface soil and content decreases with soil depth indicating low mobility of Zn through soil profiles. In uncontaminated soil, low content of DTPA-Zn was found in comparison to sewage water contaminated soil. Zn content remains more or less constant throughout the depth of soils. In light textured soils (S_3 and S_4) decline in the DTPA-Zn was higher than that in heavy textured type of soils (S_3 and S_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 result in the build-up of heavy metals in the surface soil due to higher adsorption and low permeability of these soils. DTPA-Zn in surface soil is correlated with pH (r= -0.06) and clay (r= -0.40*) were observed negative correlation, whereas, the correlation between DTPA-Zn with EC, (r=0.97**), CEC (r=0.21) and organic carbon (r=1.00**) were observed positive. These correlation studies suggest that different soil properties significantly influence DTPA-Zn in sewage contaminated soils (Table-8). 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);Akan et al.

(2010); Mani et al. (2013a) and Annu et al. (2015) also reported similar findings.

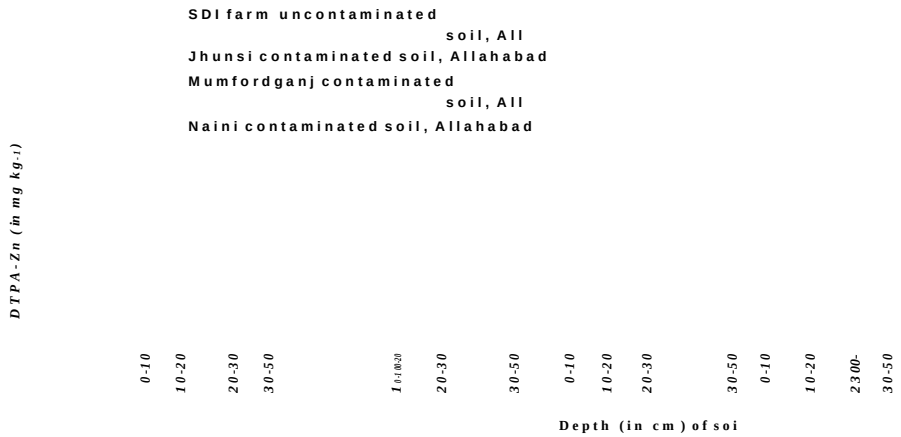

Fig. -8: Accumulation of DTPA-Zn

TABLE-7: Correlation coefficients (r values) of heavy metals with soil properties

Parameters	Total-Cd	Total-Pb	Total-Cr	Total-Zn
pH	-0.17	0.11	-0.18	-0.64*
EC	0.90**	0.92**	0.95**	0.74*
CEC	0.18	0.41*	0.28	0.76*
Organic carbon	0.98**	0.82**	1.00**	0.80**
Clay	-0.35	-0.58*	-0.46*	-0.85**

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

TABLE-8: Correlation coefficients (r- values) of heavy metals with soil properties

Parameters	DTPA-Cd	DTPA-Pb	DTPA-Cr	DTPA-Zn
pH	-0.004	-0.07	-0.19	-0.06
EC	1.00**	0.97**	0.97**	0.97**
CEC	0.29	0.46*	0.50*	0.21
Organic carbon	0.98**	0.93**	0.95**	1.00**
Clay	-0.48*	-0.64*	-0.67*	-0.40*

*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 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 macro-pores or cracks which is also referred to as preferential flow (Dowdy and Volk, 1983). The significant factors influencing the availability of heavy metals are soil pH and the quality of soil organic matter (Puschenreiter et al., 2005). 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 degreased with depth. Soil 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.

Higher concentrations of toxic metals in crops irrigated with wastewater sufficient to cause disorders in plants and clinical problems in both humans and animals consuming these plants. 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.

V. CONCLUSION

Frequent sewage irrigation on agriculture land increases the total heavy metals and DTPA-extractable (Cd, Pb, Cr and Zn) in soils. Sewage irrigated soil increases the heavy metals accumulation in soil, leading to increased plant uptake of heavy metals, which injurious to human and animal health.From the foregoing results, it was concluded that the higher accumulation of heavy metals (Cd, Pb, Cr and Zn in the surface soil (0-10 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 total Cd, Pb, Cr and Zn from 2.21±0.24-5.21±0.41 mg kg^{-1}, 3.62±0.31-4.56±0.42 mg kg^{-1}, 2.72±0.19-4.24±0.33 mg kg^{-1} and 67.58±2.34-88.47±3.89 mg kg^{-1} in surface soil (0-10 cm), respectively. A very low amount of heavy metals (Cd, Pb, Cr and Zn) were observed in (30-50 cm) depth in comparison to surface soil (0-10 cm) in all the soil examined. Similarly increased the accumulation of DTPA-extractable Cd, Pb, Cr and Zn from 0.216±0.032-0.256±0.033 mg kg^{-1}, 0.64±0.22-0.82±0.22 mg kg^{-1}, 0.38±0.17-0.54±0.22 mg kg^{-1} and 12.57±0.53-15.28±1.09 mg kg^{-1} in surface soil (0-10cm) respectively. A low amount of total heavy metals (Cd, Pb, Cr and Zn) were observed in 30-50 cm depth in comparison to surface soil (0-10 cm) in all the soil examined indicating low mobility of these metals down the depth. The total heavy metals (Cd, Pb, Cr and Zn) and DTPA-extractable heavy metals content of sewage contaminated and uncontaminated soils decreased with increasing soil depth. The soil organic carbon content in soils were positively and significantly correlated with DTPA-extractable Cd ($r=0.98^{**}$), Pb ($r=0.93^{**}$), Cr ($r=95^{**}$) and Zn ($r=1.00^{**}$), 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 uncontaminated soil, low content of heavy metals were found in comparison to contaminated soil. Under risk assessment, profile-wise study indicated accumulation of Cd, Pb, Cr and Zn below up to 50 cm. Naini contaminated soil was highly contaminated than other three sites.Thus, it may be concluded that a high concentration of extractable heavy metals in surface soils (0-10 cm) will not only reduce the plant growth but will also affect the availability of other essential elements to plants.

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