



# The Studies on the Mobility of some Heavy Metals in a Sub-urban Soil of Aligarh, U.P., India amended with an Electroplating Factory Effluent

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## Abstract

The influence of an electroplating factory effluent was studied on the mobility of Pb, Cd, Cr, Ni, Cu and Zn in a fine sandy loam soil. The technique used in these investigations was soil thin layer Chromatography (soil TLC) which is a fast, accurate, precise and repeatable method to study the metals and pesticide mobility in soil. The factory effluent was taken from the outlet of the Morris Bajaj Electroplating Factory, Aligarh and five dilutions 10 to 50% were prepared with distilled water and mixed with soil samples to make the soil TLC plate. The movement of these metals in soil was found to follow the order: Cd > Cu > Cr > Pb > Ni > Zn. The amendment made in the soil with effluent did not change the order of but enhances the mobility from 12 to 27% except for the Cu and Zn which show decreased mobility. The effect of amendment was also observed in soil samples with decomposed Soil Organic Matter, and added sesquioxide and indigenous clay minerals. The results were explained with the help of their competitive adsorption-desorption and complexation of heavy metal with the soil colloids.

**Keywords:** Clay minerals, heavy metals, MBEF effluent, mobility, soil.

## Introduction

Although, industries have major role in the overall development of a nation but, it leaves behind certain issues to be analyzed and monitored on various lines such as composition, characteristics, and short or long term effects of industrial waste on to the environmental components<sup>1-3</sup>. The presence of heavy metals in various industrial effluent and solid wastes has been the subject of great importance because of their toxic behavior, accumulation, and competitiveness in different environmental segments. It needs an increasing attention and continuous research due to growing scientific awareness in the field of environment *vis-a-vis* industrial development. The electroplating plant is an important unit of approximately all the manufacturing units of metallic products. The effluents of these units are generally composed of various heavy metals such as chromium, nickel, copper, zinc, silver, lead and cadmium etc. along with other organo-inorganic materials depending upon the nature of industries<sup>4</sup>. A number of workers have reported the effects of industrial wastes on the characteristics and behavior of soil colloids around the site of their disposal as well as urban agricultural lands where usually vegetables are most common crops<sup>5-6</sup>. These heavy metals interact with soil colloids and their bioavailability is supposed to be a function of their adsorption-desorption, leaching and translocation in the soil environment<sup>7</sup>. The translocation of these metals in soil have also been reported by a number of soil scientists and correlated them with a number of factors such as pH, soil components, presence of organic and inorganic ligands including humic and fulvic acids in soil<sup>8-10</sup>. Xiong et. al.<sup>11</sup> have reported the competitive nature of these heavy metals for their adsorption onto the soil colloids and

showed the higher adsorption in amended soil. The sorption intensities and sorption capacities of heavy metals were found to vary with the nature of heavy metals and treated soils. The present work reports the competitive mobility of certain heavy metals such as lead (Pb<sup>2+</sup>), cadmium (Cd<sup>2+</sup>), chromium (Cr<sup>3+</sup>), nickel (Ni<sup>2+</sup>), copper (Cu<sup>2+</sup>), and zinc (Zn<sup>2+</sup>) in soil as measured through soil thin layer chromatographic techniques. The objectives of the work reported here were to investigate the mobility of these heavy metals through soil treated with electroplating factory effluent. It throws a light on to the behavior of sub-urban soil in the movement of heavy metal to reach in the vicinity of the vegetable plant roots.

## Material and Methods

The soil sample used in the present study was collected from the sub-urban areas of Aligarh city of Uttar Pradesh (India). It was a fine sandy loam soil and its surface samples (depth 0 to 25 cm) were taken to dry in air, ground and passed through a 100 mesh sieves (BSS). The effluent water samples were taken from the outlet of Morris-Bajaj Electroplating Factory situated in the heart of Aligarh city and released untreated water effluent in the municipal drainage system which is thrown in the sub-urban areas of the city. It was diluted to various levels with distilled water and used to treat the soil samples. The physicochemical characteristics of soil samples and effluent are given in elsewhere<sup>12</sup>.

**Preparation of Soil Thin Layer Chromatography (Soil TLC) Plates:** The soil samples were taken in the earthenware pots and irrigated with the effluent of various dilutions (such as 10, 20,

30, 40 and 50% denoted as S<sub>1</sub>, S<sub>2</sub>, S<sub>3</sub>, S<sub>4</sub> and S<sub>5</sub> respectively) to the water holding capacity of the soil. The soil was then dried in open air at an average temperature of 30°C and homogeneously mixed, ground and passed through 100 mesh sieves (BSS). The uniform sized soil samples were slurried with demineralized water and coated on the glass plates (Sized: 20x5x0.5 cm, called as Soil-TLC plates) with TLC applicator to have a uniform layer of 0.5mm thickness in all the cases. The Soil-TLC plates were air dried as above and two lines were marked lightly at 3 and 13cm from the base of the plates. Now, a 0.5M solutions of heavy metal (Pb, Cd, Cr, Ni, Zn and Cu) as their nitrates were applied at the middle of the lower line in the form of a single spot (0.006 ml) with the help of micropipette and then air dried. A 2.5cm wide strip was also wrapped at the base of Soil-TLC plates to prevent the disintegration of soil in its development. The soil-TLC plates were developed in a chromatography chamber with distilled water as a developer up to upper lines of the plates. These plates were then taken out from the chromatographic chambers and metal spots were detected with the help of spraying 0.5% (w/v) ethanolic solutions of haematoxylene, dimethylglyoxime, and 0.1% 9 (w/v) solution of dithiazone in CCl<sub>4</sub> as the case may be. The frontal R<sub>f</sub>-values of metals were calculated as:

$$R_f = \frac{\text{Frontal distance travelled by the metal spots}}{\text{Frontal distance travelled by the developer}}$$

The whole experimental set up is shown in figure-1 and the R<sub>f</sub>-values of all the heavy metals were determined as a measure of mobility.

To observe the effect of soil organic matter (SOM), soil samples were treated with 30% Hydrogen peroxide to decompose SOM as per standard method used for decomposition of soil organic matter<sup>13</sup>. The sesquioxides of the soil samples were removed with the help of dithionate-citrate system with sodium bicarbonate buffer<sup>14</sup>. While requisite amount (ten percent weight

by weight basis) of indigenous clay separated out by dispersion method of Jackson<sup>13</sup> was added to the soil samples. These treated soil samples were used to prepare the TLC plates.

## Results and Discussion

The soil sample taken for study in these investigations was an Aerice Halaquept (fine sandy loam) having average amount of nutrients with swelling illitic clay minerals. The soil is alkaline with a pH value of 8.78 which indicates that most of the metal ions acquire their hydration states<sup>15</sup> in soil solutions. The amendment made with the effluents did not have a significant change in the pH of the soil because of self-buffering activity of the soil<sup>16</sup>. The effluent has a high concentration of suspended as 1354 (ppm) and dissolved solids as 16359 (ppm) mostly in form of salts of metal ions.

Table-1 shows the mobility of Pb, Cd, Cr, Ni, Cu and Zn in soil which was measured in terms of their R<sub>f</sub>-values. It follows the order as: Cd > Cu > Cr > Pb > Ni > Zn in soil without effluent amendments. This mobility order may be attributed to the physico-chemical characteristics of heavy metals and the substrate environment. Hydrated ionic radii, electronegativity, and hydration energy of metal solubilization in soil seems to be important factors which decides the sequence of their interactions with soil colloids. Accordingly, the Hard-Soft Acid Base (HSAB) principle<sup>17</sup> may be considered to be followed in the heavy metal-soil colloid interactions. Therefore, their mobility could be expected to follow the order of lower electronegativity, high polarizability and/or larger ionic size. Under our experimental conditions, the mobility order of heavy metals follows the increasing order of their hydrated ionic radii (table-2) except in the case of Cr and Zn whose lower electronegativity could be a reason for their better interactions with soil colloids and hence distract them from obeying the order of mobility.

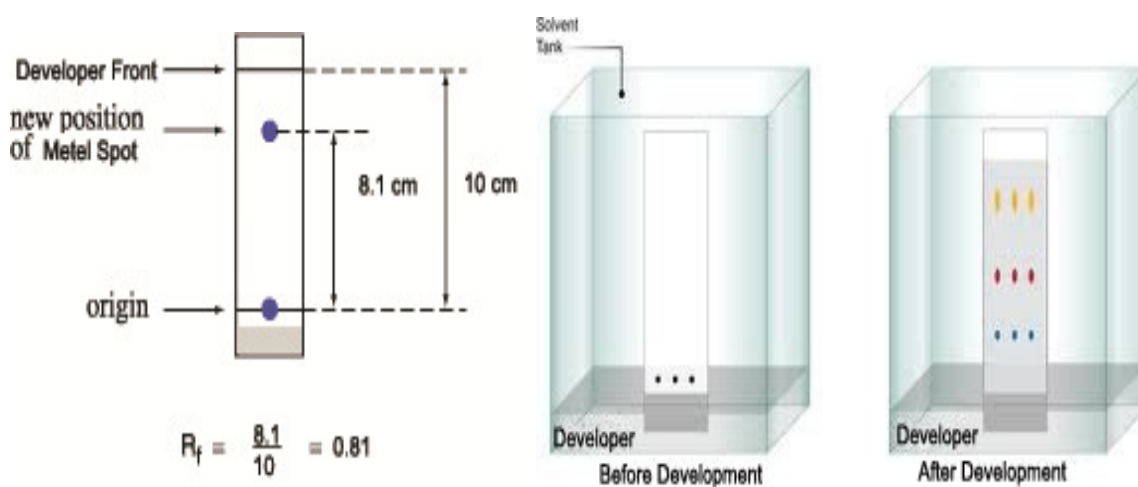


Figure-1  
 Details of Experimental set up

**Table-1**  
**The mobility of heavy metal in soil treated with factory effluent at different dilutions**

| Heavy metals | R <sub>f</sub> Values |                |                |                |                |                | CD at 5% |
|--------------|-----------------------|----------------|----------------|----------------|----------------|----------------|----------|
|              | Control               | S <sub>1</sub> | S <sub>2</sub> | S <sub>3</sub> | S <sub>4</sub> | S <sub>5</sub> |          |
| Pb           | 0.41                  | 0.43           | 0.47           | 0.51           | 0.52           | 0.52           | 0.02     |
| Cd           | 0.76                  | 0.78           | 0.81           | 0.84           | 0.85           | 0.85           | 0.02     |
| Cr           | 0.51                  | 0.53           | 0.58           | 0.59           | 0.59           | 0.59           | 0.01     |
| Ni           | 0.38                  | 0.39           | 0.44           | 0.45           | 0.45           | 0.45           | 0.01     |
| Cu           | 0.63                  | 0.57           | 0.52           | 0.51           | 0.51           | 0.51           | 0.02     |
| Zn           | 0.29                  | 0.24           | 0.21           | 0.19           | 0.19           | 0.19           | 0.01     |

Some other factors like complexing nature and variable valence states of Cr may also be a plausible reason for disturbed patterns of their mobility. Table-1 also shows that the soil amendment with factory effluent increases the mobility of Pb, Cd, Cr and Ni by 27, 12, 16 and 18 percent and decreases in the case of Cu and Zn by 19 and 34 percent respectively compared to control.

**Table-2**  
**Some physicochemical parameters of heavy metals**

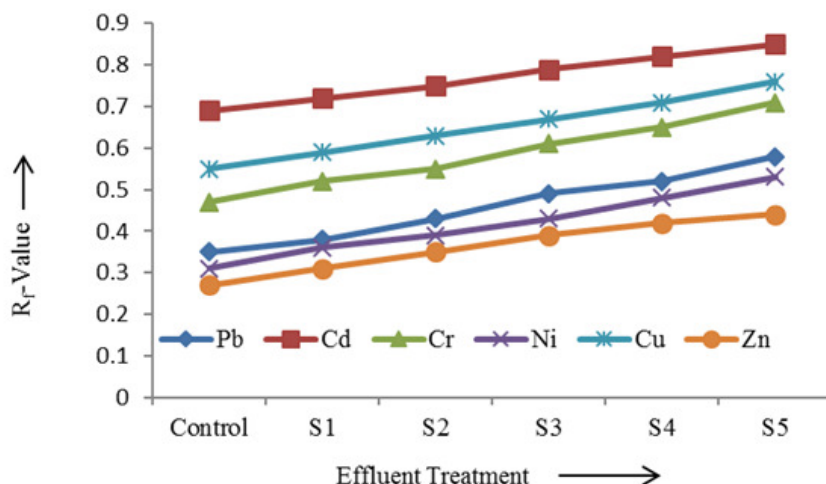
| Heavy metals | Hydrated Ionic Radii*(A°) | Electronegativity** |
|--------------|---------------------------|---------------------|
| Pb           | 4.01                      | 1.87                |
| Cd           | 4.26                      | 1.69                |
| Cr           | 4.61                      | 1.66                |
| Ni           | 4.04                      | 1.91                |
| Cu           | 4.19                      | 1.90                |
| Zn           | 4.30                      | 1.65                |

\*Lide<sup>18</sup>, \*\*Pauling Scale<sup>19</sup>

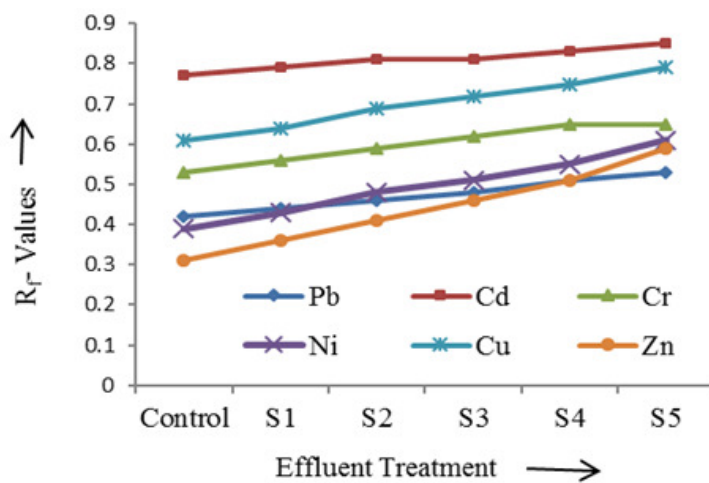
However the order of heavy metal mobility was more or less same as in the case of un-amended soil except in the case of Cr whose mobility was found to be more than Cu. This trend of increasing mobility could be explained on the basis of their reduced interactions with soil colloids due to preoccupation of interaction sites with metal ions as a result of effluent amendment. While in the case of Cu and Zn, a strong and stable humic acid – Cu/Zn complexation<sup>20</sup> could be a reason for their reduced mobility. It could also be noted that the mobility increase or decrease was found only up to a level of 30 percent effluent amendment beyond which a very less or no change was observed.

Figure-2 shows the effect of effluent amendment of soil with decomposed SOM on the translocation of heavy metals which was found to decrease in soil with decomposed SOM in comparison with soil with SOM (table-1). However the order of mobility remains the same. The decrease of mobility in respect of individual heavy metals follows the order as Ni (18.4%) > Pb (14.6%) > Cu (12.7%) > Cd (9.2%) > Cr (7.8%) > Zn (6.9%). This trend of decreasing mobility is not following the general order of their mobility in soil with or without SOM. It may be due to the fact that their interaction preferences are variable on the basis of substrate material<sup>15</sup>. According to Young Do and Park<sup>21</sup>, Pb and Cu are more selective for exchangeable sites than Cd and Zn which shows great affinity with adsorption sites. Therefore, the higher decrease in mobility of Pb and Cu in comparison of Cd and Zn results in the soil without SOM. Figure-2 also shows that the mobility of all heavy metal linearly increased with effluent concentration in soil without SOM.

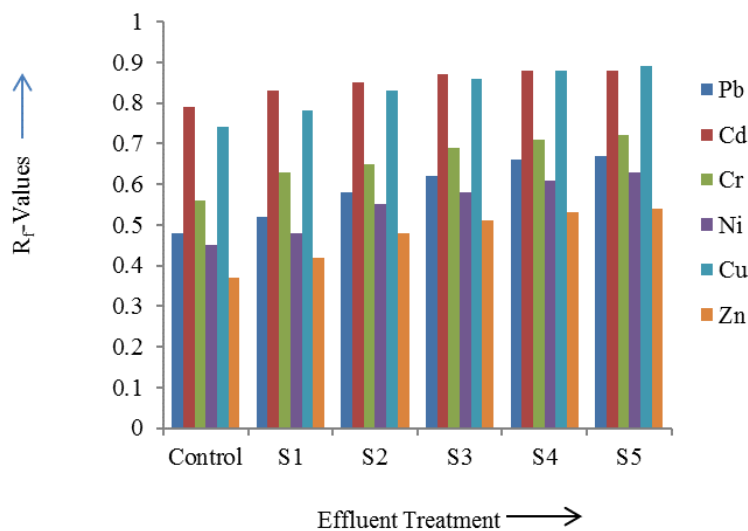
Figure-3 shows the heavy metal mobility as affected by effluent amendment in soil from which the sesquioxides have been removed. The order of heavy metal mobility was found to follow the same order and variation was negligible as compared to un-amended control soil (table-1). It indicates that under our experimental conditions heavy metal had no interactive preferences with sesquioxides and did not follow the general trends of heavy metal adsorption over the surfaces of Al- and Fe- oxy hydroxides. It also shows that the order of increase or decrease in mobility as a result of soil amendments with effluent follows the same order as in the case of soil without SOM except that of Zn and Cu which show different characteristics in their mobility behavior. It is also to be noted that the translocation of all the heavy metals was increased in uniform manner that indicates the non-availability of adsorption sites probably due to pre-occupation by indigenous metals present in effluent.



**Figure-2**  
 Influence of SOM on the Mobility of some heavy metals in soil amended with effluent



**Figure-3**  
 Influence of Sesquioxides on the Mobility of some heavy metals in soil amended with effluent



**Figure-4**  
 Effect of effluent treatment on the translocation of heavy metals in soil without SOM and sesquioxide

The movement patterns of the metals under study in effluent amended soil from which SOM and sesquioxides have been decomposed / separated is given in figure-4. It shows that the mobility of heavy metals was slightly higher than that of control soil, Soil with decomposed SOM and soil without sesquioxides. Obviously, it could be explained in terms of decreasing interaction sites in soil. The only interaction sites which are available in this case is clay minerals which might be pre-occupied by indigenous metal ions. Therefore, the uniform increase of mobility in soil samples S<sub>2</sub> to S<sub>5</sub> indicates the gradual occupation of adsorption sites in amended soils.

The mobility order of heavy metals was found to be in the same order as that in the case of control. However, the accelerating intensity of metal mobility was observed in the reverse order of their mobility as: Zn (46%) > Ni (40%) = Pb (40%) > Cr (29%) > Cu (20%) > Cd (11%). An addition of indigenous clay minerals in soil prior to the effluent amendment shows a decrease in the mobility of all heavy metals (figure-5). The order of mobility was found to be same as that in the case of control soil without amendment. It again substantiates the HSAB principle for adsorptive characteristics of metals on soil colloids. The retardation intensity of heavy metals was found to be in the order as Zn (64%) > Cr (49%) > Pb (39%) = Ni (39%) > Cu (38%) > Cd (31%). The lowest retardation of Cd mobility may be explained on the basis of its less competitive nature with other cations for adsorption such as Zn which reported to desorb Cd from adsorption sites<sup>22</sup>.

### Conclusion

The heavy metals movement in soil amended with electroplating factory effluent was observed to vary with the level of amendments. Soil amended with higher effluent dilution has very little effect on the movement of all the heavy metals. The

removal of soil organic matter and sesquioxides enhances the mobility while addition of indigenous clay minerals reduces the translocation property of all the heavy metals. Therefore, it is recommended that electroplating factory effluent disposal in its more than 40% diluted state will have less impact on the heavy metal contamination of vegetable plants grown in soil with high content of soil organic matter, sesquioxide and clay minerals.

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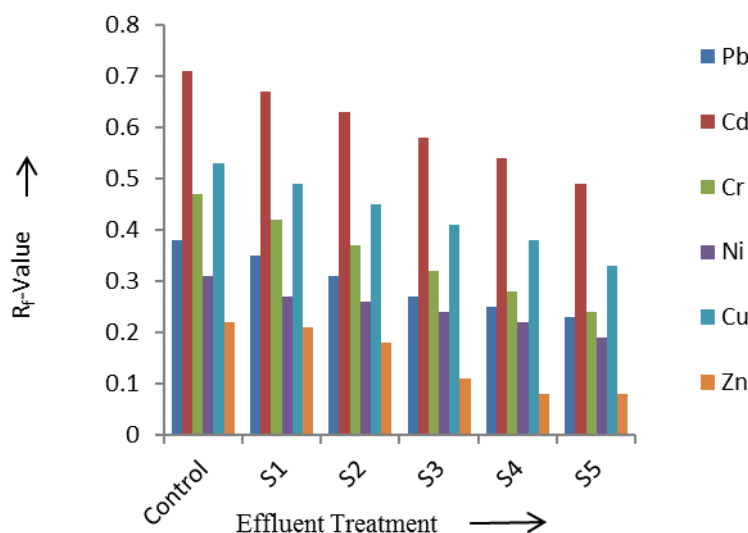


Figure-5  
 Effect of effluent treatment on the translocation of heavy metals in soil with added Clay mineral

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