# Contents and Fractionation of Heavy Metals in Soils Irrigated with Sewage Effluents

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**Summary:** Fractionation of heavy metals including Cadmium (Cd), Manganese (Mg) and Zinc (Zn) in soils of three sites in the vicinity of Lahore was carried out. These metals were irrigated for a long time with untreated sewage effluents by using selective extraction procedure to demarcate five metal fractions; exchangeable, acid soluble, reducible, oxidizable and residual. Extraction procedure showed that the total concentration of the heavy metals was largely (> 50 %) bound to residual fraction. Based on the data for Cd, Mn and Zn fractionation in various phases, the ranking of different forms of Cd Mn and Zn in soil was as follows: for Cd residual > reducible > oxidizable > exchangeable > acid soluble, for Mn residual > reducible > acid soluble > exchangeable > oxidizable and for Zn residual > oxidizable > acid soluble > reducible >

## Introduction

The natural level of metals in soil correlates with the level of these metals in parent material. However, soil forming factor can also alter this pattern to some extent. Heavy metals may be added in the soil through chemical or organic fertilizers and pesticides. Irrigation waters are also a big source of soil pollution with contaminated metals. In Pakistan sewage irrigation is very common since our sewage system caters to domestic and industrial effluents in the same sewer. These effluents are rich in organic matter and many food nutrients along with heavy metals [1]. Repeated application of effluents to farmlands, may contribute to a significant quantity of heavy metals that accumulate in the soil facilitating their significant amount, which might enter into the food chain through crops, grown on these lands. These metal ions may either remain in soil solution, taken up by plants retained in soils, or pass into the drainage water.

These transformations are controlled by a complex set of chemical reactions and a number of physical and biological processes taking place within the soils. Usually, the metal ions present in soil amounts to their total concentration. Only a few attempts have been made to classify these heavy metals into different groups and sub-groups [2-5]. Use of the total concentration as a criterion to assess the potential effects of soil contamination implies that all forms of a given metal have an equal impact on the environment, although such an assumption is not correct, because the metal availability and the mobility depend greatly on its physical forms than its total amount in soil. The understanding of metal availability and movement in soil is important for evaluating its potential environmental and health effects. With this intent, this study was designed to use chemical extraction procedure to determine different fractions of Cd, Mn and Zn in contaminated soils irrigated with sewage effluents.

## Results and Discussion

The total concentrations of metals in soils of three different sites, which have a long history of sewage irrigation from Rohi Nala in the vicinity of Lahore, are presented in Table 1.

Their relative standard deviation (rsd %) is also presented. It can be seen that the sample obtained from site 3 had the highest concentration of Cd, Mn and Zn among the three samples. Sample 2, however has the least concentration of these metals. Sequential extraction, results of metal for the samples are presented in Table 2.

The amount of non-residual fractions (exchangeable, acid soluble, reducible and oxidizable) represents the amounts of active heavy metals, while those of residual fractions may be

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considered the stable form and thus not available to plants for a reasonable period. Each metal and its successive fractions are discussed below; three concentration values given refer to sites 1, 2 and 3, respectively (Fig. 3)..

Table- 1: Total concentration of heavy metals (mg $Kg^{-1}$) and standard deviation (±) in Sewage irrigated soils.

| Sample | Cd | Mn | Zn |
|---|---|---|---|
| Site 1 | 4.2 ± 0.86 | 230 ± 2.5 | 155 ± 2.6 |
| Site 2 | 1.2 ± 0.72 | 150 ± 5.3 | 64 ± 3.2 |
| Site 3 | 6.8 ± 0.9 | 280 ± 5.8 | 180 ± 2.4 |

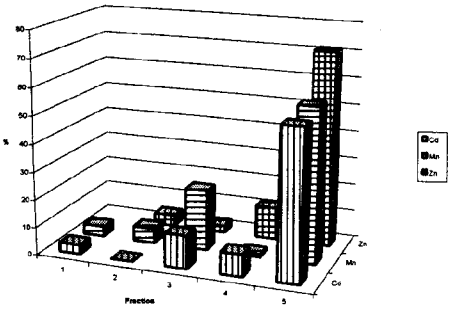

Fig. 1: Concentration of Cd, Mn and Zn in different fractions (%) from site 1.

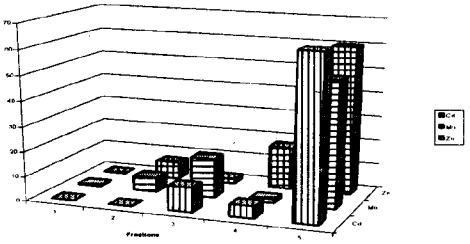

Fig. 2: Concentration of Cd, Mn and Zn in different fractions (%) from site 2.

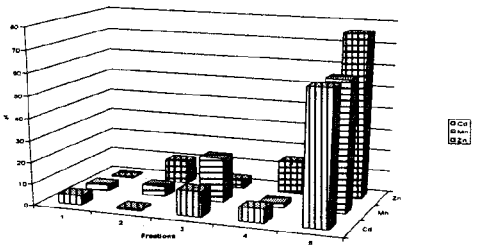

Fig. 3: Concentration of Cd, Mn and Zn in different fractions (%) from site 3.

Table- 2 Concentration of metals (mg $Kg^{-1}$) in different fractions from samples of three sites.

| Concentration (mg $Kg^{-1}$) | | | |
|---|---|---|---|
| Sample | 1 | 2 | 3 |
| Cadmium | | | |
| Exchangeable | 0.18 | N.D | 0.3 |
| Acid-soluble | N.D | - | 0.19 |
| Reducible | 0.50 | 0.12 | 0.8 |
| Oxidizable | 0.34 | 0.08 | 0.45 |
| Residual | 2.3 | 0.78 | 4.2 |
| Recovery (%) | 81.5 | 75 | 87 |
| Manganese | | | |
| Exchangeable | 8.5 | 0.8 | 7.8 |
| Acid-soluble | 12.5 | 19.0 | 13.0 |
| Reducible | 50.8 | 24.0 | 58.0 |
| Oxidizable | 2.5 | 2.3 | 6.0 |
| Residual | 118.0 | 77.0 | 168.0 |
| Recovery (%) | 83 | 81 | 88 |
| Zinc | | | |
| Exchangeable | 0.2 | N.D | 0.8 |
| Acid-soluble | 6.4 | .58 | 19.6 |
| Reducible | 3.7 | 4.5 | 6.9 |
| Oxidizable | 18.4 | 8.32 | 27.0 |
| Residual | 110.0 | 11.2 | 138.0 |
| Recovery (%) | 89 | 60 | 106 |

*Cadmium*

Cd is a non-essential metal of no benefit to humans and is the most critical element due to its easy incorporation in the food chain and its general biotoxicity [6]. The total concentration of Cd in studied soils was 4.2, 1.2 and 6.8 mg $Kg^{-1}$ despite the permissible limit being 0.5 mg $Kg^{-1}$ [7]. Generally, more than 0.5 mg $Kg^{-1}$ total cadmium in soil is considered an evidence of soil contamination. So the studied soils were observed to be heavily contaminated with Cd. The metals in sewage and soils are contributed from a number of sources, like

plastic, pigment and metallurgy industry, phosphate fertilizers and proximity to highway etc. [8].

In the soils collected from three sites, Cd was mostly present in the residual fraction i.e. 54.7 %, 65 % and 61.7 %, respectively, and these findings were consistent with many studies that highlighted the presence of Cd to be almost 50% or above in the residual fraction [9-11]. Among the non-residual fractions Cd is mostly present in reducible fraction that is bound to Fe-Mn oxides (12 %, 10 % and 11.7 %); in another study, almost 44 % of Cd was found in reducible fraction [12], as compared to be oxidizable fraction i.e., bound to organic matter (8 %, 5 % and 6.6 %) and least in exchangeable ( 3 %, 1.2 % and 4.4 % ) and acid soluble fractions( < 1 % ).

*Manganese*

Total Mn contents in soils under investigation were 230, 150 and 280 mg $Kg^{-1}$ respectively. Adhikari observed similar pattern of Mn in different layers of soil receiving sewage water [13]. Most of the Mn was present in residual fraction (56 %, 51 % and 60 %). In non-residual fraction, Mn was found to be mostly associated with Fe-Mn oxides 22 %, 16 % and 20.7 % (reducible fraction). Similar findings on this are also available in the literature [14]. The acid soluble was the next fraction and was present in 5.4 %, 6 % and 4.6 % respectively. The next fraction was exchangeable and had 3.7 %, 0.5 % and 2.8 % of the total metal concentration. The least was however, oxidizable fraction, having concentrations 1 %, 1.5 % and 2.1 %, respectively.

*Zinc*

Zinc is a heavy metal of much interest since it is not only a plant micronutrient but also a potential contaminant in soils. Although Zn has been found to have low toxicity to man, subjection to high doses for a prolonged period can result in health complications such as fatigue, dizziness and neutropenia [15]. The total zinc was found to be 155, 64 and 180 mg $Kg^{-1}$, respectively, despite the permissible limit for Zn being 80 mg $Kg^{-1}$ [ 7] In India, it was also observed that all the soils under city effluent irrigation had total Zn above the permissible limits [13]. Zinc is also present mostly in the residual fraction in 71 %, 60 % and 76 % respectively. In non-residual fraction, zinc is available in oxidizable fraction i.e. 11.8 %, 13 % and 15 %, respectively of the total metal concentration, whereas in acid soluble fraction, 4.1 %, 7 % and 10.8 %. The next fraction is reducible, which is 2.4 %, 2.0 % and 3.8 %. Exchangeable fraction was observed to be < 1 %.

## Experimental

*Sample Collection and Preparation*

The soil samples were collected using a soil auger from three different sites, where untreated sewage effluents are used for irrigation. The samples were air dried, mixed, ground with wooden article to homogenize and sieved through 2 mm sieve. Then, they were stored in labeled polyethylene bags at 4 °C for further use. The sequential extraction procedure used in this study was the one applied by Tessier *et al*, [16].

The extraction was performed in polyethylene tubes and separation was effectuated by centrifuging at 10,000 rpm for 50 minutes [H-1500FR]. The supernatant was removed with a pipette and analyzed (below) for metal concentration. The residue was washed twice after each extraction with minimum amount of water to avoid excessive solubilization of solid material. For total and residual metal analysis the solid was digested by HF and percholric acid and then solubilized in 12N HCL [17].

*Metal Analysis*

Metal concentrations were determined by AAS (Spectra AA-40) involving direct aspiration of the aqueous solution into air-acetylene flame. Triplicate analysis was carried out and the results were expressed as the mean of triplicate digestion.

## Conclusions

Total heavy metal concentrations in sewage irrigated soils are above the permissible values. Heavy metal speciation procedure showed that all the metals are dominant (> 50 %) in the residual phase. Among non-residual fractions Cd and Mn are present in reducible fraction, while zinc in oxidizable

fraction. So the idea of metal speciation is very important to study the biological activity e.g. toxicify of an element in the environment. Soil is a very complicated media and a complex set of chemical reactions with a number of physical and biological processes taking place within the soils Therefore, due care should be taken in applying sewage water to agricultural lands in the long-term.

## References


1. E. R. Fuentes, C. L.Constantino, E. E. Silva and .Dendoven, *Bioresource Techonolgy.*, **57**, 179 (2002).
2. X. Xiong, F. Stagnitti,N. Turoczy, G.Allinson and M.LeBlanc, *Environmental Contamination and Toxicology.*, **73**, 71(2004).
3. L. Yongming, *Pedosphere.*, **12**, 165 (2002).
4. T. Sherife, K. Senol and B.Geokham. *Turkish Journal of Chemistry.*, **27**, 333 (2003).
5. A. Khan, M. Ibrahim, N. Ahmad and S. A Anwar, *Journal of Agriculture Research.*, **32**, 525 (1994).
6. J. E. Girard. *Principles of Environmental Chemistry.* 424, Jones and Bartlett Publishers. USA (2005).
7. D. L. Rowell., *Pesticides and Metals.* 303, Longman Singapore Publishers Ltd. Singapore (1944).
8. M. B. McBride., *Environmental chemistry of Soils.* Oxford University Press N.Y. USA. (1994).
9. K. Ridvan and A. Tayfun., *Archives of Agronomy and Soil Science.* **48**, 263 (2002).
10. A. A. Olajire, T. E. Ayodele, G. O. Oyedirdam and E.A Oluyeni. *Environmental Monitoring and Assessment.*, **85**, 135 (2003).
11. K. Marika and Y. Markku. *Environmental pollution.*, **126**, 225 (2003).
12. A. Kashem and B. R. Singh, Trace Element in soil; *Bioavailability, Flux, and Transfer, Proceeding of workshop.*, 213, (2001).
13. S. Adhikari, A. Mitra, S. K. Gupta and S. K. Banargee, *Journal of Indian Society of Soil Science.*, **46**, 153 (1998).
14. B. Q. Wang, B. Huang and L. Shuping, *Analytical Science.*, **17**,1561 (2001).
15. R. Hess and B. Schmid. *Journal of Pediatric Haematology/ Oncology.*, **24**, 582, (2002).
16. A. Tessier, P. G. C. Campbell and M. Bisson, *Analytical Chemistry.*, **51**, 844 (1979).
17. Standard methods for the Examination of Water and Waste Water, 20th Edition. APHA, AWWA. WPCE, Newyork.,(1998).