

Chemical fractionation of heavy metals in wastewater-irrigated soils

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Abstract : The present study was carried out to assess the distribution pattern of heavy metals and their chemical fractionations in wastewater-irrigated agricultural soils. Surface soil samples were collected from different locations from the wastewater-irrigated agricultural fields and analyzed for pH, organic matter, cation exchange capacity along with some heavy metals. The experiment showed that the mean Pb (85.998 ± 4.537 mg/kg), Cd (8.98 ± 1.619 mg/kg), Fe (195 ± 33.8 mg/kg), Cu (59.142 ± 9.109 mg/kg), Mn (145.5 ± 7.728 mg/kg) and Cr (39.88 ± 5.676 mg/kg) exhibited the high concentrations in the studied soils. The speciation study revealed that the overall percentage of metal content in different fractions was in the sequence of Residual > Fe-Mn Oxides > Exchangeable > Organic > Carbonate. The investigation showed pronounced spatial distribution and significant accumulation of heavy metals in the agricultural soils. The trend of metal accumulation in wastewater-irrigated soil was in the order : Fe > Mn > Pb > Cu > Cr > Cd. The study revealed that a significant portion of metals from wastewater sources mainly occur in the labile fraction in the studied soils and may be taken up by organisms as the environmental parameters change. Eco-toxicological assessment of the studied soil using the mobility factor indices indicated high degree of metal mobility and therefore, poses a serious threat to ecosystem health.

Keywords : Wastewater irrigation, soil, heavy metal distribution, chemical fractionation, metal mobility.

Introduction

The use of industrial or municipal wastewater in suburban areas, for irrigation purpose is a common practice¹⁻⁴ which poses a set of environmental problems⁵. Wastewater generated from different origins, carries appreciable amounts of toxic metals which may leads to degradation of soil health and contamination of food chain mainly through the vegetable/crops grown on that soils. So the long-term application of treated and untreated wastewater has resulted in a significant accumulation of heavy metals in soils over time^{6,7}. Dispersion of heavy metals from the contaminated soil to the vegetables and cereals and their subsequent transfer to the food chain causes a potential health risk to humans and animals^{8,9}. Heavy metals in agricultural soils may be introduced from natural as well as anthropogenic sources, such as mining, smelting, chemical industries, urban efflu-

ent, waste disposal, sewage sludge, vehicle exhausts, pesticides and fertilizers¹⁰⁻¹⁴. Contamination of soils by heavy metals is now widespread¹⁵ and also increased dramatically during the last few decades¹². Heavy metals are very harmful due to their non-biodegradability, persistence nature, long biological half-life and their potentiality to accumulate in humans and animals¹⁶. Excessive accumulation of heavy metals in agricultural soils through irrigation of wastewater may not only result in soil contamination but also leads to elevated heavy metal uptake by plants.

Soil can be considered as a source and sink of pollution with the capacity to transfer pollutants¹⁷⁻²⁰. The determination of total heavy metal content does not provide useful information about the bioavailability, risks of environmental hazards, the capacity for remobilization and the behavior of the metals in the environment. On the other hand the study of metal

speciation in the solid fraction may therefore, help us to understand the contribution of different sources and biogeochemical processes in the formation and mobility of metal in the solid phases. Sequential extraction procedure is a well-established approach for the investigation of different forms of trace metals in soils and sediments. Several sequential extraction procedures have been suggested to identify the distributions of elements in operationally defined pools. The metals may also found in soils in different forms, including soluble and exchangeable, carbonate form, as an amorphous material (Fe/Mn oxides), complexed with organic matter and sulfides, or bound to mineral lattices (residual)^{21,22}. The main objectives of the present study were : (1) to determine the distributions of metals in surface soils and (2) to identify the chemical phases present in the wastewater-irrigated soils using the sequential extraction protocol, and hence to ascertain their mobility.

Experimental

Materials and methods :

Surface soil samples ($n = 8$) were collected from cultivated fields impacted by the industrial wastewaters. The investigation was carried out on the agricultural soils in Asansol industrial zone of the state West Bengal, India. Soils were collected from plant root zone of cultivated vegetables with the help of a spatula and kept in zipped polyethylene bag and immediately sent to the laboratory for physico-chemical analysis and metal estimation. Soil pH was measured by preparing soil suspension (1 : 5, w/v) with deionised water²³. Organic matter (OM) content by Walkey and Black method²⁴ and soil cation exchange capacity (CEC) of soil (1 g dry weight) was determined in flame photometrically by extracting exchangeable sodium with ammonium acetate solution (1 mol/L)²⁵. The soil samples were air-dried, ground, and sieved with a 0.5-mm sieve, and further physico-chemical analysis was carried out. For the analysis of total metals 1 g of the sieved soil samples were digested with 5 : 1 mixture of concentrated HNO₃ and HClO₄²⁶. Tessier method²² was applied to fractionate the metal

content from three soil samples (S1, S2 and S3) into exchangeable fraction, carbonate fraction, fraction bound to Fe-Mn oxides, fraction bound to organic matter and residual fraction. Elemental concentrations from each sequential extraction step were measured using atomic adsorption spectrophotometer (GBC, Avanta).

Quality control assurance :

Care has been taken for sample collection and preservation during every experimental procedure.

AR grade reagents were used during experimental process, and analysis of soil samples were triplicated to ensure the reliability of results. E. Merck (AR grade, Germany) standard solutions (1000 mg ml⁻¹) were used to calibrate the instrument for metal analysis. Intermediate solutions were prepared carefully by diluting stock standard solution with freshly prepared distilled water. For further enhancement of experimental results, the mean values for each parameter along with standard deviation (SD) were considered.

Results and discussion

pH, organic matter, CEC and total concentrations of metals in soils :

The summarized information of pH, organic matter, cation exchange capacity (CEC) and total concentrations of metals is shown in Table 1. The pH value ranged from 5.99–6.65 with a mean value of 6.42 ± 0.201 indicating slightly acidic nature of the studied soil. The organic matter content (%) of soils ranged from 1.557–3.215 with a mean value of 2.556 ± 0.611 in the study area. The organic matter of the studied soil exhibited lower to moderate load. According to Adriano *et al.*²⁷, the organic matter contents influence the bioavailability of metals. The cation exchange capacity (CEC) value (meq of Na/100 g soil) ranged from 10.254–12.534 with a mean value of 11.428 ± 0.846 in the studied soil. Some soil quality parameters like pH, organic matter content, cation exchange capacity affects the availability of heavy metals for uptake by plants^{28–30}. The concentrations of Pb, Cd, Fe and Cr in the studied region

Table 1. pH, OM, CEC and heavy metal concentrations in wastewater-irrigated soils

Sites	pH	OM	CEC	Pb	Cd	Cu	Fe	Mn	Cr
S1	6.65	2.965	12.349	91.241	10.536	61.854	198	142	43.253
S2	6.45	2.247	11.952	87.258	9.852	63.635	210	158	41.634
S3	5.99	3.175	12.534	92.342	11.359	69.185	264	142	49.921
S4	6.32	3.215	11.357	87.126	8.251	71.126	178	139	37.538
S5	6.39	2.634	10.663	83.841	8.937	46.527	169	141	40.832
S6	6.51	1.867	10.637	78.368	6.634	54.224	152	151	30.124
S7	6.48	1.557	10.254	84.865	9.147	47.953	204	137	38.398
S8	6.57	2.786	11.681	82.942	7.125	58.628	185	154	37.336
Min.	5.99	1.557	10.254	78.368	6.634	46.527	152	137	30.124
Max.	6.65	3.215	12.534	92.342	11.359	71.126	264	158	49.921
Ave.	6.42	2.556	11.428	85.998	8.980	59.142	195	145.5	39.880
SD	0.201	0.611	0.846	4.537	1.619	9.109	33.8	7.728	5.676

Units : Organic matter (OM) in %; cation exchange capacity (CEC) in meq of Na/100 g soil; heavy metals are in mg/kg.

ranged from 78.368–92.342 mg/kg, 6.634–11.359 mg/kg, 152–264 mg/kg and 30.124–49.921 mg/kg with an overall mean of 85.998 ± 4.537 mg/kg, 8.98 ± 1.619 mg/kg, 195 ± 33.8 mg/kg and 39.880 ± 5.676 mg/kg respectively. The elevated level of total Pb, Cd, Fe and Cr was observed in S3 and can be due to the recent input of these elements. The concentrations of Cu and Mn in the studied region ranged from 46.527–71.126 mg/kg, and 137–158 mg/kg with an overall mean of 59.142 ± 9.109 mg/kg, and 145.5 ± 7.728 mg/kg respectively. The trend of metal accumulation in wastewater-irrigated soil was in the order : Fe > Mn > Pb > Cu > Cr > Cd. pH value of the S3 site is low which also may favours the metal mobility. Spatial distributions analysis of heavy metals indicated that the wastewater irrigation might also have

influence on heavy metal contamination in the studied region.

Statistical analysis :

Pearson correlation coefficient among the chemical constituents of the studied soil is represented in Table 2. There was no positive correlation observed in the Cd ($r = -0.458$), Pb ($r = -0.429$), Cu ($r = -0.434$), Fe ($r = -0.648$) and Cr ($r = -0.579$) concentrations with the pH of the studied soils. Organic matter ($r = -0.391$) and cation exchange capacity (CEC) ($r = -0.270$) also showed negative correlations with soil pH. Organic matter content is significantly correlated with some heavy metals : Pb ($r = 0.616$), Cu ($r = 0.701$) and Cr ($r = 0.544$). Correlation between OM and Cd is not so high ($r = 0.344$) than the other metals like Cu as because the Cd can-

Table 2. Pearson correlation coefficient matrix of analyze variables

	pH	OM	CEC	Pb	Cd	Cu	Fe	Mn	Cr
pH	1								
OM	-0.391	1							
CEC	-0.270	0.711	1						
Pb	-0.429	0.616	0.770	1					
Cd	-0.458	0.344	0.605	0.914	1				
Cu	-0.434	0.701	0.773	0.609	0.334	1			
Fe	-0.648	0.307	0.645	0.799	0.826	0.468	1		
Mn	0.286	-0.165	0.244	-0.329	-0.320	0.110	-0.129	1	
Cr	-0.579	0.544	0.696	0.903	0.928	0.397	0.876	-0.250	1

Values in bold are significant at P = 0.05.

not easily bound with organic matters. Strong positive correlation between Cu and OM ($r = 0.701$), due to high complexing tendency of Cu for organic matter. Similar observations were also reported by Zhai *et al.*³¹, where they found a strong affinity between organic matter and Cu. Statistical analysis revealed the existence of significant correlation among metals : Pb-Cd ($r = 0.914$), Pb-Cu ($r = 0.609$), Pb-Fe ($r = 0.799$), Cr-Pb ($r = 0.903$), Cd-Fe ($r = 0.826$), Cd-Cr ($r = 0.928$) and Cr-Fe ($r = 0.876$), indicating that all of them have the same origin which may come from industrial wastewater.

Partitioning of metals in soils :

To determine the chemical phases of heavy metals in the wastewater-irrigated soils, the Tessier sequential extraction method²² was applied, and the average percentages of Pb, Cd, Fe, Cu, Mn and Cr associated with the exchangeable fraction (F1), carbonate fraction (F2), reducible fraction (F3), oxidizable fraction (F4) and residual fraction (F5) were shown in Fig. 1. These categories have different behaviors with respect to remobilization under changing environmental condition. The study of metal speciation helps to determine the (1) binding character and mineralogical forms of metals, (2) extent of retention and (3) mobility/mobilization in surface soils.

Pb fraction in the studied soils was observed as follows : I – Exchangeable species (6.954%), II – Carbonates (11.952%), III – Fe-Mn oxides (22.3433%), IV – Organic fraction (16.751%) and

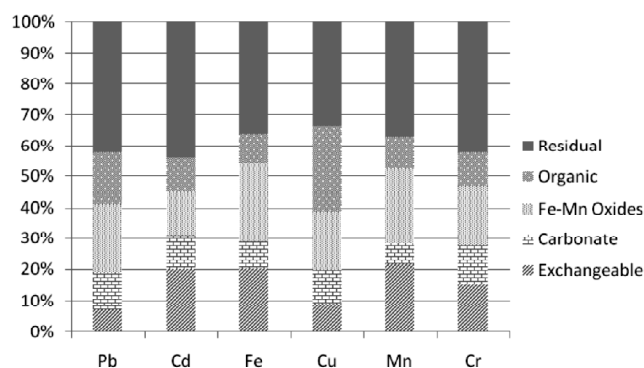


Fig. 1. Chemical fractionation of heavy metals by Tessier (1979).

V – Residual fractions (42.02%). The study revealed that the Fe/Mn oxides (F3) phase contains a significant amount of Pb in comparable with the amounts associated with other non-residual phases due to the fact that Pb can form stable complexes with Fe and Mn dioxide³². The study of some workers^{33,34} also suggested that the reducible Pb is more abundant than other two non-residual fractions. Cd fraction in the studied soils was observed as follows : I – Exchangeable species (20.043%), II – Carbonates (11.158%), III – Fe-Mn oxides (14.210%), IV – Organic fraction (10.963%) and V – Residual fractions (43.665%). Cd was mostly present in the residual fraction of all the samples. Though, significant amount of Cd was observed in the exchangeable fraction indicated that the bioavailability of Cd was high³⁵. The elevated level of chemically reactive forms of Cd implies a high ecological risk.

The association of Fe with the different sequential fractions was observed as follows : I – Exchangeable species (20.320%), II – Carbonates (8.526%), III – Fe-Mn oxides (25.685%), IV – Organic fraction (9.441%) and V – Residual fractions (36.027%). Among all the fractions Fe was mostly present in the residual fraction. Though, significant amount of Fe was observed in the Fe-Mn oxides/reducible fraction. Reducible form of metal is one of the metal fractions bound to Fe-Mn oxides and can release into dissolved form under changing environmental condition. With respect to the other metals studied, Mn presented a different exchangeable speciation distribution pattern than the other metals, as observed. Mn fraction in the studied soils was observed as follows : I – Exchangeable species (21.941%), II – Carbonates (6.571%), III – Fe-Mn oxides (24.281%), IV – Organic fraction (10.460%) and V – Residual fractions (36.751%). Generally Mn is not identified as dangerous metal for soils, though it can elicit a variety of serious toxic responses on human beings upon long-term exposure to high concentrations. According to Keen *et al.*³⁶, the central nervous system is the primary target of Mn, so for this reason manganese is taken into consideration for this study. The proportion associated

with the acid exchangeable fraction for Mn was higher than the other non-residual fractions.

The fraction bound to the organic matter for Cu was more abundant than the other elements. Cu fraction in the studied soils was found in the order : residual fraction (33.34%) > fraction bound to organic matter (27.697%) > fraction bound to Fe-Mn oxides (19.26%) > fraction bound to carbonates (10.783%) > exchangeable fraction (8.928%). The moderately high percentage of Cu in the oxidisable (organic bound) fraction is an indicative of strong binding ability of the heavy metal to form complexes with organic matter³⁷. The fractionation study revealed that copper was mainly bound to organic fraction and this high stability constant of organic-Cu compounds results in stable complex formation between Cu and organic matter³⁸. The sequential extraction of Cr showed that its major fractions were associated with residual fraction (41.837%) followed by Fe-Mn oxides fraction (19.145%), exchangeable fraction (15.199%), carbonate fraction (12.729%) and organic fraction (11.099%). Among all the chemical fractions Cr was mostly present in the residual fraction. Though, significant amount of Cr in the exchangeable fraction is an indicative of anthropogenic pollution in the wastewater-irrigated soil.

Mobility and bioavailability :

The bioavailability and environmental mobility of the metals are dependent upon the form in which the metals are associated with the soil particles. Exchangeable fraction involves weakly adsorbed metals retained on the solid surface by weak electrostatic adsorption force onto the soil and much more available to the biological organisms. Exchangeable fraction (F1) of metals followed the sequence of Mn > Fe ≥ Cd > Cr > Cu > Pb indicating very high mobility and lability and can exhibit environmental hazardous. According to Kabala and Singh³⁹, high values of mobility factor for a heavy metal is an indicative of relative high bioavailability. The mobility of heavy metals in soils can be calculated on the basis of absolute and relative content of fractions weakly bound to soil components with the following equation : MF = (F1 +

F2)/(F1 + F2 + F3 + F4 + F5) × 100. Where MF = mobility factor, F1 = exchangeable fraction, F2 = carbonate bound fraction, F3 = ferrous-manganese bound fraction, F4 = organic matter bound fraction, F5 = residual fraction. The study showed that high mobility factor was observed for Cd (30.994%) indicating high environmental mobility. Mobility factor metals followed the sequence of Cd (30.994%) > Fe (28.846%) ≥ Mn (28.511%) > Cr (27.925%) > Cu (19.709%) > Pb (18.904%), suggesting the potential long-term risk of these elements (especially Cd) in the wastewater-irrigated soils.

Conclusion

The study revealed that the distribution and partitioning phases of the studied metals are of major environmental concern in relation to chemical fractionation and eco-toxicological aspect. The pH of the studied soil was slightly acidic with lower to moderate organic matter load, while cation exchange capacity (CEC) values are at moderate range. Pronounced spatial distribution and significant accumulation of heavy metals was observed in the wastewater-irrigated soils. The trend of metal accumulation in the studied soil was in the order : Fe > Mn > Pb > Cu > Cr > Cd. The speciation study revealed that the overall percentage of metal content in different fractions was in the sequence of Residual > Fe-Mn Oxides > Exchangeable > Organic > Carbonate. Like Fe and Mn a significant amount of Cd was observed in the exchangeable fraction indicating very high mobility and lability and can become readily available to plants and other living organisms. Mobility factor of the metals followed the sequence of Cd > Fe ≥ Mn > Cr > Cu > Pb, suggesting the potential long-term risk of these elements (especially Cd) in the wastewater-irrigated soils.

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