Total Concentration and Chemical Speciation of Heavy Metals in Sewage Sediments

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Summary. Bottom sewage sediments from six locations of Lahore city were studied to evaluate total concentration of selected heavy metals and also their chemical speciation using sequential chemical extraction method. Analysis of the extracts were carried out by atomic absorption spectroscopy. The total concentration of metals were in the sequence Fe >Mn> Ni> Cu> . Zn> Co.The metals were partitioned into five operationally defined fractions i.e. exchangeable, bound to carbonates, associated with Fe-Mn oxides, associated with organic fractions and residual. Speciation analysis showed that most of the metals were in the residual fraction. The next considerable proportion is associated with Fe-Mn oxides, than with organic fraction and least with carbonate and exchangeable fractions.

Introduction

Mmany human activities in the last decades have contributed to increase the metal mobility in the environment. Heavy metals are one of the main pollutant which cause serious threat to human and environment. Rapid industrialization and urbanization are the major causes of metal contamination. In Pakistan sewage system is of combine type that it contains domestic sewage, industrial liquor and storm water. In general industrial water may not be discharged into public sewer, unless they are free from non-biodegradable agents. Of all the possible pollutants in water heavy metals are non degradable and when present in sufficient quantities, pose the most serious, long term environmental threat [1].

Metals in sewage water remain soluble or in suspended form, may precipitate or get adsorbed on solids. When the water slows, the particles and the burdens of toxic metals settle out and accumulate in bottom as sediment containing high concentration of metals. Sediments are known to be the sinks of heavy metals where they concentrate according to the level of pollution [2]. Some of the metals occurring at low concentration in the surface water are found in high concentration, high in corresponding sediments [3, 4].

The behavior and concentration of metals in sediment can play a important role in detecting sources, degree of pollution and also their distribution mechanism in aquatic environment. Different metals may be distributed among many components of the sediment and may be associated with them in different ways. Chemical speciation is defined as distribution of an individual chemical element among different species or groups. Usually metal ions studied in sediment are their total concentration, only few attempts have been made to evaluate the speciation of heavy metals i,e partitioning among the various forms in which they might exist [5-8]. So this study was carried out to determine the chemical speciation or fractionation of Cu, Ni, Zn, Fe, Mn, Co in sewage sediments to characterize their level in environment. Although iron is not a heavy metal but it is so designed to simplify the presentation of the results.

Results and Discussion

Results of total metal contents in sewage sediments of six different sites of Lahore are presented in Table-1. Their relative standard deviation (rsd %) also presented. Of all the metals examined in the sewage sediment, the following sequences is obtained Fe> Mn> Ni> Cu> Zn> Co. Almost same trend is found in sediment of sewage contaminated canal [9]. Sequential extraction results of different fractions of metals for the samples are presented in Table-2 and are discussed below. Figs. 1 (a-f) show the same data in percentage for Fe, Mn, Ni, Cu, Zn and Co.

Exchangeable

Fe, Co and Zn in exchangeable fraction are the lowest in studied sediments. The low concentration is probably due to the fact that metals in this form can

Table-1: Total contents (ug/g) and relative standard deviation (rsd %) of metals in Sewage Sediments (n = 4)

Site	Fe		Mn		Ni		Cu		Zn		Co	
	ug/g	rsd %	ug/g	rsd %	ug/g	rsd %	ug/g	rsd %	ug/g	rsd %	ug/g	rsd %
1.	16420	0.46	370	1.8	168	0.60	109	1.37	43.5	0.30	13.7	0.64
2.	17014	0.28	576	3.40	381	3.60	74	1.20	52.5	4.90	22.0	0.30
3.	16190	1.14	271	0.35	151	1.80	119	5.3	61.5	3.40	17.2	1.37
4.	20150	1.93	516	4.9	306	0.53	88	1.28	59.2	1.00	23.3	1.9
5.	18025	2.1	406	0.93	283	4.10	112	0.98	48.6	0.30	26.5	2.1
6.	19070	1.45	486	0.87	201	2.13	95	4.3	54.0	0.70	24.0	1.0

Table-2: Concentration (ug/g) of metals in different fractions from sewage sediments

	1	2	3	4	5	6
			Iron			
Exchangable	3.28	N.D.	N.D.	6.04	N.D.	N.D.
Carbonate	147.7	204	184	503	360	438
Fe- Mn oxide	2085	2518	2881	3224	3208	3165
Organic	344	306	275	403	324	305
Residual	13136	13951	12790	1601	13879	13730
Σ	15716	16979	16130	20155	17771	17638
Recovery (%)	96	99	99	100	98	92
			Manganese			
Exchangable	28.5	25.0	35.8	67	30.3	44
Carbonate	44.5	126	32.0	86	90	58
Fe- Mn oxide	92.4	140	38.0	119	85	92
Organic	6.8	17.2	4.0	15.8	13.6	9.7
Residual	165	241	140	223	163	225
Σ	337.2	549.2	250	510	382	428
Recovery (%)	91	95	92	98	94	88
			Nickel			
Exchangable	4.0	7.3	ND	6.0	4.9	ND
Carbonate	6.4	13.0	5.7	12.2	11.0	8.8
Fe- Mn oxide	36.8	84.3	29.8	69.7	59.2	49.0
Organic	8.2	17.0	7.5	20.0	16.5	8.3
Residual	101	242	94	190	16.7	115
Σ	156	363	137	235	258	181
Recovery (%)	93	95	90	76	91	90
			Copper			
Exchangable	0.6	0.3	0.7	0.4	0.6	0.5
Carbonate	12.8	11.3	19.8	13.6	15.5	13.3
Fe- Mn oxide	17.2	12.6	21.0	16.8	18.0	17.3
Organic	24.8	19.2	31.0	21.6	23.5	22.3
Residual	35.2	26.6	41.4	32.8	37.8	33.0
Σ	90.6	70	113.6	85.2	95.4	86.4
Recovery (%)	83	94	95	96	85	91
			Zinc			
Exchangable	ND	ND	ND	ND	ND	ND
Carbonate	3.5	4.3	7.2	12	3.8	4.8
Fe- Mn oxide	11.6	15.2	18.7	16.2	14.0	17.0
Organic	2.0	3.0	4.0	2.6	3.2	2.9
Residual	25.0	27	27.8	28.0	23.5	29.0
Σ	42.2	49.3	57.7	59.8	44.5	53.7
Recovery (%)	96	94	94	100	92	99
			Cobalt			
Exchangable	ND	ND	ND	ND	ND	ND
Carbonate	ND	ND	0.3	ND	0.37	ND
Fe- Mn oxide	3.9	4.7	4.2	5.7	4.93	5.52
Organic	0.4	0.5	0.52	.98	0.98	0.88
Residual	6.7	11.2	8.8	14.8	18.0	12.2
Σ	11	16.4	13.8	21.4	24.3	18.6
Recovery (%)	80	75	80	92	91	77

Fig. 1a: Concentration of Iron in different fractions of six samples.

Fig. 1b: Concentration of Manganese in different fractions of six samples.
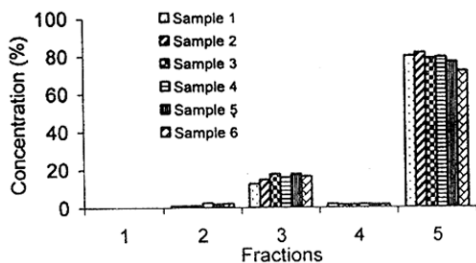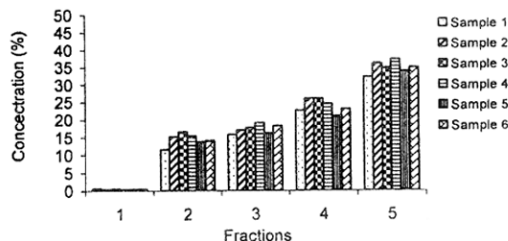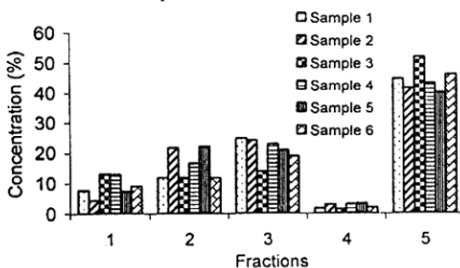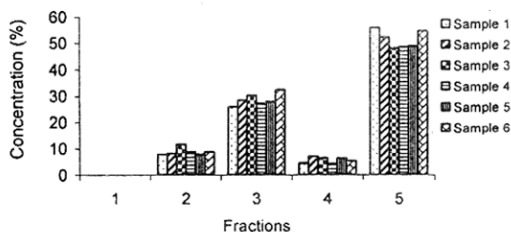

Fig. 1c: Concentration of Nickel in different fractions of six samples.

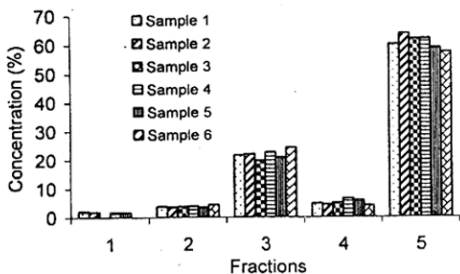Fig. 1d: Concentration of Copper in different fractions of six samples.

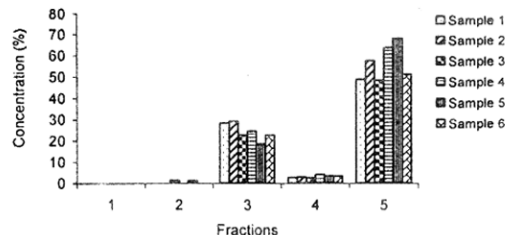Fig. 1e: Concentration of Zinc in different fractions of six samples.

Fig. 1f: Concentration of Cobalt in different fractions of six samples.

easily be absorbed and utilized by the organisms in the aquatic environment. From available evidence on the extraction of exchangeable metals from sediment [10-14] these results are to be expected. Ni and Cu concentration in exchangeable fraction account for 1.7-2.0 % and 0.4-0.6 % of the total metal concentration respectively. The relative percentage range for Mn is 4.4 % to 12.2 % and is probably due to Mn (II). It is recognized that in most natural waters, Mn (II) oxidation is much slower process than Fe (II) oxidation [13, 14].

Bond to carbonates

The concentration of Co in this fraction are below the detection limit, while Ni and Fe bonding carbonates are the lowest in this fraction. The relative percentage of Cu, Mn and Zn are 11.7-16.6 %, 11.9-22.1 % and 7.9-11.78 %, respectively. The metal species in first two fractions i.e. exchangeable and carbonate bond fraction are mobile in environment and are called bioavailable species [15].

Bond to iron and manganese oxide

The metal concentration in this fraction are relatively high and represent a major fraction of total metal concentration. The range of relative percentage of Cu, Ni, Mn, Zn, Fe and Co are 15.8-19.3 %, 19.7-24.3 %, 13.9-24.9 %, 13.9-24.9 %,26-32.5 %, 12.7-17.8 % and 2.25-29.3 %. The surface of Fe and Mn oxides have special affinity with the cations to natural pH [10, 14]. The results illustrate the strong scavenging efficiency of Fe-Mn oxide for metals.

Bond to organic matter

The concentration of Mn, Fe and Co in this fraction are the lowest i.e. 1.5-3.3 %, 1.6-2.1 % and 2.7-4.2 % respectively. The concentration of copper is highest (21-26 %) in this fraction followed by Zn (4.3-7.14 %) and Ni (4.0-6.5 %). The fulvic and humic acids and other sources of organic matter with complexant properties explain the high level concentration of of copper associated to this fraction. The stability constant of Cu-organic matter complex is higher than other ions with similar oxidation state [16, 17].

Residual

Metal concentration found in this fraction are higher than those observed in any of the proceeding fraction. Fe level reaches as high as (72-82 %). In the case of Ni, Mn. Zn and Co almost 50 % or above is residual fraction and these findings are according to many studies available in literature[10, 12, 13].

A major proportion of heavy metals studied being associated with mineral lattice (residual), is essentially unavailable and it is not expected to be released into solutions over a reasonable time span under the conditions normally encountered in the natural environment. The next considerable proportion of the metals Cu (15.8-19.3 %), Ni (19.7-24.3 %), Mn (13.9-24.7 %), Zn (26-32.5 %), Fe (12.7-17.8 %) and Co (18.6-29.3 %) is associated with ferro-manganese coating and is probably available as Fe-Mn oxides. The organic associated fraction represents the minor fraction (1.6-7.4 %) except Cu, which represents the 21-26 % association, this fraction is also available. First two fractions although readily available represents minor fractions in case of Co, Fe and Ni while represents some high concentration in case of Mn (11.9-22.1 %), Cu (11.7-16.6 %) and Zn (7.9-11.7 %).

Thus the chemical speciation evaluate the potential environmental availability of metals associated with specific sediment phases under various environmental conditions.

Experimental

a) Sample collection and preparation

Sediment samples were collected from six sewer drains of Lahore city, Main Mir drain, Misri Shah drain, Mc Lord Road drain, Bhati drain, Jail Road drain and Ravi drain in polyethylene bags that were previously soaked in 10 % HNO_3 for 48 hours followed by rinsing with distilled water and then allowed to drain to dryness. The samples were air dried, ground and sieved to 200 mesh size then stored at 4°C for further analysis.

The fractionation analysis of metals in sediments was performed by the method described by Tessier *et. al.,* [14]. The metals were partitioned into five operationally defined fractions i,e exchangeable, bound to carbonates, associated with Fe-Mn oxides (reducible), associated with organic matter (oxidisible) and residual.

The extraction was performed in 50 ml polypropylene centrifuge tubes, separation was affected by centrifuging at 10,000 rpm for 50 minutes (H-1500 FR). The supernatant was removed with a pipette and analyzed (below) for metal concentration. The residues was washed twice after each fraction with minimum amount of deionised water to avoid excessive solubilization of solid material.

b) Metal Analysis

Metal concentrations were determined by atomic absorption spectrometer (Varian model Spectr-40) involving direct aspiration of the aqueous solution into an air-acetylene flame. The concentration were obtained directly from appropriate calibration curves prepared for each metal. For total and residual metal analysis the solid was digested with perchloric acid HF and HCl [18]. Triplicate analysis of each sample was carried out and results were expressed as the mean of triplicate digestion.

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