

Speciation of Heavy Metals in Bed Sediments of Wetlands in Urban Coimbatore, India

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In water bodies sediment forms an important repository of heavy metals. Sediment plays a very important role in the physicochemical and ecological dynamics of heavy metals in aquatic systems. The physicochemical nature of sediment bound heavy metals are important in bioaccumulation in plants and animals in aquatic system. This is because different physicochemical forms of metals have different bioavailability and toxicity (Kumaresan and Riyazudin 2001). It is widely believed that easily bioavailable or free metal ion forms in aquatic system causes biological responses (Boruvka et al 1997, Brown and Markich 2000, Markich et al 2000). These forms of metals leads to biological responses by diffusion into cell membrane, sorption/complexation of metal at binding sites in cell membrane and uptake into the organism. The Biological responses of heavy metals are related with chemical speciation of metals (Ramos et al 1999). The chemical speciation that determines their bioavailability and mobility depends upon the physico-chemical conditions in the local micro environment such as pH, redox conditions, and competition for absorption sites among metal ions and absorptive area (Kabata-Pendias and Pendias 1984). Several methods are in use to study the chemical speciation of metals (For example, Tessier et al 1979, Sanchez et al 1993, Kersten and Forstener 1986), among which the sequential extraction method by Tessier et al (1979) is widely used. In the present study, heavy metal speciation in sediments of polluted lakes of Coimbatore, India was determined.

Coimbatore is an industrial city of India (11° 7'N lat. and 77° 15'E long.), ranking 11th in terms of urban population (about 1.8 millions) in the country. About 17000 registered small-scale industries operate in Coimbatore. Of these, nearly 450 are foundries, 300 electric motor manufacturing units and 200 wet grinder manufacturing units (Azeez et al 2000). There are 28 wetlands located in and around Coimbatore. Most of these wetlands are fed by river Noyyal, flowing through the city on its south. The river originates in the Vellingiri hills in Western Ghats, located on the southwestern side of the city. The river and the river-fed wetlands support a large number of plants and animals including migratory birds (Chandrabose and Nair 1988). Since the city is devoid of an integrated sewerage system, the prevailing drainage and sewerage are open type joining the near by lakes, wetlands and river without any appropriate treatment.

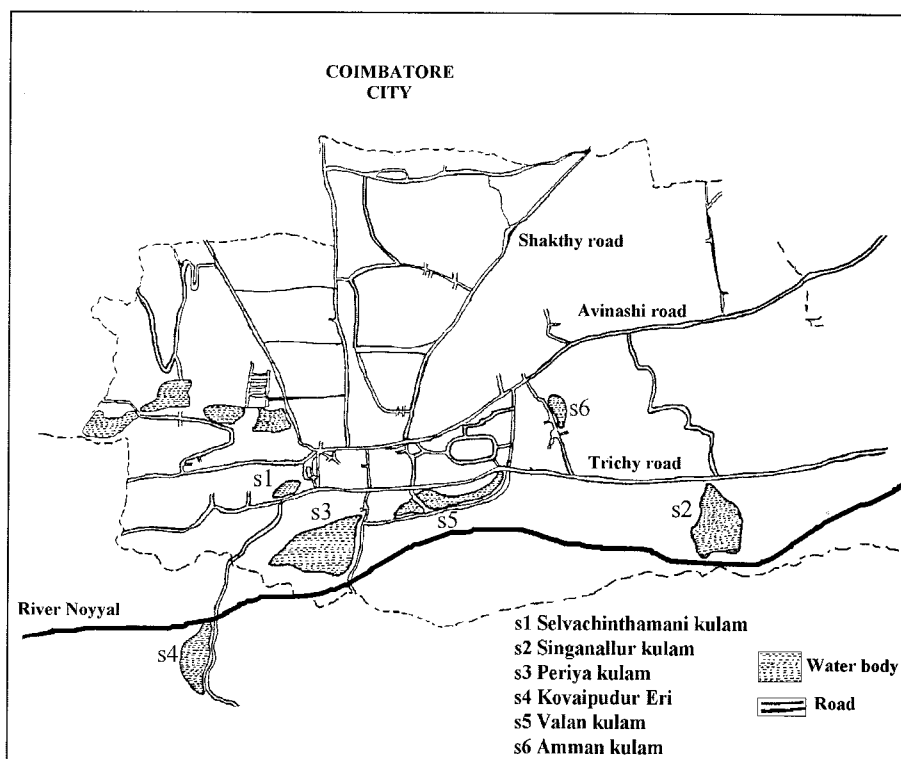


Figure 1. Map showing sampling stations

Most of the wetlands in the city get dried in summer and are used as a dumping yard for garbage, municipal and industrial wastes. During rainy season these wetlands receive substantial quantity of urban runoff. The surface water of most of these wetlands is polluted from various sources and none of them were found to comply the WHO standards for drinking water (Mohanraj et al 2000). In the current study, to understand the extent of contamination in wetland sediments of Coimbatore, an attempt was made to determine its physico-chemical characteristics and heavy metal speciation for select wetlands within the urban limits.

MATERIALS AND METHODS

Sediment samples from six wetlands, of which five are located close to motor ways, were collected for the present study (Figure 1). The water spread area of the wetlands, physico-chemical composition of its surface waters, the agricultural lands irrigated by each of the wetlands, present status of wetland with reference to pollution source and current use are described in erstwhile study (Mohanraj et al 2000).

The sediment samples from the wetlands were collected using 25 cm long clean

Table 1. Sequential extraction procedure for heavy metals.

Fraction Description		Extraction procedure
F-I	Exchangeable	1 hr agitation 8ml of 1 M Magnesium chloride at pH 7.
F-II	Bound to carbonate	8ml of 1 M sodium acetate adjusted to pH 5 with acetic acid and agitated for 5 hrs.
F-III	Bound to amorphous Fe and Mn hydroxides	20 ml of 0.04 M hydroxylamine hydrochloric acid in 25% acetic acid at 96 ⁰ C with occasional agitation for 6 hrs.
F-IV	Bound organic matters and sulphides	5 ml of 30% Hydrogen peroxide and 0.02 M nitric acid at 85 ⁰ C with occasional agitation for 5 hrs.
F-V	Residual	Digested with concentrated HNO ₃ and HClO ₄ .

Table 2. Physico- Chemical characteristics of sediment samples.

Parameters	S1	S2	S3	S4	S5	S6
PH	7.7	7.7	8.9	7.5	9.3	7.1
EC (m mhos)	1433	1137	586.7	490	456	650
Alkalinity (mg/g)	2.8	1.7	2.5	1.4	2.8	4.6
Chloride (mg/g)	24.8	12.3	11.6	11.6	11.2	15.3
Calcium (mg/g)	1.3	0.9	1.4	0.3	0.6	1
Magnesium (mg/g)	0.28	0.17	0.28	0.1	0.17	0.34
Total Organic Carbon (%)	4.7	8.6	8.3	8.9	5.5	10.3
Phosphate (mg/g)	0.48	0.37	0.24	0.23	0.28	0.29
Sulfate (mg/g)	4.81	3.74	2.4	2.43	2.36	2.35
Sodium (mg/g)	1.8	0.41	1.5	0.2	0.82	0.32
Potassium (mg/g)	0.92	1.18	0.7	0.35	0.4	0.46

PVC tubes of 3.5 cm internal diameter. Surface sediment samples up to depth of 15 cm were taken at three different places in each wetland and thoroughly mixed for the study. The samples were spread out and allowed to dry in the air at 40⁰C. The dried sediment samples were analysed for physico-chemical characteristics using methods described by Black et al (1965) and Trivedi et al (1987). pH, Electrical Conductivity (EC), alkalinity and chloride in the sediment samples were estimated in 1:5 sediment/water suspension. pH and EC, in the suspension of sediment in water were tested using respective electrodes. Total Organic Carbon (TOC) was estimated following Walkley and Black method. Exchangeable Ca²⁺ and Mg²⁺ were estimated separately after leaching with ammonium acetate solution by EDTA titrimetric method. Available nitrogen was determined using alkaline KMnO₄ and available phosphorus by stannous chloride method. Sulphate was estimated turbidometrically using BaCl₂. Sodium and potassium were estimated using flame-photometer, after extracting with neutral ammonium

Table 3. Concentration of heavy metals ($\mu\text{g/g}$) in sum of five fractions

Metals	S1	S2	S3	S4	S5	S6
Copper	120.4	106.3	75.4	38.5	91	168.7
Zinc	322.2	181.5	223	172.5	165.5	171.5
Nickel	167.8	163.5	166.6	111.9	117	140.6
Lead	360	126.2	122	105.5	107	215.5
Cadmium	2.2	1.5	1.7	1.5	1.5	0.5
Iron	8097	8345	8112	7827	8285	8867
Manganese	662.4	795	684	754.4	1166	802

acetate. The sequential extraction procedure suggested by Tessier et al (1979) was applied to extract heavy metals (Cu, Zn, Ni, Pb, Fe and Mn) from a gram of dried sediment samples. The summary of the sequence is given in Table 1. The supernatant of each fraction was analysed for metal concentrations using atomic absorption spectrophotometer (Model Pye Unicam SP 9). Drying the sediment samples in air may add a bias towards increasing carbonate and oxide forms of the elements, mainly due to the exposure to gases in the air. No attempt was made to quantify this bias in terms of concentration of various fractions.

RESULTS AND DISCUSSION

The pH of the sediment samples ranged between 7.1 to 9.3 (Table 2). Only in samples of S3 and S5 pH to the basic side was seen. Alkalinity of samples was in the range of 1.4 to 4.6 mg/kg. Highest electrical conductivity (EC) was observed in station S1 (1433 mmho) and lowest in S5 (456 mmho). High sodium and chloride content found in sample S1 may due to dyeing effluents (Senthilnathan and Azeez 1999) known for its high salt content from the dyeing industries present in the vicinity. The lowest quantity of calcium and magnesium were found in sample S4, while highest magnesium and calcium was in samples S6 and S1 respectively. An average of 0.315 mg/kg of phosphate was found in the sediments. No notable variation was seen in the case of phosphate among the samples. Higher values of organic carbon noticed in sample S6 suggest that the lake may be receiving effluents rich in organic load.

The total sum of heavy metal composition of samples analysed through sequential extraction procedure are showed in Table 3, while Fig 2 illustrates the percentage of fractional concentrations. The total concentration of metals in samples; the sum of the concentrations in all the fractions, was in the order $\text{Fe} > \text{Mn} > \text{Zn} > \text{Pb} > \text{Ni} > \text{Cu} > \text{Cd}$.

Copper in samples ranged between 38 – 168 $\mu\text{g/g}$. Residual fraction (F-V) was found to be the highest carrier of copper in all samples (64 – 86%), followed by F-III (5.6 – 29.6 %). High percentage of Cu in residual fraction is reported in most of the studies (Tessier et al 1979, Ramos et al 1994, Ramos et al 1999). Sample of S3 showed relatively high proportion of Cu in F-III (29%). Cu is more or less equally distributed in F-I and F-II in the case of all samples.

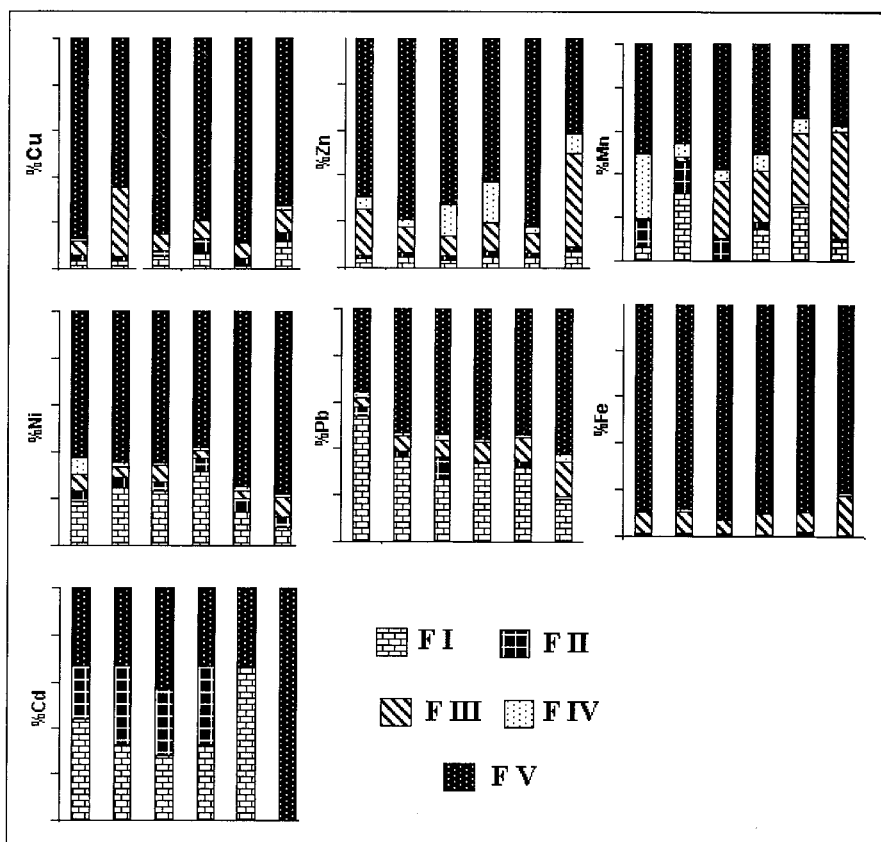


Figure 2. Fractional distribution of heavy metals in sampling stations (S1-S6).

An inverse correlation was observed between F-V and F-III, where as in most of samples F-I and F-II showed a positive correlation. Cu associated with F-III increases from 2 to 30% with increase in electrical conductivity up to 1137 mmhos, and beyond 1137 mmhos the trend reverses. In general, sediments having concentrations of copper higher than 50 mg/kg and 25 - 50 mg/kg dry weight are classified as "heavily polluted" and "moderately polluted" respectively (Irwin 1997). If the present study were classified accordingly, except S4 all other sediment samples would come under "polluted" category.

Zinc bound to F-V was observed as predominant (41- 78%) in the study, followed by F-III (8.4 – 40.4%). However some studies have reported that Zn bound to carbonates as a major fraction (Tsai et al 1998, Charlsworth and Lees 1999). Sample S6 was found with very high concentration of Zn (1715 $\mu\text{g/g}$). S6 also contained larger fraction of Zn in F-III, which is bound to anion phases of Fe and Mn hydroxides (40.4%) compared to other samples. In general Zn present as comparatively mobile form (the exchangeable form) is low. If Zn concentration decreases in F-V, either F-III or F-IV acquires higher values of Zn. The study

also reveals that as the pH increases percentage of Zn in the residual fraction increases gradually, indicating low rate of mobility at elevated pH 7 (Maskall et al 1995). Organic carbon content of the sediment, >8 mg/g, is inversely correlated with F-V and positively correlated with F-III. Such a positive correlation between organic carbon content of sediment and F-III fraction is apparently unusual. However, in surface sediments, overlaid with a water column, it is possible that an organic rich overlying water column may promote a relatively reducing conditions with subsequent migration of Fe and Mn to the surface of the sediments and formation of their hydroxides that can bind Zn from the sediment media. A gradual decrease in Zn associated with F-IV is observed as the electrical conductivity of sediment decreases. Calcium and Magnesium content of sediment does not seem to modify the Zn speciation substantially. The overall fractional profile of Zn in the present study appears to be more or less similar to many studies in freshwater sediments (Ramos et al 1994, Ramos et al 1999, Datta and Subramanian 1997).

Lead associated with fraction F-I (17 – 54%) and F-V (35 – 62 %) was found higher followed by F-III, F-II and F-IV. Lead concentrations in S1 and S6 were extremely higher compared to the other studies in urban sites. For example Lee et al (1997b) recorded only 43 µg/g in sediments at 12-16 cm depth of a retention pond along the motorway in Sologne, France. Lead bound to F-I is found higher compared with other metals, indicating its current anthropogenic sources. Such a distribution is common in sites of urban activities and industrial operations (Ramos et al 1999). Many studies have also recorded comparatively low percentage of lead in exchangeable fraction (For example, Charlesworth and Lees 1999, Tsai et al 1998). In an earlier study, the association of lead with F-I is found higher in samples of lower pH (Maskall and Thorton 1998). The study also reported rapid migration of lead bound to F-I to a depth of several meters in contaminated soils. Vehicular traffic, industrial and urban activities are the major sources for lead in sediment samples. The highest concentration of lead was in sample S1 (360 µg/g), which also had 54% of lead in exchangeable form (F-I). The wetland (S1) is situated close to a busy motorway and have a number of automobile maintenance centres in its catchment. The overall level of lead in S1 is high compared to other wetlands included in the present study. Sediments having concentrations higher than 60 mg/kg dry weight are included in the class "heavily polluted" by Irwin (1997). However, higher level, as high as 620 mg/kg dry weight of lead, are reported in detention pond sediments receiving runoff from highways elsewhere (Irwin 1997).

Nickel concentration among samples does not show much variation (111.95 – 167.8 µg/g). All wetland sediments lower than 20 µg/g is classified as "non polluted" (Irwin 1997). In the present study none of the wetlands fall "Non polluted" category. In samples, about 61.7 – 77.7% of Ni is associated with residual fraction F-V followed by F-I (7.4 – 31.8%). Ni bound to F-IV was found very low (0.8% - 7.4%). The samples of S2, S3 and S4 exhibited higher proportion of Nickel in exchangeable form. Fraction I was inversely correlated

with fraction V. An increase in sediment organic carbon from 5.5-8.9% has positive correlation with metal concentration in F-I.

Cadmium concentrations in samples ranged between 0.5 µg/g to 2.25 µg/g. In most of the samples F-I, F-II and F-V carried close quantity of Cd. This kind of distribution agrees to the previous observations of Lee et al (1997a). The fractions F-III and F-IV are devoid of cadmium content in all samples. Residual Cd remained more or less in close range in all the samples, despite their variations in other physicochemical parameters. In the case of samples S1 and S3 that have higher concentrations of Cd among all the wetlands, had this element in F-I and F-II fractions apart from the residual fraction.

About 80 – 93% and 5 –17% of iron is associated with residual fraction (F-V) and fraction III respectively. Overall concentration of Fe in the samples was in the range of 7.8-8.8 mg/g without much variation among the samples. Increase in pH from 7.1 to 9.3 showed only 5% increase in residual bound Fe and decrease in Fe–Mn oxide bound Fe, indicating the stability of scavenging action of Fe – Mn oxides at this range of pH. The iron content of overlying water in these wetlands (520 - 8020 µg/L) exceeded the prescribed WHO limit (300 µg/L) for drinking water (Mohanraj et al 2000).

Mn in samples varied between 662.5 to 1166 µg/g among the samples. The fractional distributions were 32–50% bound to F-V, 2–30% bound to F-IV, 1-48% bound to F-III, 1–14 % bound to F-II and 0.8–23 % bound to F-I. At pH 7.7 Mn bound to F-III was only 1%, while decrease in pH seems to increase Mn bound to F-III by 30-50% in the samples. For Mn, fraction F-V was found to be a major carrier. Fractional distribution of Mn exhibited wide variation among samples. For example in sample S6, 48% of Mn is associated with F-III, which is very high compared to other samples. Likewise only the sample S1 had high Mn (30%) in F-IV, while all other samples showed very low Mn concentration (2 – 6.5%) in this fraction. In a study conducted by Lee et al (1997b) in detention ponds the sediments of surface had higher values in F-I, while with increasing depth F-V recorded a proportionately higher concentration. Since, the samples in the present study are taken up to a depth 15 cm and made composite the results appear to be comparable with that of Lee et al (1997b).

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