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Retention of fly ash-derived copper in sediments of the Pandu River near Kanpur, India

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Abstract A coal-based thermal power plant is situated on the bank of the Pandu River, which is a tributary to the Ganges near Kanpur. River sediments downstream from the ash pond outfall are contaminated by fly ash. In order to establish the role of soils and sediments in retaining fly ash-derived heavy metals, copper was investigated as a model metal. A maximum concentration of 70 ppm Cu could be leached from the fly ash, confirming that it is a major source of this metal. Soil samples and river sediments were examined for Cu adsorption in the natural state as well as after treatment with H_2O_2, EDTA, and H_2O_2 followed by EDTA. The organic fraction of the samples was determined, and it had a major control on removal of Cu from a solution with 10^{-4} M initial concentration. Further characterization of organic matter indicated that with reference to natural samples, the humic acid fraction had a copper enrichment factor in the range 9.1–15.1. The factor for fulvic acids, in contrast, was between 3.5 and 5.5. This leads to the conclusion that river deposits rich in humic acids would withstand relatively high metal loads. Only when the metal input exceeds the maximum retention potential, would the metal be fractionated into the aqueous phase and act as a potential biocide.

Key words Fly ash · Copper adsorption · River sediments · Soil organic matter

Introduction

The Pandu River is a small tributary within the Ganges basin. It originates near Kanpur in the state of Uttar Pradesh and flows for about 64 km in a southeasterly direction before joining the Ganges. Typical discharge values are 78 MLD in the dry season and 130 MLD during monsoon (Arora and Routh 1980). A thermal power plant (TPP) is located at Panki on the left bank of the river (Fig. 1). This power plant utilizes around 600,000 tons of coal leading to the production of 210,000 tons of fly ash annually. The ash is disposed of by the wet method into ash ponds covering an area of 16 ha. While the ash settles down in the ponds, the supernatant slurry passes through filters, mixes with domestic wastewater from the residential colony of the TPP, and finally reaches the Pandu river.

It is well known that coal fly ash is rich in heavy metals. At the same time, soils and sediments are effective sinks for these metals. For example, Patel and Pandey (1987) observed that Cu, Co, Ni, Pb, Zn, Bi, and Sb carried in fly ash fallout from a TPP had permeated soil horizons up to a depth of 0.9 m. In the present study, copper was investigated as a model metal. Soil and sediment samples were collected from a stretch of the Pandu River before and after the TPP outfall. The main objective was to establish the fractionation of copper into the river sediment and to characterize the inorganic (mineral) and organic sites for adsorption. Experiments were designed to study the kinetics of copper adsorption and to correlate copper removal with cation exchange capacity (CEC). Some details have been discussed below.

Methods

Table 1 gives a brief description of various samples collected for this study. As the fly ash was relatively coarse grained, it was observed under a binocular microscope. In addition, the finer fraction of all samples which passed through ASTM 270 sieve (less than 53 μm) was used for mineral identification by x-ray diffraction. All other experiments were performed with the size fraction between ASTM 170 and 270 sieves (88–53 μm).

The organic matter content was determined by weight

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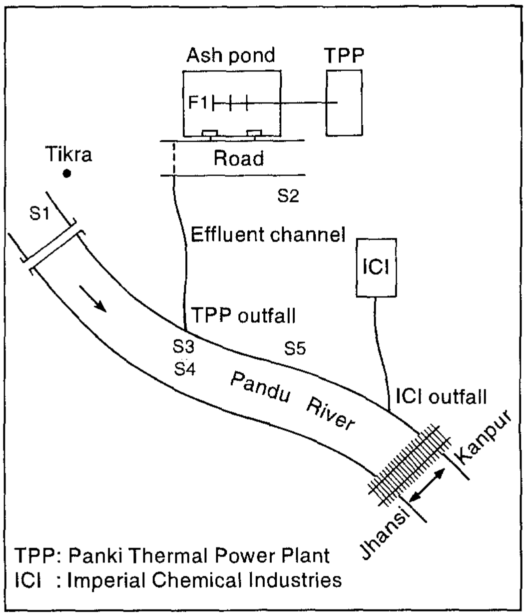


Fig. 1 Schematic map for sampling points

Table 1 Description of samples

Sample code	Description
F_1	Fly ash from ash pond
S_1	Benthic deposit at sediment-water interface, Pandu River at road bridge near Tikra village upstream from thermal power plant (TPP) outfall
S_2	Topsoil from embankment near ash pond
S_3	Benthic deposit at sediment-water interface, Pandu River at the confluence of TPP outfall
S_4	Benthic deposit 10 cm below interface, Pandu River at the confluence of TPP outfall
S_5	Soil below root zone, flood plain downstream of TPP outfall

loss due to oxidation by H_2O_2 (Jackson 1958). CEC was determined by acid saturation followed by potassium exchange and titration of the liberated H^+ ions by standard NaOH (modified after Chapman 1965). CEC determined after H_2O_2 treatment gave the value due to the inorganic constituents. Therefore, the difference in CEC between the untreated sample and the sample after removal of organic fraction was attributed to soil/sediment organic matter (SOM).

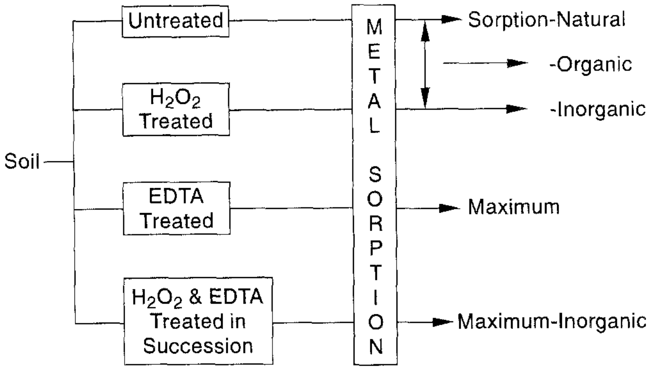
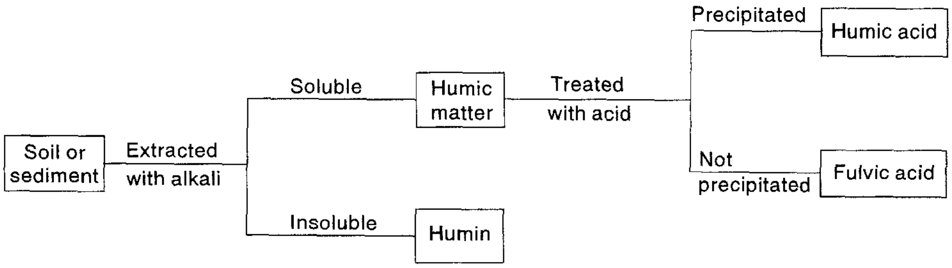


Fig. 2 Scheme for soil/sediment treatment for determination of metal sorption

Copper adsorption was measured with reference to an initial Cu(II) concentration of 10^{-4} M in a solution at 25°C with pH maintained at 5.0 by an acetate buffer. Total Cu(II) in solution was estimated by the colorimetric Cuprithol method (Standard Methods 1971). The analyses for a few selected samples were repeated by atomic absorption spectrometry. Kinetics and extent of Cu removal was studied after various treatments, which have been schematically represented in Fig. 2. It is obvious that adsorption of Cu after destruction of organic matter by H_2O_2 can be attributed to the mineral constituents. The difference between uptake by untreated samples and that after H_2O_2 treatment gave the adsorption by the organic fraction. Similarly, the value after leaching with EDTA represents the maximum metal adsorption because EDTA forms a strong complex with the metal bound to all sites on the soil or sediment surface (Mouvet and Bourg 1983). However, treatment of the sample with EDTA after H_2O_2 clears the binding sites as well as destroys organic matter. Therefore, the adsorption after H_2O_2 and EDTA treatment in succession represents the maximum removal by the inorganic fraction. More drastic treatment, such as digestion with acids, was not employed as they destroy the clay mineral structure.

The role of SOM in Cu adsorption was further investigated by characterizing the humic acid (HA), fulvic acid (FA), and humin fractions according to the scheme presented in Fig. 3.

Fig. 3 Fractionation of SOM



Results and discussion

Mineralogy and copper content of fly ash

The appearance of the fly ash particles under the binocular microscope has been summarized in Table 2. The nomenclature of Watt and Thorne (1965) has been followed for this purpose. It was realized that, unlike crystalline mineral grains, the cenospheres would not give x-ray peaks because of their amorphous nature. On the other hand, these amorphous and spongy particles may be of great significance for retention X-ray of heavy metals.

A typical X-ray diffractogram of fly ash is shown in Fig. 4. The mullite peak can be used as diagnostic of fly ash in a mixture with soil or sediment because this mineral with composition $3Al_2O_3 \cdot 2SiO_2$ is believed to be the product of thermal breakdown of clay minerals originally associated with coal (Watt and Thorne 1965). For example, the X-ray pattern of sample S_4 (Fig. 5) contains mullite peaks at 5.42, 3.43, and 3.39 Å along with standard soil mineral peaks of chlorite, illite, kaolinite, and quartz. This confirms that the benthic deposit of the river has been contaminated by fly ash.

Copper was extracted from the fly ash by various leaching agents listed in Table 3. It is obvious that the value of 70 ppm obtained by EDTA leaching represents the maximum Cu released. This falls within the range of 49–270 ppm listed by Ferraiolo and others (1990) as typical Cu content of fly ash.

Table 2 Characterization of fly ash particles

Description	Identification
Irregular transparent particles	quartz
Transparent spheres	silicates
Irregular white particles	clay minerals
Opaque spheres	iron minerals
Dark, irregular particles	partially burnt coal
Opaque, spongy particles	cenospheres

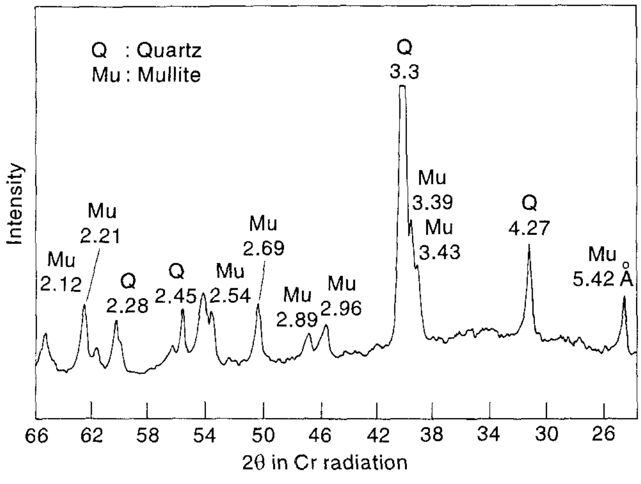


Fig. 4 X-ray diffractogram of fly ash

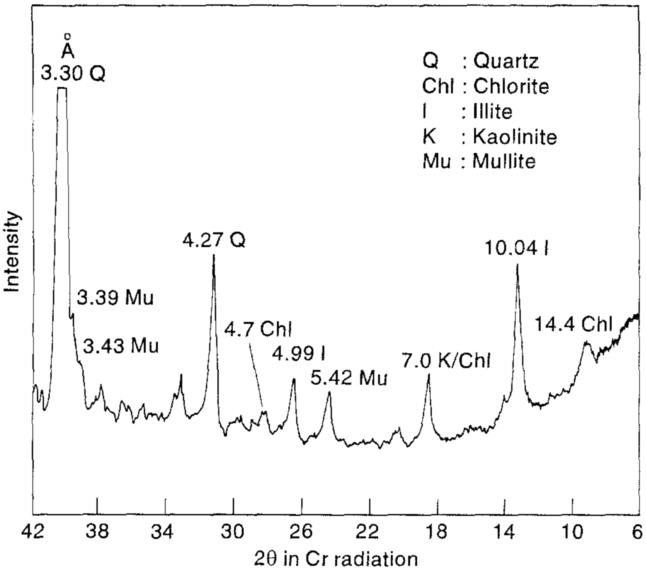


Fig. 5 X-ray diffractogram of sample S_4

Table 3 Release of Cu from fly ash by various leaching agents

Leaching agent	Amount of Cu in leachate in ppm of fly ash
Distilled water	32
0.1 N HCl	60.8
10^{-3} M EDTA	70

Organic matter content and CEC of soil and sediment

The results presented in Table 4 show that there is a wide variation in SOM. The minimum value of 0.17 percent was determined in sample S_1 collected upstream of the TPP outfall. However, sample S_3 from the sediment–water interface at the confluence of the TPP outfall with the Pandu River contains the maximum amount of 3.0 percent organic matter. This points to the contribution of domestic wastewater, which mixes with the ash pond effluent.

CEC of the natural soil or sediment generally increases with the organic matter content. Moreover, it is interesting to note that CEC due to the organic fraction is several times higher than that due to the inorganic fraction.

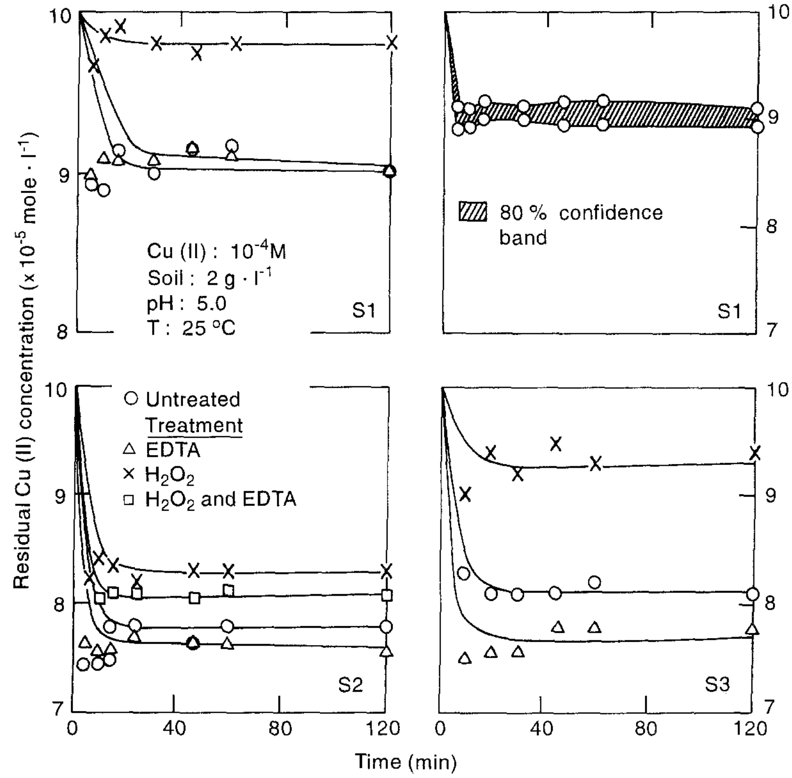
Metal adsorption studies

The kinetic plots presented in Figs. 6 and 7 indicate that the adsorption of Cu is rapid and the equilibrium plateau is established within 2 h. In general, Cu adsorption was higher for EDTA-treated samples compared with H_2O_2-treated samples. Typical adsorption curves for various

Table 4 Organic matter content and CEC of soils/sediments

Sample	H_2O_2 oxidizable organic matter (%)	CEC of natural soil/sediment (meq/100 g)	CEC due to inorganic fraction of sample (meq/100 g of inorganic part)	CEC due to organic fraction of sample (meq/100 g of organic part)
S_1	0.17	2.44	2.04	235.3
S_2	1.37	6.38	5.67	41.6
S_3	3.00	5.50	4.74	30.0
S_4	0.50	2.00	1.25	152.0
S_5	1.74	4.13	2.93	71.8

Fig. 6 Kinetics of Cu(II) adsorption by samples S_1, S_2, and S_3 and kinetic plot for S_1 with 80% confidence band



fractions of samples S_2 and S_4 are presented in Fig. 8. Table 5 summarizes the adsorption of Cu from a solution with initial 10^{-4} M Cu(II) by natural samples and various fractions. Copper adsorption by natural samples ranged between 0.261 and 0.921 mg of Cu(II) per gram of sample. This is similar to the range 0.318–0.510 mg/g recently reported by Msaky and Calvet (1990) for soil samples from France and Tanzania under identical experimental conditions of pH 5.0 and initial Cu concentration of 10^{-4} mol/l.

Table 6 compares Cu adsorption with CEC of various components of the soil or sediment. In all cases, the metal adsorption due to inorganic fraction was less than its CEC and ranged between 9.5 and 46.2 percent of CEC. Metal adsorption by the organic fraction, in contrast, had a variable relationship with its CEC. For example, adsorption was more than CEC for samples S_1 and S_2, almost equal to CEC for sample S_3, and less than CEC for samples S_4 and S_5. These results suggest that processes other than simple ion exchange are important for adsorption of Cu by soils and sediments. For example, complexation of metal with organic matter may be responsible for adsorption in excess of CEC. Similarly, the nature of organic matter and its affinity towards Cu may be important in other cases.

A plot of organic matter content against CEC (Fig. 9) gives a regression line with slope 1.4. From a similar plot for coastal plain soils, Kamprath and Welch (1962) had obtained a slope of 2.86. In order to depict the influence on metal adsorption, the organic matter content has been plotted against maximum Cu removal after EDTA treatment on the same figure. This confirms the importance of SOM in cation exchange as well as in metal adsorption.

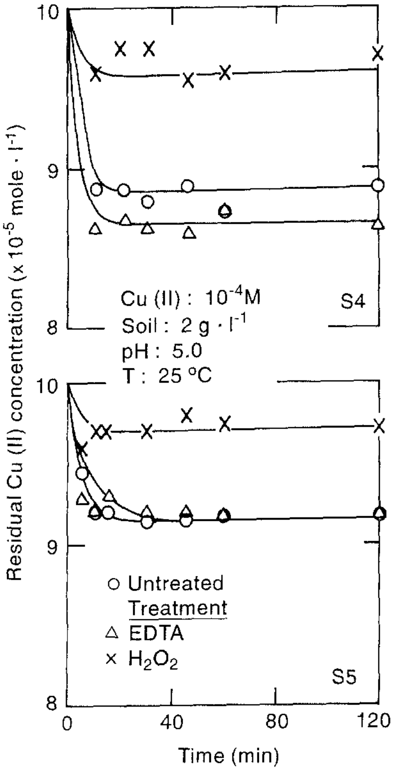


Fig. 7 Kinetics of Cu(II) adsorption by samples S_4 and S_5

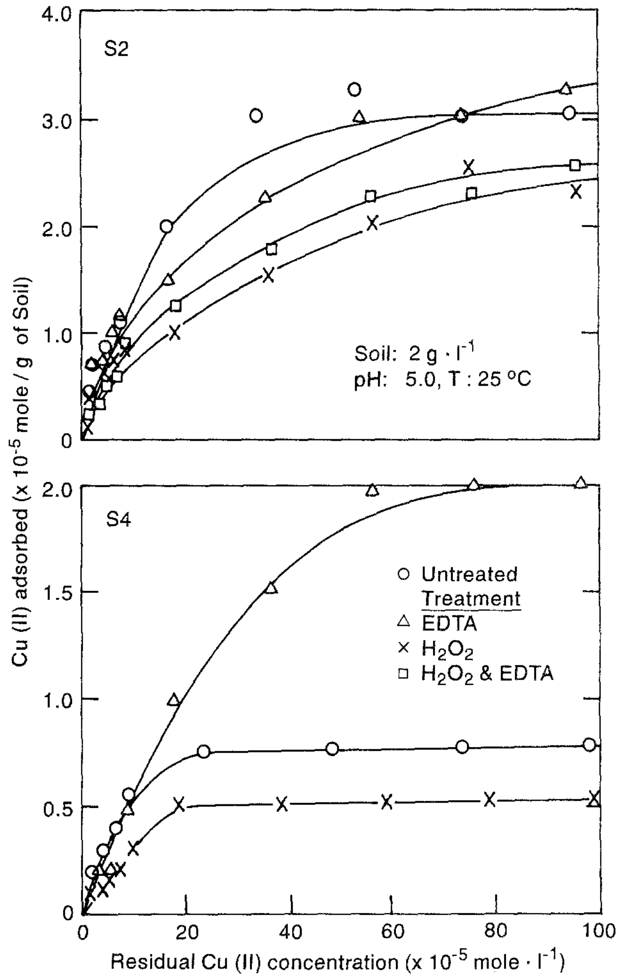


Fig. 8 Cu(II) sorption curves for samples S_2 and S_4

Characterization of SOM

HA, FA, and humin fractions were characterized for alluvial soil samples S_2 and S_5, which had relatively high organic matter contents. These fractions in SOM are highly stable and nonbiodegradable. Therefore, they can bind metals permanently. Sample S_3 was avoided in spite of its higher SOM because contamination by domestic wastewater would have introduced unstable species of biodegradable organic matter. The ratio of optical densities in the visible range at 465 and 665 nm (E4/E6 ratio) as well as absorption bands at the 2900 to 2800 cm^{-1} region in IR spectra were used for this purpose, as suggested by Schnitzer and Khan (1972). The Cu adsorption values have been listed in Table 7. This table also gives the enrichment factors for HA and FA with respect to adsorption by natural soil. The results clearly show that HA is able to retain three times more Cu compared with FA. This is possibly due to the greater affinity of HA for Cu. For example, the stability constant of the Cu–HA complex is reported to be around 8.65 (Takamatsu and Yoshida 1978), whereas the value for Cu–FA varies from 5.64 to 7.65 depending on the type of binding site (Hirata 1981). Thus soils and sediments containing higher amounts of HA are likely to show greater Cu adsorption. This conclusion is similar to that drawn by Nriagu and Coker (1980).

Table 5 Distribution of Cu between various constituents of soils/sediments at initial concentration of 10^{-4} M

Sample	Organic matter content (%)	Adsorption by natural soil/ sediment (mg of Cu/g of sample)	Adsorption by inorganic fraction (mg of Cu/g of inorganic part)	Adsorption by organic fraction (mg of Cu/g of organic part)	Adsorption maximum (mg of Cu/g of sample)
S_1	0.17	0.261	0.064	115.90	0.280
S_2	1.97	0.921	0.487	22.54	0.762[a]
S_3	3.00	0.560	0.309	8.67	0.590
S_4	0.50	0.330	0.191	28.00	0.365
S_5	1.74	0.369	0.097	15.75	0.305

[a] Maximum adsorption by inorganic fraction after subjecting sample S_2 to H_2O_2 and EDTA treatment is 0.615 mg of Cu/g of inorganic part

Table 6 Comparison of CEC and copper adsorption by soils/sediments

Sample	Organic matter content (%)	CEC of natural soil/ sediment (meq/ 100 g)	Maximum copper adsorption (meq/ 100 g of sample)	CEC due to inorganic part (meq/ 100 g of inorganic part)	Metal adsorption inorganic (meq/ 100 g of inorganic part)	CEC due to organic part (meq/ 100 g of organic part)	Metal adsorption organic (meq/ 100 g of organic part)
S_1	0.17	2.44	0.88	2.1	0.20	235.3	364.8
S_2	1.97	6.38	2.40	5.7	1.53	41.6	70.9
S_3	3.00	5.50	1.86	4.7	0.97	30.0	27.3
S_4	0.50	2.00	1.15	1.3	0.60	152.0	88.1
S_5	1.74	4.13	0.96	2.9	0.31	71.8	49.6

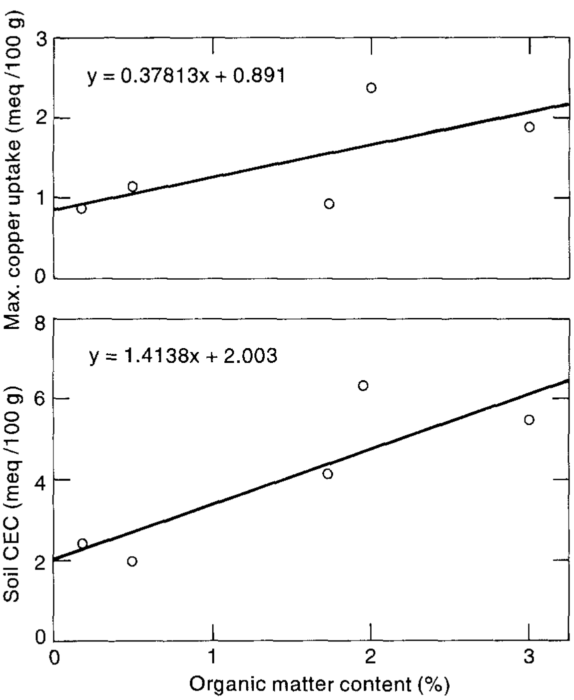


Fig. 9 Relationship between SOM and CEC and SOM and copper adsorption

Concluding remarks

This case study demonstrated that TPP fly ash can release up to 70 ppm Cu. This might be typical of heavy metal input from this source into river systems. The X-ray technique enabled the use of mullite peaks as fingerprints for fly ash contamination of river sediments. The various chemical treatments given to the sediment and soil samples effectively stripped the binding sites of metals retained earlier. This was followed by adsorption of Cu under controlled laboratory conditions. The kinetics and extent of Cu removal indicated that the river sediments and nearby soils have high metal retention potential. Among the various constituents of the samples, organic matter has relatively high Cu adsorption and cation exchange capacities. For the inorganic fraction, represented by minerals such as illite, chlorite, kaolinite, and quartz, Cu adsorption was less than CEC. However, the organic fraction showed a variable relationship between Cu adsorption and CEC. This is apparently controlled by the nature of organic matter. For example, the humic acid fraction of SOM has a higher adsorption compared with fulvic acid and humin. Therefore, river deposits rich in HA could assimilate metal doeses up to their maximum retention potential. Heavy metal toxicity in river water would occur only when metal input exceeds this level.

Acknowledgments This paper is based on an M. Tech, thesis submitted by D. V. Ravi Chander to the Department of Civil Engineering, I.I.T. Kanpur.

Table 7 Distribution of copper and enrichment factor in various organic fractions

Sample	Adsorption by humic substances		Adsorption by humin (µg Cu/g humin)	Adsorption by soil/ sediment (µg Cu/g sample)	Enrichment factor for[a]		
	Cu (µg/g HA)	Cu (µg/g FA)			HA	FA	Humin
S_2	8370	3180	635	921	9.1	3.5	0.69
S_5	5580	2032	254	369	15.1	5.5	0.69

[a] HA = humic acid; FA = fulvic acid.

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