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## Distribution And Chemical Speciation Of Select Transition Metals In The Waters Of River Yamuna, New Delhi

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### ABSTRACT

Select metals Fe, Mn, Cu, Pb, Zn, Ni and Cr were investigated in the water samples collected from river Yamuna. Although free metal ion concentrations of Cu, Pb and Cd were probed using ion selective electrodes, they were found below the detection limits of the electrodes. Among the total dissolved metals, zinc was found to be highest, i.e. 304.85µg/l at najafgarh drain, while lead was seen in the lowest concentration(0.05µg/l) at site ramghat, the entry point of the river into New Delhi. Lead concentration ranged between 0.05 to 1.37µg/l. The lowest level was found at ramghat and highest level at nizamuddeen bridge and okhla barrage. As expected Zn, Fe and Mn were seen in very high concentrations compared to the other elements namely Cu, Cr, Ni and Pb. In each site, the variation among the metal concentrations was highly significant. Similarly each of these metals also differed significantly(LSD, P<0.05) among the sampling sites. At down stream sites the percentage concentrations of chelex-labile metals, particularly Fe, Mn and Cu were lower than that of the upstream sites. This is attributed to the varied nature and amount of colloidal matter in the waters at these sites. Copper in the river water differed from the other metals in its behavior towards chelex-resin, probably for its strong association with the organic films on Fe and Mn colloids.

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### KEYWORDS

Speciation;  
ISE;  
Chelex-labile;  
Complexation;  
Organic film.

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### INTRODUCTION

River processes form a major link in the geochemical cycle. An understanding of the pathways of pollutants through the riverine environment depends on their geochemical cycling. Nevertheless, heavy metal pollution and its environmental and biological implications have been widely studied. Following a number of catastrophic episodes of metal pollution and several observations from experimental studies, investigations led to the detection of certain forms of metals being responsible for toxicity and fate of metal contaminants in the medium such as water. It is accepted that the quantification of these chemical forms would be more meaningful than measurement of total metal concentrations<sup>[1-6]</sup>. Study of chemical speciation of metals is very valuable to understand the responses of biological communities to metal exposures<sup>[7]</sup> and could appreciably help solving many modern environmental and ecotoxicological issues posed by toxic metals<sup>[8-9]</sup>. However, in spite of the high importance of chemical speciation of metals in ecotoxicology and pollution management, such studies remain rare in countries like India.

Two different approaches have been used to study chemical speciation of trace metals in natural waters<sup>[1]</sup> and an array of techniques are used for such studies<sup>[4,10-15]</sup>. One approach is experimental and attempts to place various metal species in operationally defined classes based on their behavior during separation and chemical analysis. The second approach involves computation of the equilibrium concentrations of all metal-ligand species using experimentally determined values for total metal and ligand concentrations and published values of the relevant metal-ligand stability constants. In the cases where stability constant data are not available, particularly for various natural ligands, stability constants are determined through complexometric titrations after chemically isolating them.

Regarding the experimental approach, very few methods are available, which will analytically respond to only one particular chemical form of an element. Integrating some of the preliminary physico-chemical separation techniques in sequence, several authors have proposed and examined speciation

schemes to distinguish the different chemical forms of metals in aquatic systems<sup>[13,16-22]</sup>. The schemes separate various forms of metals into assorted fractions according to size/density (ultra-filtration, ultra centrifugation and dialysis), charge (electrophoresis), electrochemical behavior (ASV labile or non-labile) or chromatographic characteristics (Chelex-resin, XAD-2, Sephadex). Some of the schemes include photo-oxidation also. While the significance of the individual fractions is not clearly understood, researchers during the past few decades have made use of one or the other schemes and have reported speciation of metals in many aquatic systems<sup>[23-30]</sup>. The present study examines speciation of select metals in the water of river Yamuna, flowing by the side of New Delhi. The distribution of free metal ion and chelex-labile metals were particularly examined.

### Study area

The river Yamuna in New Delhi, the capital city of India, receives large quantities of effluents from thermal power plants, numerous industrial units and 18 major drains that bring in municipal and domestic wastes<sup>[31]</sup>. For several decades, effluents and wastes are being dumped in large scale into the river and its environs. It is very likely that the river has accumulated large quantities of recalcitrant pollutants in the bygone years and possible steady mobilization of toxic metals from sediments is likely to cause health risk to the downstream population. Pollution load in the river has been reportedly increasing due to several point and non-point sources of waste discharges<sup>[32-35]</sup>. Although the river Yamuna has been extensively studied for heavy metals by various researchers<sup>[36-37]</sup>, studies on their speciation in this riverine environment are rare.

### EXPERIMENTAL

Water samples were collected from six locations along the river stretch, namely Ramghat (site 1), Najafgarh drain (site 2), Old Yamuna bridge (site 3), Yamuna barrage (site 4), Nizamuddin bridge (site 5) and Okhla (site 6) (Figure 1) for a period of one year. The sampling site at Ramghat is an upstream location where Yamuna enters New Delhi. The largest drain

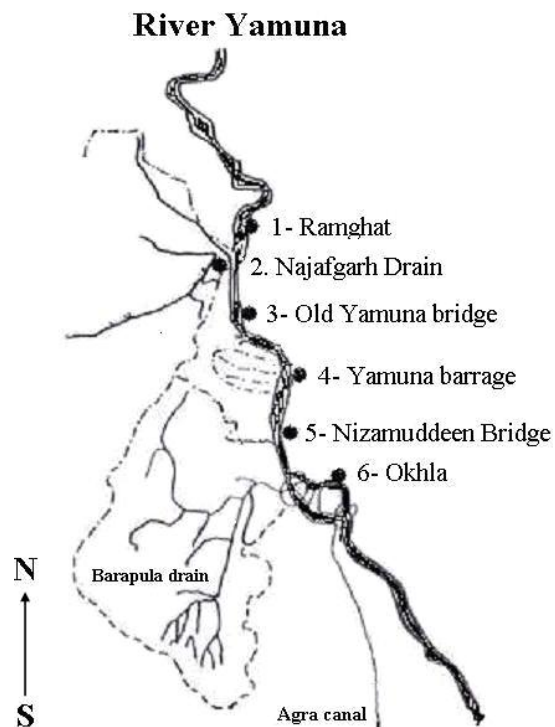


Figure 1: Sampling sites in the river Yamuna

that carries almost 50% of sewage from the city, the najafgarh drain, joins the river just earlier to the old yamuna bridge. The effluents from indraprastha thermal power plant, one of the major power plants in the city, joins the river nearby the old yamuna bridge site. At okhla, the point at which the river leaves New Delhi, it receives a major drain carrying domestic and industrial effluents, and effluents from several non-point sources. The non point sources of pollution in this riverine environment are mostly those of urban runway runoff and waste water from automobile garages.

Water samples were collected in metal free laboratory cleaned polyethylene bottles. The glasswares used in the experiment were cleaned with detergents, soaked in 10% nitric acid for 48 hours, then washed in deionized distilled water and dried in an oven at 70°C<sup>[38]</sup>. The samples were filtered through 0.45µm membrane filters(Whatman) and stored at 4°C for speciation analysis. atomic absorption spectrophotometer (Model philips, PU 9200X) was used for esti-

imating total concentration of Fe, Mn, Cu, Pb, Zn, Ni and Cr in the filtered samples, after the samples were pre-concentrated via APDC-MIBK procedure. Another set of filtered samples was analyzed for free metal ion concentrations, by ion selective electrode (ISE) potentiometry. The ion-analyzer (Model orion-901) fitted with the respective ISE was standardized using a standard solution of strength comparable to the total concentration of the metal. To each sample(50ml), 1ml of ion strength adjustor(ISA) was added and kept stirred by a teflon coated magnetic bead while concentration measurements are made. A third set of filtered samples was used to estimate the chelex labile metal. Chelex-100(Bio-rad) is a styrene-divinyl benzene copolymer containing paired imino-diacetate ions, which act as chelating group in binding polyvalent metal ions. About 1-2g of the sodium form of chelex(100-200mesh) was made into slurry with deionized distilled water. The slurry was poured in to 0.8cm internal diameter metal free glass columns fitted at the bottom with fritted glass and teflon stopcock. A flow rate of 2.5ml/min was maintained giving a contact time of 7sec<sup>[39]</sup>. Around 1 to 2 liters of each sample were passed through the column and the labile metal taken up by chelex was eluted by 1N HCl in a 50ml volumetric flask and analyzed further by atomic absorption spectrophotometer. Standard addition technique was used to reduce the matrix effects in these analyses. The estimated detection limits of the metals in the water(µg/ml) and the recovery rate of all the metals are given in TABLE 1. Analysis of pre-analyzed water samples showed an average recovery rate of 95.1%. A test of least significant difference (LSD) was performed, using 'MEGASTAT', to evaluate the variability of metals among the sampling sites. The  $\alpha=0.05$  criterion was followed for the test.

## RESULTS AND DISCUSSION

The average concentrations of total dissolved metals at different sites are given in TABLE 2. The total concentration of the metals varied among the

TABLE 1: Detection limits for transition metals

Metal	Fe	Mn	Zn	Cu	Pb	Cr	Ni
Detection level in water (µg/ml)	0.08	0.06	0.05	0.007	0.005	0.03	0.02
Recovery rate (%)	97.1	96.3	96.9	95.1	93.4	91.9	95.2

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sampling sites and months. The industrial and domestic effluents of varying compositions and quantities are responsible for these spatial and temporal variations. Many metal ions are released into the environment as a result of civilizatory activities. Whenever the rate of release exceeds the natural rate of cycling, contamination of the ecosystem may result. Among the total dissolved metals zinc was seen in the highest concentration (304.85 µg/l at site 2), while lead was seen in the lowest concentration (0.05 µg/l at site 1). Lead, one of the most pernicious heavy metals, ranged in concentration from 0.05 to 1.37 µg/l. The lowest level was found at site 1 and highest level at sites 5 and 6. Zn, Fe and Mn were seen in very high concentrations compared to other elements namely Cu, Cr, Ni and Pb. The recorded concentrations of the metals in this river water were compared with that of the values reported from river Gomti that flows by Lucknow, another major industrial city in the northern India<sup>[40]</sup> (TABLE 2). Of all the metals, only Cu and Zn were found to be higher than that reported from river gomti. Almost all the metals showed elevated levels in the down stream points

than that of upstream ones. Singh et al.<sup>[40]</sup> also reported similar findings. It appears established that on a global scale, the flux of Zn exceeds the natural rate of cycling<sup>[41]</sup>. In each site, the variation among the metals was highly significant. Similarly each of these metal concentrations also differed significantly (LSD, P<0.05) among the sampling sites along the river stretch.

Measurement of metals in the water samples using ISE did not yield any results. This indicated that concentrations of free metal ions were below the detection limits (in the range of 10<sup>-9</sup>M) of the electrodes. The average concentrations of chelex-labile metals at different sites are given in TABLE 3. The corresponding percentage levels of chelex-labile metals are given in TABLE 4. As in the case of the total dissolved metals, Zn was seen to have the chelex labile forms in highest concentration. However, in terms of percentage it did not occupy the highest position: the chelex-labile form of the element was only about 73%. Highest percentage of chelex labile form was seen in the case of Cu (93%), while the lowest was seen in the case of Fe (51%). In

**TABLE 2: Annual average concentration (µg/l) of total dissolved metals in river Yamuna**

Metals	Site 1*	Site 2	Site 3	Site 4	Site 5	Site 6	River average concentration	Reported values #
Fe	114.71	291.14	181.1	145.82	207.04	205.7	190.9 ± 60.8	79.0-319.0
Mn	111.83	87.23	80.61	82.21	69.02	69.22	83.3 ± 15.7	4.0-97.0
Cu	6.19	16.22	12.25	12.37	16.6	18.73	13.7 ± 4.5	1.3-4.0
Pb	0.05	1.3	0.96	1.01	1.37	1.37	1.01 ± 0.5	15.8-27.0
Zn	155.27	304.85	216.61	227.77	241.61	212.15	226.4 ± 48.5	14.0-28.7
Ni	2.26	9.21	7.59	7.48	7.89	8.03	7.1 ± 2.4	7.0-11.0
Cr	5.36	18.78	18.14	20.35	20.4	18.37	16.9 ± 5.7	2.0-68.0

\*Site 1: Ramghat, Site 2: Najafgarh drain, Site 3: Old Yamuna bridge, Site 4: Yamuna barrage, Site 5: Nizamuddeen bridge, Site 6: Okhla #Singh et al., 2005

**TABLE 3: Annual average concentration (µg/l) of chelex labile metals**

Metals	Site 1*	Site 2	Site 3	Site 4	Site 5	Site 6
Fe	86.62	161.83	119.46	98.64	117.72	104.53
Mn	93.98	64.51	50.74	53.43	46.93	48.1
Cu	5.75	13.78	10.43	10.38	13.36	14.04
Pb	0.04	1.1	0.78	0.83	1.15	1.1
Zn	114.82	214.97	158.14	169.68	174.9	155.29
Ni	1.85	7.66	6.39	6.02	6.27	6.6
Cr	4.62	16.13	14.98	17.76	18.23	15.32

\*Site names are given in Table 2

**TABLE 4: Annual average percentage concentration of chelex labile metals**

Metals	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6
Fe	75.51	55.58	65.96	67.65	56.86	50.82
Mn	84.04	73.95	62.95	64.99	67.99	69.49
Cu	92.89	84.96	85.14	83.91	80.48	74.96
Pb	80	84.62	81.25	82.18	83.94	80.29
Zn	73.95	70.52	73.01	74.5	72.39	73.2
Ni	81.86	83.17	84.19	80.48	79.47	82.19
Cr	86.19	85.89	82.58	87.27	89.36	83.4

\*Site names are given in Table 2

the case of Cu, the percentage of chelex labile forms across the months and sites was in the range of 75 to 93 %.

Though complexes of log stability constant greater than 14.0 are not expected, at down stream sites the percentage concentrations of labile metals have been found to be considerably lower than the upstream site (Ramghat, Site 1). As noted earlier, the fraction of chelex-labile metals varied across months and sites. The resin kinetics cannot be accountable for the observed changes as experimental conditions, like flow rate and temperature, remained identical all through the study. A range of factors would influence the adsorption on/or occlusion of colloids resulting in differing concentrations of labile species as observed in the present study. Among such factors important are the quantities of colloids and their nature at various sites, and the differences in the characteristics of the metal ions and their complexes [such as charge, size, and extent of complexation<sup>[42]</sup>. Similar observations were reported in certain earlier studies also<sup>[43]</sup>.

The percentage of chelex-labile metal concentrations of Fe, Mn and Cu showed sharp differences (8-20%) between the first upstream sampling site and the rest of the sampling sites, while Pb, Zn, Ni and Cr showed relatively lower differences. It is possible that addition of domestic/municipal sewage downstream and the resulting higher formation of colloidal forms of Fe and Mn may be an important reason for these changes. Nevertheless, river systems constitute a multimetal-multiligand system and hence studies on the speciation of trace metals in rivers remain one of the interesting aspects owing to the natural pathways of metals in such systems. Copper being capable of forming strong complexes with organics would associate itself with organic films covering the iron and manganese colloids becoming itself unavailable to the chelex resin<sup>[44]</sup>. Other elements that did not show notable differences between the first and the other locations have lesser affinity to organic complexans. Speciation of organic ligands (distribution of the chemical species of ligands) in water, which is very complex, has significant role in determining the speciation of metals<sup>[45]</sup>.

## REFERENCES

- [1] T.M.Florence, G.E.Batley; CRC, Crit.Rev.Anal.Chem., **9**, 219-296 (1980).
- [2] M.R.Twiss, O.Errecalde, C.Fortin, P.G.C.Campbell, C.Jumarie, D.Denizeau, E.Berkelaar, B.Hale, K.van Rees; Canadian Network of Toxicology Centre (CNTC), **27** (2000).
- [3] P.Svete, R.Milacic, B.Pihlar; J.Environ.Monit., **3**, 586-590 (2001).
- [4] W.Baeyens, F.Monteny, M.Leermakers, S.Bouillon; Anal.Bioanal.Chem., **376**, 890-901 (2003).
- [5] B.Michalke; Ecotoxicol.Environ.Safety., **56**, 122-139 (2003).
- [6] J.O.Okonkwo, M.Mothiba, O.R.Awofolu, O.Busari; Bull.Environ.Contam.Toxicol., **75**, 1123-1130 (2005).
- [7] M.Ramirez, S.Massolob, R.Frache, J.A.Correa; Mar.Pollut.Bull., **50**, 62-72 (2005).
- [8] A.Sanz-Medel; Pure.Appl.Chem., **70**, 2281-2285 (1998).
- [9] A.S.Hursthouse; J.Environ.Monit., **3**, 49-60 (2001).
- [10] P.Benes, E.Steinnes; Water Res., **8**, 947 (1974).
- [11] B.T.Hart, S.H.R.Davies; Aust.J.Mar.Freshwater Res., **28**, 105-112 (1977).
- [12] H.Oda, S.Okabe; J.Faculty, Mar.Sci.Technol, Tokai Univ., **10**, 89 (1977).
- [13] A.Tessier, P.G.C.Campbell, M.Bission; Anal.Chem., **51**, 844-851 (1979).
- [14] G.E.Batley, S.E.Apte, J.L.Stauber; Aust.J.Chem., **57**, 903-917 (2004).
- [15] E.Fernandez, R.Jimenez, A.M.Lallena, J.Aguilar; Environ.Pollut., **131**, 355-364 (2004).
- [16] G.E.Batley, T.M.Florence; Anal.Lett., **9**, 379-388 (1976).
- [17] S.F.Sugai, M.A.Healy; Mar.Chem., **6**, 291-308 (1978).
- [18] Y.Sugimura, Y.Suzuki, Y.Miyake; J.Oceanogr. Soc.Japan, **34**, 93-96 (1978).
- [19] R.M.Harrison, D.P.H.Laxen; Nature, **286**, 791-793 (1980).
- [20] J.R.Hasle, M.I.Abdullah; Mar.Chem., **10**, 487-503 (1981).
- [21] H.W.Nurnberg, C.J.M.Kramer, J.C.Duinker; Eds.Nihoff/Junk Publ., The Hague, 95 (1984).
- [22] C.Ianni, N.Ruggieri, P.Rivarolo, R.Frache; Anal.Sci., **17**, 1273-1278 (2001).
- [23] L.J.F.Sanchez, R.Rubio, G.Rauret; Int.J.Environ.Anal. Chem., **51**, 113-121 (1993).
- [24] D.K.Datta, V.Subramanian; Environ.Geol., **36**, 93-101 (1997).
- [25] L.Ramos, M.J.Gonzalez, L.M.Hernandez; Bull. Environ.Contam.Toxicol., **62**, 301-308 (1999).
- [26] S.J.Markich, P.L.Brown, R.A.Jeffrey, R.P.Lim;

## Current Research Paper

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- Aquat.Toxicol., **51**, 155-175 (2000).
- [27] H.P.van Leeuwen, J.P.Pinheiro; Pure Appl.Chem., **73(1)**, 39-44 (2001).
- [28] M.Mathew, R.Mohanraj, P.A.Azeez, S.Pattabi; Bull.Enviro.n.Contam.Toxicol., **70**, 800-808 (2003).
- [29] Y.Zhang, W.T.Frankenberger Jr; Int.J.Enviro.n.Anal.Chem., **83**, 315-326 (2003).
- [30] S.Meylan, N.Odzak, R.Behra, L.Sigg; Anal.Chim.Acta, **510**, 91-100 (2004).
- [31] [WWF] World Wide fund for Nature; Delhi Environmental Status report-an information handbook for citizen action, World Wide fund for Nature-India and Government of NCT, Delhi, 326 (1995).
- [32] K.M.M.Dakshini, J.K.Soni; Indian J.Enviro.n.Health, **21**, 354-360 (1979).
- [33] R.Sitasawad; Ph.D.dissertation, J.N.University, New Delhi, India (1984).
- [34] V.Subramanian, R.Sitasawad; Water Qual.Bull., **9**, 219 (1984).
- [35] R.M.Sharma, P.A.Azeez, P.S.Hameed, M.M.S.Hameed, S.Ravikumar, V.Masilamani; Eds. 'Proceedings of the National Seminar on Atomic Energy, Ecology and Environment', Journal Muhammad College, Bharathidasan University, India, 160-165, (2001).
- [36] M.Ajmal, M.A.Khan, A.A.Nomani; Environ.Monitor.Assess, **5**, 305-314 (1985).
- [37] M.Singh; Environ.Geol., **40**, 664-671 (2001).
- [38] D.P.Laxen, R.M.Harrison; Anal.Chem., **53**, 345-350 (1981).
- [39] P.Figura, B.McDuffie; Anal.Chem., **52**, 1433-1439 (1980).
- [40] V.K.Singh, K.P.Singh, D.Mohan; Environ. Monit. Assess., **105**, 43-67 (2005).
- [41] W.Stumm, H.Bilinski; in 'Proceedings of Sixth International Conference on Advances in Water Pollution Research', 1972 June 08-23, Jerusalem, 39-49 (1973).
- [42] M.S.Shuman, G.P.Woodward; Jr.Enviro.n.Sci. Technol., **11**, 809-813 (1977).
- [43] T.M.Florence, G.E.Batley; Talanta, **23**, 179-186 (1976).
- [44] W.Salomons, U.Forstner; Springer-Verlag, Berlin, 349 (1984).
- [45] T.Midorikawa, E.Tanoue; J.Oceanogr., **52**, 421-439 (1996).