Physico-chemical Studies of heavy metals as pollutants in river water of KHARKAI - SWARNREKHA river near Ghatshila - Jharkhand, India

Dr. Namrata Sinha, University Department of Chemistry, Ranchi University, Ranchi

ABSTRACT:

Heavy metals such as Iron, Chromium, Manganese, Cobalt, Nickle, Copper, Zinc, Cadmium and Lead were studied as pollutants in river. Wastewater discharge samples of rivers around steel and copper plants around Jamshedpur and Ghatshila were collected from April 2004 to October 2006. Atomic absorption, spectrophotometric analysis of non-filterable residue of sediments of the metals were made. The fractional analysis of the sediments was made in four phases, adsorbed and/or ion exchangeable, oxide coating, organic solids and crystalline. Along with total metal concentration, sum of concentration in each phase was determined. The concentration of metal available to biota have been estimated.

KEY WORDS:

Metal transport phases, surface sediments, pollutants, biota, Atomic Absorption Spectrophotometer (AAS) and self-purification

INTRODUCTION:

The chemical composition of the surface sediments and its variation at different sites in river receiving the treated and untreated waste water from domestic and industrial sources have a profound impact on the water quality of the river basin. Water chemistry only assesses the effluent impact at the time of sampling while the surface sediments geo-chemistry gives a cumulative assessment of pollution. Surface Sediments analysis has been used to trace pollutant inputs and to anticipate the affects of these pollutants on water quality.

In this work, the surface sediments from different sites on the rivers Swarnrekha and Kharkai around steel City of Jamshedpur and Industrial establishment of Hindustan Copper Corporation Limited at Moubhandar. Ghatshila were analysed for their multi element composition with a view to establish the relationship between the pollution of the rivers and the discharge of domestic ad industrial waste waters.

EXPERIMENTAL - SAMPLING SITES:

i) SWARNREKHA RIVER

Site III A	Waste Water discharge from copper plant at Ghatsila.
Site III B	River Water sample at Ghatsila.
Site II A	Discharge sample near Baridih.
Site II B	River water sample near Baridih.

ii) KHARKAI RIVER (NEAR ADITYAPUR)

Site I A	Discharge Sample.	Site I B	River water sample.

A) PARTITIONING OF WASTE WATER DISCHARGE SAMPLE:-

The sample was transferred into two 1L measuring flasks separately and then filtered through Whatman filter paper (NO - 42) separately. Filtrate in all the cases was rejected. The residues in the above two cases were collected separately and treated as follows.

RESIDUE – I :

The residue obtained after filtration of the waste water discharge sample along with the filter paper was treated with 20 ml Aqua regia and heated for 0.5 hour over water bath. It was then filtered through

Whatman filter Paper (NO - 42) and the volume was made up-to 500ML with distilled water in a volumetric flask. The metals determined in this filtrate were the total metal concentration in the sample.

RESIDUE – II :

The residue obtained after filtration of 1 L of waste water discharge sample along with the filter paper was leached with 50 ml 0.5N MgC12. 6H20 solution for 7 hr stirring from time to time and it was then filtered through Whatman filter paper (No. - 42). The filtrate was then made up to 500 ml with distilled water in a volumetric flask for the determination of adsorbed and / or ion exchangeable heavy metals (Eisenreich - 1980). The residue left over on the filter paper along with the filter paper itself was then leached with 0.4N sodium pyrophosphate solution for 10 hours stirring from time to time and then filtered. The filtrate was then made up to 500ml and heavy metals associated with organic solid were estimated from this filtrate. The residue along with the filter paper is treated with 50ml 0.3 N HC1 solution and heated at 90^0C for 0.5 hr. and then filtered. The filtrate was then made up to 500ml. Heavy metals in oxide coating were determined in the filtrate. The residue left on the filter paper along with the filter paper was then treated with 20ml Aqua regia and heated over water bath for 0.5 hr. It was then filtered and the volume of the filtrate Made upto 250m1. The metal determined in this last filtrate was designated metal in crystalline state.

B) <u>PARTITIONING OF RIVER WATER SAMPLE:</u>

Similar procedure was followed for the determination of total concentration heavy metals and concentration of heavy metals in different phases.

The samples obtained as above were analysed for estimation of heavy metals such as Fe, Mn, Cr, Ni, Co. Cu, Zn, Cd and Pb by Atomic Absorption spectrophotometer.

RESULTS AND DISCUSSIONS:-

Chemical Parameters for the Samples from Six Sites are given in the tables:-

Site – IIIA	→	Moubhandar, Ghatsila	River	→	Subarnarekha
Month	→	November	Year	→	2004
Sample	→	Discharge	pH	→	2.26

	Fe	Cr	Mn	Co	Ni	Cu	Zn	Cd	Pb
Total metal concentration (in mg/L)	71.00	0.077	0.14	0.068	2.18	-	0.31	-	0.053
Concentration of metal available to biota (in mg/L)	28.1295	0.069	0.105	0.0575	1.167	-	0.253	-	0.0525
Percentage of metal available to biota.	36.62%	89.60%	75.00%	84.56%	53.53%	-	81.6%	-	99.06%

Site – IIIB	→	Moubhandar, Ghatsila	River	→	Subarnarekha
Month	→	November	Year	→	2004
Sample	→	Discharge	pH	→	6.22

	Fe	Cr	Mn	Co	Ni	Cu	Zn	Cd	Pb
Total metal concentration (in mg/L)	10.905	-	0.135	0.19	0.32	0.257	0.467	-	0.055
Concentration of metal available to biota (in mg/L)	4.11	-	0.116	0.160	0.31	0.207	0.417	-	0.038
Percentage of metal available to biota.	37.69%	-	84.06%	84.21%	97.00%	80.54%	89.3%	-	69.10%

Site – IIA	→	Bardiha Housing Colony	River	→	Subarnarekha
Month	→	May	Year	→	2005
Sample	→	Discharge	pH	→	7.76

	Fe	Cr	Mn	Co	Ni	Cu	Zn	Cd	Pb
Total metal concentration (in mg/L)	17.825	0.605	0.329	0.021	0.0614	0.0565	0.824	-	-

Concentration of metal available to biota (in mg/L)	9.82	0.258	0.298	0.0195	0.0535	0.045	0.766	-	-
Percentage of metal available to biota.	55.10%	42.64%	90.60%	92.86%	87.13%	79.65%	92.96%	-	-

Site – IIB → IIB River → Swarnrekha
Month → May Year → 2005
Sample → River Water pH → 7.96

	Fe	Cr	Mn	Co	Ni	Cu	Zn	Cd	Pb
Total metal concentration (in mg/L)	12.935	0.060	0.231	-	0.070	0.022	0.29	-	-
Concentration of metal available to biota (in mg/L)	4.539	-	0.2135	-	0.0645	0.019	0.262	-	-
Percentage of metal available to biota.	35.1%	-	92.42%	-	92.14%	86.36%	90.34%	-	-

Site – I A → I A River → Kharkai
Month → June Year → 2006
Sample → Discharge pH → 8.32

	Fe	Cr	Mn	Co	Ni	Cu	Zn	Cd	Pb
Total metal concentration (in mg/L)	2.62	-	0.164	0.238	0.056	0.086	0.24	-	-
Concentration of metal available to biota (in mg/L)	1.2305	-	0.149	0.226	0.0385	0.07	0.206	-	-
Percentage of metal available to biota.	47.00%	-	90.85%	94.96%	68.75%	81.40%	85.83%	-	-

Site → I B River → Kharkai
Month → June Year → 2006
Sample → River Water pH → 8.44

	Fe	Cr	Mn	Co	Ni	Cu	Zn	Cd	Pb
Total metal concentration (in mg/L)	1.862	-	0.126	0.045	0.145	0.045	0.154	-	0.031
Concentration of metal available to biota (in mg/L)	0.6985	-	0.099	0.0425	0.073	0.0315	0.1155	-	0.030
Percentage of metal	37.51%	-	78.60%	94.44%	50.34%	70.00%	75.00%	-	96.77%

available to biota.									

Among the heavy metals, iron occurs in much higher concentration. Site - IIB (Swarnrekha river water at Baridih site) and site - IIIB (Subarnarekha River water at Moubhandar, Ghatsila) have higher values of total iron. Site - IB (Kharkai River Water near Adityapur) has relatively lower value of total iron content. Sites - IB and IIB are near the waste water discharge from the industrial establishments in Jamshedpur, the Steel City. Site - IIIB is about 1 Km downstream from the waste water discharge from Ghatsila copper plant. Sites-IIB and IIIB samples have high iron content. Reddish brown suspensions were usually found at Sites IIB and IIIB which might be due to the formation of Fe (OH)3, formed by the acidic waste water mixing the natural river water having bicarbonate alkalinity. The dissolved or ferrous iron can also be oxidized into insoluble ferric compounds (mostly ferric oxide) as the effluents are oxygenated and neutralized by river water. This type of condition was also found by Brush, Kalinowski and Miller (reference No. - 11) in their work. In this work, The total iron content as determined by Atomic Absorption Spectrophotometer in river water samples varies from 1.862 mg/L to 12.935 mg/L and in discharge samples, varies from 2.62 mg/L to 71 mg/L. According to environmental pollution norms the general standard of iron concentration for discharge as environmental pollutant is 3 mg/L. According to WHO standard permissive value of Fe for drinking water is 0.3 ppm and 1 ppm is excessive.

Total chromium metal content as determined by Atomic Absorption Spectrophotometer was in the range from 0.077 mg/L to 0.605 mg/L in the discharge sample. In the river water sample chromium was found at Baridih site only and the concentration was 0.060 mg/L in the crystalline state. Chromium (VI) is the most toxic one. Waste water from different industries involving steel manufacture, chrome plating etc., is rich in Chromium content. Chromium enters into the water bodies in the form of chromate from cooling towers. CrO_4^{2}- solution is used in passivating the steel surface through the formation of a protective coating. The stable oxidation states of chromium are +3 and +6. Cr (III) can exist as $Cr(OH)_2^+$, $Cr(OH)_2^+$, $Cr(OH)_3$, $Cr(OH)_4$- depending on the P_H. In aquatic environment, MnO_2 present in the sediment can oxidise Cr (Ill) to Cr (VI). Normal level of Cr (IV) in drinking water is 3 to 40 ppb. The normal permissible limit being 5Oppb.

Total manganese content in the river water samples as determined by Atomic Absorption Spectrophotometer were in the range from 0.126 mg/L to 0.231 mg/L. In the waste water discharge samples, total manganese content varies from 0.14 mg/L to 0.329 mg/L. Manganese frequently encounters in iron bearing water, although it is present usually to a much lesser extent than iron. According to WHO standard permissive value of Mn for drinking water is 0.1 ppm and 0.5 ppm is excessive.

Total cobalt (Co) concentration in river water samples varies from 0.045 mg/L to 0.19 mg/L with sites IB and IIIB as determined by Atomic Absorption Spectrophotometer. Site IIIB has higher total cobalt content. At site IIB (Subarnarekha river water, Baridih Site), the cobalt concentration was almost Nil. In discharge samples total Cobalt ion concentration varies from 0.021 to 0.238 mg/L.

The total nickel (Ni) content in river water samples as determined by Atomic Absorption Spectrophotometer was in the range from 0.070 mg/L to 0.32 mg/L. In the discharge samples Ni ion concentrations varies from 0.056 mg/L to 2.18 mg/L. The general standard of Ni for discharge as pollutant (inland surface water) is 3.0 mg/L.

In river water sample the total copper concentration as determined by Atomic Absorption Spectrophotometer varies from 0.022 mg/L to 0.257 mg/L. In the discharge sample, total copper concentration varies from 0.0565 mg/L to 0.086 mg/L. The values of Cu^{++} ions are due to suspended solids, (M.J. Stiff-reference No. - 13). M. J. Stiff has shown that copper may be present in polluted surface fresh waters, both associated with suspended solid and in different soluble chemical states. An analytical scheme was devised by him to differentiate quantitatively these soluble forms of copper. Analytical results showed that much of copper present in the river waters is associated with suspended solid and that soluble copper consists almost entirely of complexed forms. Site IIIB has highest copper content. According to WHO standard permissible value of copper in drinking water is 1. mg/L and 1.5 mg/L is excessive.

Aquatic environments are very sensitive to the presence of many trace elements. It has been shown that the growth rate of algae is affected by the presence of free Cu++ concentrations as low as 10^{-10} to 10^{-12M}. The presence of copper in the samples is a definite indication of its effect on aquatic environment in these rivers. The site IIIB water samples have low pH value. This low pH value of the site IIIB water sample is an indication to the absence of control on the treatment of waste water in the industrial establishment. Therefore urgent attention of the authorities is required for the treatment of the waste water.

The discharge of the metal ions like Cu^{++} at this pH (2.26) at site IIIA must have affected the aquatic environment of Subarnarekha to a very large extent rendering the water even unfit for agricultural purposes.

Total zinc concentration as determined by AAS varies from 0.24 mg/L to 0.824 mg/L in the discharge sample and in river water sample varies from 0.154 mg/L to 0.467mg/L. According to WHO standard permissive value for drinking water is 5 ppm and 15 ppm is excessive. Hence the values of zinc concentration in river water samples lie below the permissive value for this purpose, but the effect of the concentration of zinc to fishes and algae growth should be evaded. Zinc is very toxic to fish. According to Schott (reference no. 12), owing to an increase in the free CO_2 concentration of water supply to fish tanks containing trout, sufficient zinc was dissolved from newly galvanised pipes to give a zinc concentration of 0.15 ppm, which proved fatal to the fishes. A number of cases of mortality among fishes caused by the presence of zinc in solution have also been found by him.

Both in water and in aquatic floating plants, the trace element decreases in the order of Fe, Mn, Zn, Cu........., but in submerged and free floating plants, the order is Mn, Fe, Zn, Cu............. Free floating plants accumulate high trace elements, but after their short life cycle, the trace elements return to the water and also accumulate partially in bottom sediments, where they serve as source of secondary pollution of the reservoirs. The Mn and Cu uptake by aquatic plants play the main role in decreasing the pollution of water and sediments with these trace elements. Fe and Zn are removed both by their biogenic accumulation by the plants and by physio-chemical factor of Fe precipitation as Fe-hydroxide and Zn-Sorption on fine particles suspended in water (reference no. 4).

Lead metal concentration was determined by Atomic Absorption Spectrophotometer. Lead was found to be almost nil at sites IA, IIA and IIB but found at the sites IB, IIIA and IIIB. The total lead metal concentration in river water samples varies from 0.031 mg/L to 0.055 mg/L. Total lead content in the discharge sample of site IIIA was 0.053 mg/L.

In fresh water, $PbCO_3$ and $Pb(CO3)_2^{2}$- are the major species. Carbonates increase with increase in pH between "6 — 8"; at higher pH the hydroxy species dominate. Lead carbonates (and basic carbonates) are found in sediments in rivers and lakes. In the water bodies, the soluble Pb-compounds are gradually converted into insoluble PbS in part. Lead compounds are also sorbed by iron-manganese oxides.

CONCLUSION: These data about the occurrence of Fe, Cr, Mn, Co, Ni, Cu, Zn and Pb in the various available and unavailable metal phases would help in determining the effect of these metals on the crops and other biota. The higher concentration of the heavy metals in water also prevents the self purification of water and produces adverse effect on aquatic lives. During the evolution process, life did not meet these toxic elements and this is why it did not evolve any efficient mechanism to cope with these elements. Consequently, the tolerance limit given by the threshold value for a toxic element is generally very low and toxicity, i.e. deleterious effect, starts even for a minuscule concentration. However, it needs further study on the co-relation of the concentration of these metals in the various phases and their toxicological and other effects.

REFERENCES

[1] Goel, P. K, Water Pollution – Causes, Effects and Control, New age Int. (P) Ltd. , New Delhi. (2000).

[2] Brown, E., Skougstad, M.W. and Fishman, M. J., Method for Collection and Analysis of Water Sample for Dissolved Minerals and Gases, US Department of Interior, Book No. 5(1974),

[3] APHA:, Standard Methods for Examination of Water and Waste Water,19th edn., American Public Health Association, Washington, D.C(1995),.

[4] Weber, W. J. Jr. and Stun, W.:, 'Mechanism of hydrogen ion buffering in natural waters', J. American Water Works Association. 55 , 1553–1555, (1963).

[5] Saha, T. K. and Bose, S. K.:, 'Observations on diurnal variations in Hydrobiological factors at Hazaribagh lake, Jharkhand' in: Proceedings of 74th Indian Science Congress, Part – III, Abstract, paper 39, 1987.

[6] Abdul Jameel, A.:, 'Evaluation of drinking water quality in Tiruchirappalli, Tamil Nadu', Indian J. Env. Hlth. 44(2), (2002), pp108–112.

[7] Azeez, P. A., Nadarajan, N. R. and Mittal, D. D.:, 'The impact of monsoonal wetland on ground water chemistry', Poll. Res. 19(2), (2000),pp 249–255.

[8] Shyamala, R., Shanthi, M. and Lalitha, P., Physicochemical analysis of bore well water samples of Telungupalayam area in Coimbatore District, Tamilnadu, India. E-Journal of chemistry, Vol.5, No.4, (2008), pp.924-929.

[9] Tiwari, D. R.:, 'Physico-chemical studies of the Upper lake water, Bhopal, Madhya Pradesh, India', Poll. Res. 18(3), (1999), pp323–326.

[10] Pradeep Jain, K.:, 'Hydrogeology and quality of ground water around Hirapur, District Sagar (M.P.)', Poll. Res. 17(1), (1998), pp91–94.

[11] Srinivas, C. H., Ravi Shankar Piska, Venkatesan, C., Sathya Narayan Rao, M.S. and Ravinder Reddy, R.: , 'Studies on ground water quality of Hyderabad', Poll. Res. 19(2), (2000), pp 285–289.

[12] Harilal, C.C., Hashim, A., Arun, P.R. and Baji, S., J Ecology Environ Conservation, 10(2), (2004), pp187-192.

[13] Bhanja, K. Mohanta and Ajoy KU Patra: , 'Studies on the water quality index of river Sanamachhakandana at Keonjhar Garh, Orissa, India', Poll. Res. 19(3), (2000), pp377–385.

[14] Thomson Jacob, C., Azariah, J. and Viji Roy, A. G.:, 'Impact of textile industries on river Noyyal and riverine ground water quality of Tirupur, India', Poll. Res. 18(4), (1999), pp 359–368.

[15] Trivedy, R.K. and Goel, P.K, Chemical and biological methods for water pollution studies. Environmental Publication, karad(1986).

[16] National Seminar on (Man and the Environment pollution ,January 29 -30 1979.

[17] Chattopadhyaya, R.M.Studies in river sediment around Jamshedpur' Ph.D Thesis, R.U. Ranchi , Bihar, India (1985)

[18] Reddy. M.M.Environment international, Vol. - 2 (1979)

[19] Vanderwerff, M.and M. J. Pruyt Chemosphere, eng., 11 (8) 727 - 739 (1982)

[20] Moraitou - Apostolopoulour, M., and G. verriopoulos. Hydrobiology, eng. 11(8), 727 -39 (1982)

[21] K lein, 1. River Pollution 2 - causes and effects, 151 - 152 (1967)

[22] Ingots, R.S.Sewage industrial wastes, 26-33 (1955)

[23] Khangarot, B.S. Acta hydrochem hydrobiology Eng., 10(4), 401- 4 (1982)

[24]Brush, E.E.J., M.Kalinowski and T. Miller Proceedings of The Pennsylvania Academy of sciences; 53,179,188 (1979)

[25] Schott, W. Dtsch. Labensmitt Rdsch, 48,62-63 (1952)

[26] Stiff, M.J.,Water res, 5(8), 585 - 599 (1971)

[27] Kadukin, A.I., V.V. Krasintseva, G.I. Romanova and L.V.Tarasonko.Gidribiol Zh, 18(1), 79 - 82 (1982)

[28] Nakhshina, F.P., L.A. Malinoveskaya and G.I. Strokatenko Gidribiol Zh, 18(1), 106 - 9 (1982)

[29] Roy, N.N. and P.Narayan. Upadhyaya Toxilogical and Environmental Chemsitry (1985) (Vol -10) p.p . 285 - 298.

[30] Eisenreich , S.J., M.R. Hoffman, D. Rastetter, E. Yost and W.J.Maier, Particulates in water, Adv.in. Chem.Ser., 189, 135-176 (1980)

[31] Stummn, W. and J.J. Morgan Aquatic chemistry (John Wiley and Sons, New York, 1981) 2nd edition, chapter.6, pp 378, 385 -386.

[32] Mishra , H.S. Studies in metals transport phases in rivers around Jamshedpur, Ph.D. thesis, R.U. Ranchi 1988.

[33] Vogel, Al. A text book of quantitative Inorganic Analusis. ELBS Edition'of fourth edition 1978, Longman group. (U.K.)Ltd pp-743-744-738-739,739-740,746,747-748,161,155- 156.

[34] APHA, 1967 Standard methods for examination of water and waste water (12th edn; Part - I)American Public health Association, New York,pp 317 -320

[35] Subramaniam,V., Van Grieken and L. Van't Dack, 1987 Env. Geol. water Sci 9 (2); 93 -103