Assessment of heavy metal pollution in surface water

[1]D. Kar; [1]P. Sur; [1]S. K. Mandal; [2]T. Saha; [2]*R. K. Kole

[1]*Department of Agricultural Chemistry and Soil Science Faculty of Agriculture, Bidhan Chandra Krishi Viswavidyalaya, Kalyani-741235, West Bengal, India*

[2]*Department of Agricultural Chemicals, Faculty of Agriculture, Bidhan Chandra Krishi Viswavidyalaya, Kalyani-741235, West Bengal, India*

ABSTRACT: A total of 96 surface water samples collected from river Ganga in West Bengal during 2004-05 was analyzed for pH, EC, Fe, Mn, Zn, Cu, Cd, Cr, Pb and Ni. The pH was found in the alkaline range (7.21-8.32), while conductance was obtained in the range of 0.225-0.615 mmhos/cm. Fe, Mn, Zn, Ni, Cr and Pb were detected in more than 92% of the samples in the range of 0.025-5.49, 0.025-2.72, 0.012-0.370, 0.012-0.375, 0.001-0.044 and 0.001-0.250 mg/L, respectively, whereas Cd and Cu were detected only in 20 and 36 samples (0.001-0.003 and 0.003-0.032 mg/L). Overall seasonal variation was significant for Fe, Mn, Cd and Cr. The maximum mean concentration of Fe (1.520 mg/L) was observed in summer, Mn (0.423 mg/L) in monsoon but Cd (0.003 mg/L) and Cr (0.020 mg/L) exhibited their maximum during the winter season. Fe, Mn and Cd concentration also varied with the change of sampling locations. The highest mean concentrations (mg/L) of Fe (1.485), Zn (0.085) and Cu (0.006) were observed at Palta, those for Mn (0.420) and Ni (0.054) at Berhampore, whereas the maximum of Pb (0.024 mg/L) and Cr (0.018 mg/L) was obtained at the downstream station, Uluberia. All in all, the dominance of various heavy metals in the surface water of the river Ganga followed the sequence: Fe > Mn > Ni > Cr > Pb > Zn > Cu > Cd. A significant positive correlation was exhibited for conductivity with Cd and Cr of water but Mn exhibited a negative correlation with conductivity.

Key words: *River Ganga, spatial and temporal changes, heavy metal, water quality*

INTRODUCTION

Ganga, the most sacred and important river of India, is regarded as the cradle of Indian civilization. About 2506 km of the river stream gives life to twenty-nine cities, seven towns and thousands of villages which are contaminating the river by over 1.3 billion L waste water per day (Khan, *et al.*, 1998). Among the inorganic contaminants of the river water, heavy metals are getting importance for their non-degradable nature and often accumulate through tropic level causing a deleterious biological effect (Jain, 1978). Anthropogenic activities like mining, ultimate disposal of treated and untreated waste effluents containing toxic metals as well as metal chelates (Amman, *et al.*, 2002) from different industries, e.g. tannery, steel plants, battery industries, thermal power plants etc. and also the indiscriminate use of heavy metal containing fertilizers and pesticides in agriculture resulted in deterioration of water quality rendering serious environmental problems posing threat on human

beings (Lantzy and Mackenzie, 1979; Nriagu, 1979; Ross, 1994) and sustaining aquatic biodiversity (Ghosh and Vass, 1997; Das, *et al.*, 1997). Though some of the metals like Cu, Fe, Mn, Ni and Zn are essential as micronutrients for life processes in plants and microorganisms, while many other metals like Cd, Cr and Pb have no known physiological activity, but they are proved detrimental beyond a certain limit (Marschner, 1995; Bruins, *et al.*, 2000), which is very much narrow for some elements like Cd (0.01 mg/L), Pb (0.10 mg/L) (ISI, 1982) and Cu (0.050 mg/L). The deadlier diseases like edema of eyelids, tumor, congestion of nasal mucous membranes and pharynx, stuffiness of the head and gastrointestinal, muscular, reproductive, neurological and genetic malfunctions caused by some of these heavy metals have been documented (Johnson, 1998; Tsuji and Karagatzides, 2001; Abbasi, *et al.,* 1998). Therefore, monitoring these metals is important for safety assessment of the environment and human health in particular. Regrading this background, this survey monitored the surface water

✉ *Corresponding Author Email: dipankarkar@gmail.com*
Tel./Fax: +91 33 2580 9767

D. Kar, et al.

in the Bhagirathi-Hooghly stretch of the river Ganga in west Bengal, India, considering the spatial and temporal variations in heavy metal content and also to evaluate the status of the river water quality with respect to drinking and agricultural irrigation purposes.

MATERIALS AND METHODS

Water samples were collected once in every month during April 2004 to March 2005 from two sites (middle of the river stretch and a discharge point) at four monitoring stations viz. Berhampore (BH), Palta (PA), Dakshineswar (DK) and Uluberia (UL) on the river Ganga, a 300 km stretch known as Bhagirathi-Hooghly in West Bengal, India (Fig .1). The samples were collected from a depth of 1ft below the surface using Nansen type water sampler and kept in polythene containers (500 mL) with the addition of 2 mL concentrated HNO_3 at 2 mL in order to preserve the metals and also to avoid precipitation. The pH of water samples was determined using pH-meter with electronic glass electrode (LI 127 of Elico, India) and conductivity was measured by conductivity-meter (Systronics 304). For the analysis of total heavy metals (dissolved and suspended), water (200 mL) samples were digested with 5 mL of di-acid mixture (HNO_3: $HClO_4$ :: 9: 4 ratio) on a hot plate and filtered by Whatman No. 42 filter paper and made up the volume to 50 mL by double distilled

water for analysis of eight heavy metals viz. Fe, Cu, Mn, Zn, Pb, Cd, Cr and Ni using atomic absorption spectrophotometer (GBC-902, Australia) (APHA, 1995). The obtained data were subject to statistical analysis to test the analysis of variance (ANOVA) and correlation among all the parameters using SPSS statistical package.

RESULTS AND DISCUSSION

The river water samples exhibited an alkaline pH in the range of 7.21 to 8.32 with an overall mean of 7.80. Seasonal mean values of pH varied from 7.7 in monsoon to 7.9 during summer and winter (Table 1). The lowest pH value was always observed in monsoon at all the four locations which may be due to the dilution effect of rain water (John, 1991). No significant difference was noted in the observed pH during the summer and winter and the variation in pH due to change in sampling location was also insignificant (Table 1). The observed values, however, were well within the safe limit for drinking (WHO, 1973) as well as for crop production (FAO, 1975). Similar trend was also observed in case of conductivity. The values of conductivity ranged from 0.225 to 0.615 with an overall mean of 0.395 mmhos/cm. Table 1 shows the mean seasonal values of conductivity in the range of 0.330 to 0.460 mmhos/cm and the mean locationwise values within 0.376 to 0.407 mmhos/cm.
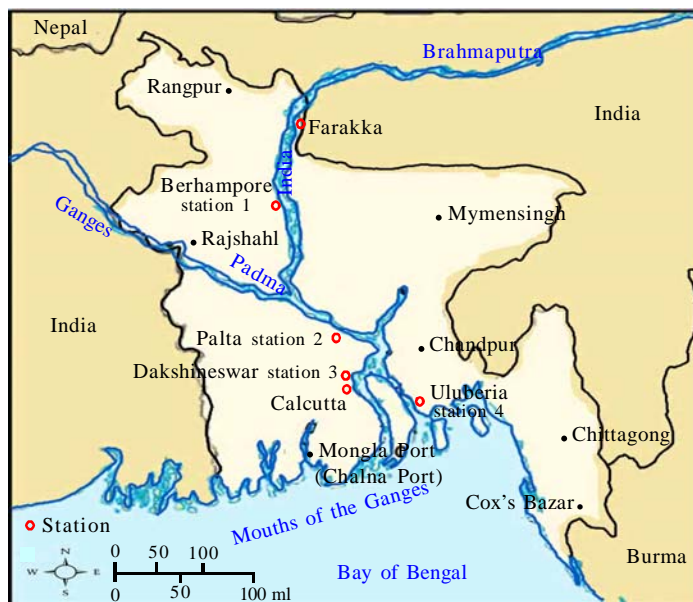

Fig. 1: Locations of the monitoring stations on river Ganga (Bhagirathi-Hooghly stretch) in West Bengal

120

Regarding the highest conductivity at Uluberia, the downstream station may be due to the inundation of sea water from Bay of Bengal during the tidal time (Gupta and Gupta, 1999). The lowest conductivity in monsoon may be due to the dilution effect of rain water. However, the locationwise change in conductivity was statistically insignificant. All the 96 surface water samples of the river Ganga were analyzed for Fe, Mn, Zn, Cu, Cd, Cr, Pb and Ni. The presence of four essential micronutrients viz. Fe, Mn, Zn and Cu was detected in 95, 93, 95 and 36 samples with concentrations within the ranges of 0.025-5.490, 0.025-2.720, 0.012-0.370, 0.003-0.032 mg/L with an overall mean of 1.052, 0.266, 0.716 and 0.005 mg/L, respectively (Table 2). Besides, the presence of four toxic heavy metals viz. Pb, Cd, Cr and Ni were detected in 93, 20, 93 and 93 samples in the range of 0.001-0.250, 0.001-0.003, 0.001-0.044 and 0.012-0.375 mg/L with an overall mean of 0.140, 0.002, 0.170 and 0.450 mg/L, respectively. The seasonal average concentrations of various heavy metals viz. Fe, Mn, Zn, Cu, Pb, Cd, Cr and Ni at four locations in the surface water of the river Ganga were observed in the range of 0.353-2.345, 0.085-0.712, 0.042-0.111, 0.003-0.008, 0.005-0.097, 0.001-0.003, 0.010-0.022 and 0.035-0.084 mg/L, respectively (Table 2). Except for Fe and Mn, the concentrations of other metals in the Ganga water were lower than the observed metal concentrations of the river Bhadra at Karnataka and of the river Purna (Shah, *et al.,* 2005). The mean concentrations of the metals were observed in the order: Fe > Mn > Ni > Cr > Pb > Zn > Cu > Cd. Similar result was also observed by Khan, *et al.,* (1998) in Ganga-Brahamputra-Meghna Estuary. The mean concentrations of Fe, Mn, Zn, Cu, Cd, Cr, Ni and Pb in the surface water at four locations varied from 0.586-1.485, 0.150-0.420, 0.055-0.085, 0.004-0.006, 0.001-0.002, 0.016-0.018, 0.034-0.054 and 0.008-0.024 mg/L (Table III). Out of these four experimental stations, the highest mean concentrations of Fe (1.485 mg/L), Zn (0.085 mg/L) and Cu (0.006 mg/L) were observed at Palta where as Mn (0.42 mg/L) and Ni (0.054 mg/L) were maximum at Berhampore and Cr (0.018 mg/L) at both Dakshineswar and Uluberia and Pb (0.024 mg/L) at Uluberia. The highest concentrations of most of the heavy metals (Fe, Zn and Cu) at Palta may be due to the discharge of heavy metal loaded industrial waste water (Shah, *et al.,* 2005). The spatial changes in the concentrations of Zn, Cu, Cr, Ni and Pb, however, were not statistically significant. Throughout the year, the mean concentrations of Fe, Mn, Zn, Cu, Cd, Cr, Ni and Pb in the surface water of the river Ganga in three different seasons varied from 0.76-1.52, 0.132-0.423, 0.063-0.084, 0.005-0.006, 0.001-0.003, 0.014-0.020, 0.030-0.060 and 0.007-0.020 mg/L, respectively (Figs. 2 and 3). Similar trends of results were also observed by Haque, *et al.,* (2005) in the surface water of the river Ganga at Sundarban estuary. The highest concentrations of Cu, Cd, Cr, Ni and Pb (Fig. 2) were observed in winter, while those of Mn and Zn were observed in monsoon (Fig. 3) which may be due to a sudden rainfall followed by high river discharge from upstream environment (Khan, *et al.,* 1998). But the maximum for Fe was observed in summer (Fig. 3). Among the eight heavy metals, significant seasonal change was noted in the concentrations of Fe, Mn, Cd and Cr, whereas in case of Zn, Cu, Ni and Pb, the seasonal change was not significant. The correlation among the physico-chemical properties (pH and conductivity) of water and different heavy metal concentrations were also studied and the results are presented in Table 4. There was no significant correlation observed in the changes of heavy metal concentrations with the pH of water. But Cd and Cr exhibited a significant positive correlation with conductivity, while Mn indicated a negative correlation with conductivity (Table 4).

Table 1: Changes in pH and conductance of surface water of the river Ganga in west Bengal

Parameters	Season	Mean value of the parameters				Average	
		BH	PA	DK	UL		
pH	Summer	7.83	7.91	7.85	7.93	7.88	
	Monsoon	7.63	7.72	7.71	7.59	7.66	SEM = 0.039; CD = 0.110
	Winter	7.97	7.75	7.90	7.84	7.87	
	Average	7.80	7.79	7.80	7.79	7.80	
	SEM = 0.045; CD = 0.127						
EC (mmhos/cm)	Summer	0.382	0.394	0.401	0.426	0.401	
	Monsoon	0.313	0.341	0.338	0.319	0.330	SEM = 0.014; CD = 0.039
	Winter	0.431	0.457	0.467	0.477	0.460	
	Average	0.376	0.398	0.402	0.407	0.395	
	SEM = 0.017; CD = 0.048						

121

Table 2: Average concentrations of heavy metals in surface water of the river Ganga

Metal	Season	Average concentration of metals (mg/L) at			
		BH	PA	DK	UL
	Winter	0.651	1.234	0.792	0.353
Fe	Summer	1.744	2.345	1.413	1.584
	Monsoon	0.365	0.884	1.120	1.155
	Winter	0.181	0.123	0.085	0.152
Mn	Summer	0.369	0.251	0.177	0.172
	Monsoon	0.712	0.417	0.436	0.139
	Winter	0.085	0.068	0.042	0.084
Zn	Summer	0.065	0.084	0.053	0.082
	Monsoon	0.095	0.111	0.083	0.058
	Winter	0.007	0.006	0.007	0.004
Cu	Summer	0.003	0.004	0.008	0.006
	Monsoon	0.004	0.007	0.004	0.003
	Winter	0.002	0.003	0.002	0.003
Cd	Summer	0.001	0.001	0.003	0.002
	Monsoon	0.001	ND	ND	ND
	Winter	0.084	0.042	0.035	0.083
Ni	Summer	0.041	0.035	0.044	0.034
	Monsoon	0.045	0.053	0.038	0.035
	Winter	0.021	0.005	0.005	0.052
Pb	Summer	0.008	0.006	0.097	0.003
	Monsoon	0.014	0.015	0.009	0.017
	Winter	0.018	0.021	0.022	0.024
Cr	Summer	0.010	0.013	0.017	0.018
	Monsoon	0.017	0.014	0.016	0.013

ND: not detected

Table 3: Spatial changes in heavy metal content in the surface water of the river Ganga

Locations	Heavy metal concentration in water (mg/L)							
	Fe	Mn	Zn	Cu	Cd	Cr	Ni	Pb
BH	0.586	0.420	0.075	0.005	0.001	0.016	0.054	0.014
PA	1.485	0.260	0.085	0.006	0.001	0.017	0.041	0.009
DK	1.110	0.023	0.055	0.006	0.002	0.018	0.034	0.008
UL	1.030	0.150	0.071	0.004	0.002	0.018	0.049	0.024
SEM	0.231	0.081	0.014	0.002	0.000	0.002	0.011	0.006
CD	0.651	0.228	0.039	0.006	0.000	0.006	0.031	0.017

Table 4: Correlation of different heavy metals, pH and EC of the surface water of the river Ganga

	pH	EC	Fe	Mn	Zn	Cu	Cd	Cr	Ni	Pb
pH	1.00									
EC	0.18	1.00								
Fe	-0.06	-0.11	1.00							
Mn	-0.19	-0.30[*]	0.01	1.00						
Zn	-0.01	0.01	-0.15	0.09	1.00					
Cu	-0.13	-0.02	0.05	-0.02	0.09	1.00				
Cd	0.16	0.43[*]	-0.07	-0.17	-0.01	0.18	1.00			
Cr	0.09	0.34[*]	-0.23[*]	-0.04	0.13	0.01	0.25	1.00		
Ni	0.01	-0.06	-0.08	0.26[*]	0.29[*]	-0.07	-0.06	0.17	1.00	
Pb	0.06	0.04	-0.12	0.07	-0.05	0.07	-0.1	0.12	0.12	1.00

Indicates correlation is significant at the 0.05 level (2-tailed)

Among the heavy metals themselves, a significant negative correlation was observed between Fe and Cr, whereas Ni exhibited a significant positive correlation with Mn and Zn. This will help to understand the nature of these metals and their species speciation in the aquatic environment.

The concentrations of Zn, Cu, Cd and Cr were within the safe limit for both drinking as well as for crop production but the concentrations of Fe, Mn, Pb and Ni exceeded the BIS, (1991) standard for drinking (0.3 mg/L for Fe, 0.1 mg/L for Mn, 0.05 mg/L for Cu and Pb, 0.01 mg/L for Cd) in 79, 67, 24 and 84% of the analyzed samples, respectively (Fig. 4). Whereas, only the concentration of Mn exceeded the safe limit for crop production (5.0 mg/L for Fe, 0.2 mg/L for Mn, 0.2 mg/L for Cu, 5.0 mg/L for Pb and 0.01 mg/L for Cd ; FAO, 1975) in 29% of the total samples (Fig. 4).

The river water exhibited a slightly alkaline pH and the conductivity apparently increased along the downstream due to the tidal effect of Bay of Bengal. The observed pH of the river water was well within the safe limit for drinking (WHO, 1973) as well as for crop production (FAO, 1975). Although conductivity increased towards the downstream of the river attributable to the tidal effect of Bay of Bengal (Gupta and Gupta, 1999) the change was not significant. The lowest conductivity in monsoon may be due to the dilution effect of rain water. The relative dominance of the heavy metals in water was observed in the following sequence: Fe > Mn > Ni > Cr > Pb > Zn > Cu > Cd. The highest concentrations of most of the heavy metals (Fe, Zn and Cu) at Palta may be due to the discharge of heavy metal loaded industrial waste water (Shah, *et al.*, 2005). There was no significant correlation observed in the changes of heavy metal concentrations with the pH of water. But Cd and Cr exhibited a significant positive correlation with conductivity, while Mn indicated a negative correlation with conductivity. Considering the status of heavy metal concentrations in water, it may be concluded that the river water as such is not suitable for drinking purpose due to the excess concentrations of Fe, Mn, Pb and Ni and it may not be suitable for irrigation due to the excess concentration of Mn. The excess heavy metal load of river water can be attributed to the discharge of industrial effluents and municipal wastes, geology of river bed and catchment area. Though some of the detected heavy metals are beneficial for human and
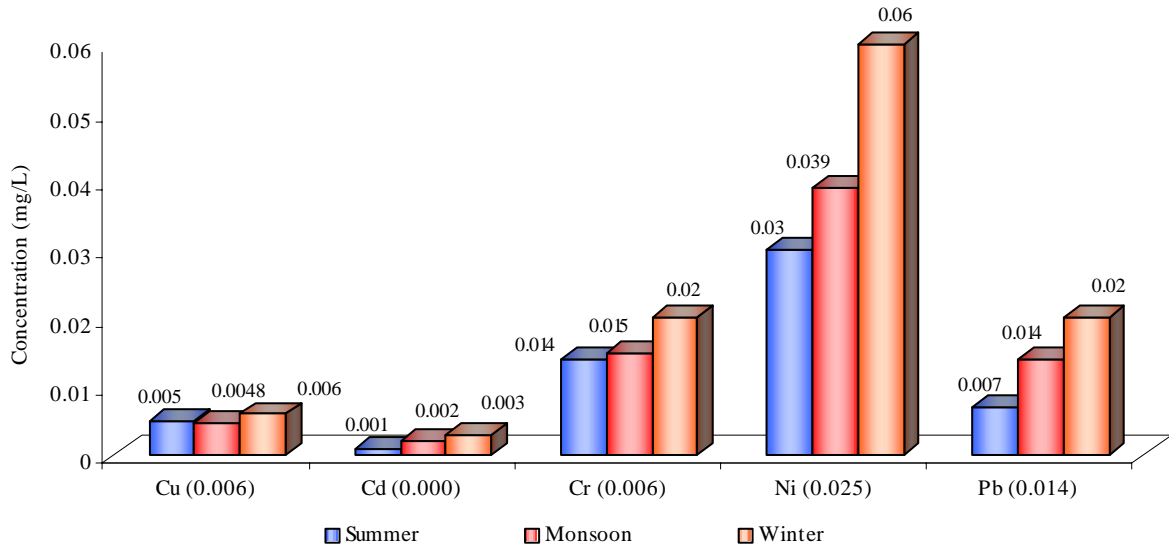
Fig. 2: Seasonal variation in the concentrations of Cu, Cd, Cr, Ni and Pb (values in the parentheses indicate the corresponding CD value)
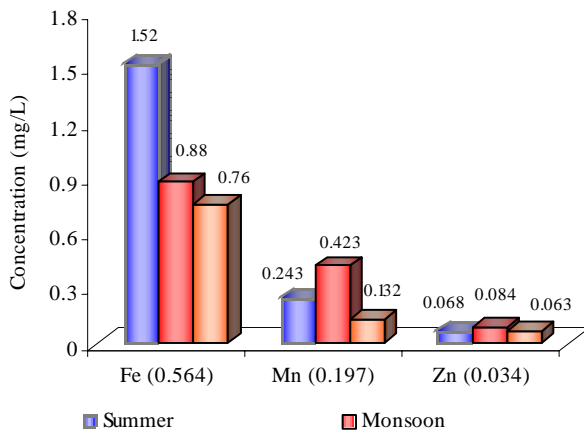
Fig. 3: Seasonal variation in the concentrations of Fe, Mn and Zn (values in the parentheses indicate the corresponding CD value)
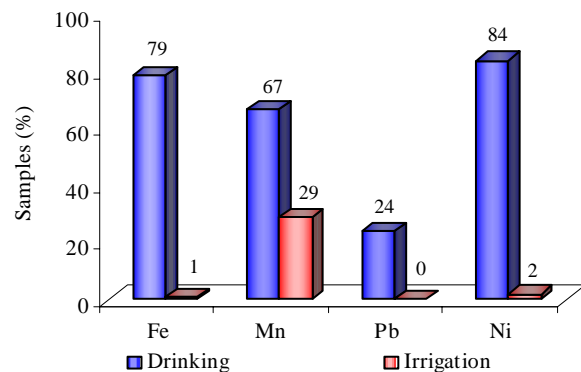
Fig. 4: Percentage of samples not suitable for drinking and crop production

plants up to a certain limit, it may be harmful beyond that. Adoption of adequate measures to remove the heavy metal load from the industrial waste water and renovation of sewage treatment plants are suggested to avoid further deterioration of the river water quality.

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AUTHOR (S) BIOSKETCHES
Kar, D., M.Sc., Ph.D. Research student, Department of Agricultural Chemistry & Soil Science, Faculty of Agriculture, Bidhan Chandra Krishi Viswavidyalaya, Kalyani-741235, West Bengal, India.
Email: *dipankarkar@gmail.com*

Sur, P., M.Sc., Ph.D. Rresearch student, Department of Agricultural Chemistry & Soil Science, Faculty of Agriculture, Bidhan Chandra Krishi Viswavidyalaya, Kalyani-741235, West Bengal, India.
Email: *pintu_soil@yahoo.com*

Mandal, S. K., M.Sc., Ph.D. Research associate, Department of Agricultural Chemistry & Soil Science, Faculty of Agriculture, Bidhan Chandra Krishi Viswavidyalaya, Kalyani-741235, West Bengal, India.
Email: *santanukumarmandal@rediffmail.com*

Saha, T., M.Sc., Ph.D. Research associate, Department of Agricultural Chemicals, Faculty of Agriculture, Bidhan Chandra Krishi Viswavidyalaya, Kalyani-741235, West Bengal, India. Email: *t.saha@rediffmail.com*

Kole, R. K., M.Sc., Ph.D. Reader, Department of Agricultural Chemicals, Faculty of Agriculture, Bidhan Chandra Krishi Viswavidyalaya, Kalyani-741235, West Bengal, India. Email: *rkkole@yahoo.com*