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Seasonal variation of heavy metals in Subarnarekha River at Jamshedpur, East Singhbhum, Jharkhand

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Abstract : The present investigation is aimed at assessing the amount of heavy metals and current water quality standard along the Subarnarekha river in Jharkhand. Three samples were collected along the stretches of Subarnarekha basin during the period : Jan-Dec, 2015, on the first week of every month. The concentrations Cu, Pb, Ni, Zn, Cr, Co, Sr, Cd and Fe were determined using inductively coupled plasma mass spectrometry for seasonal fluctuation, source apportionment and heavy metal pollution indexing. The results demonstrated that concentrations of the metals showed significant seasonality. To assess the composite influence of all the considered metals on the overall quality of the water, heavy metal pollution indices were calculated. The deterioration of water quality and enhanced concentrations of certain metals in the Subarnarekha River near industrial and mining establishments may be attributed to anthropogenic contribution from the industrial and mining activities of the area. Various physicochemical parameters like pH, TDS, EC, DO, BOD, Total Hardness, Total alkalinity sodium, potassium, calcium, magnesium etc. were also analysed. Eight parameters namely pH, Dissolved Oxygen, Biochemical Oxygen Demand, Nitrate, Phosphate, Total Dissolved Solids and Faecal Colliform were considered to compute Water Quality Index (WQI) based on National Sanitation Foundation studies and discussed.

Keywords : Heavy metals, Subarnarekha river, NSF water quality index, TDS, EC, DO, BOD, Total hardness.

INTRODUCTION

River Water quality monitoring is necessary especially where the water serves as drinking water sources and threatened by pollution resulting from various human activities along the river course (Ahmad et al. 2010; Amadi 2011). Heavy metals contamination in river is one of the major quality issues in many fast growing cities, because maintenance of water quality and sanitation infrastructure did not increase along with population and urbanization growth especially for the developing countries (Karbassi et al. 2007; Akoto et al. 2008; Ahmad et al. 2010). Metals enter into river from variety of sources; it can be either natural or anthropogenic (Wong et al. 2003; Adaikpoh et al. 2005; Akoto et al. 2008). Identification and quantification of these sources should form an important part of managing land and water resources within a particular river catchment (Bellos and Swaidis 2005). Simultaneously, seasonal variations in agricultural activity, stormwater runoff, interflow and atmospheric deposition have strong effects on river water quality (Singh et al. 2004; Ouyang et al. 2006; Cidu and Biddau 2007). Thus, characterization of seasonal variability in surface water quality is imperative for evaluating temporal variations of river pollution from natural or anthropogenic contributions.

Usually in unaffected environments, the concentration of most of the metals is very low and is mostly derived from the mineralogy and the weathering (Karbassi et al. 2008). Main anthropogenic sources of heavy metal contamination are mining, disposal of untreated and

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partially treated effluents containing toxic metals as well as metal chelates from different industries and indiscriminate use of heavy metal-containing fertilizer and pesticides in agricultural fields (Ammann et al. 2002; Nouri et al. 2006, 2008). Rivers in urban areas have also been associated with water quality problems including metal contamination due to the practice of discharging of untreated domestic and small-scale industrial effluent into the water bodies (Rim-Rukeh et al. 2006; Khadse et al. 2008; Juang et al. 2009; Venugopal et al. 2009; Sekabira et al. 2010).

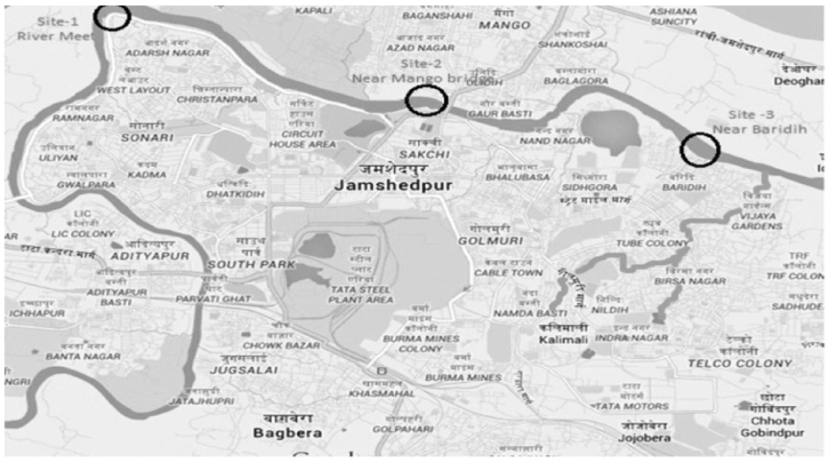
However, in recent years much attention has been given towards the evaluation of heavy metal pollution in ground and surface waters with development of heavy metal pollution index (HPI) (Reddy 1995; Mohan et al. 1996). The metals monitored for the assessment of the water quality of any system give an idea of the pollution with reference to that particular metal only. HPI is a method that rates the aggregate influence of individual heavy metal on the overall quality of water and is useful in getting a composite influence of all the metals on overall pollution. In the HPI, a similar approach is adopted as Horton (1965) and NSFWQI. However, the weighted factors of the metals correspond to the inverse of the recommended standard of the metal and the summation of the weighted factors does not equal to 1. Moreover, in HPI higher values indicate deteriorated water quality with respect to metals as opposed to other WQI where higher values represent the better quality. In contrast to other WQI, where sub-indices are calculated using only standard values, HPI uses both the ideals values and the standard values.

MATERIALS AND METHODS

Site Description

The study is carried out in Subarnarekha River which flows through the East Singhbhum district, which is one of the India's important industrialized areas known for ore mining, steel production, power generation, cement production and other related activities. The Subarnarekha river is the eighth river in India by its flow (12.37 billion m3/year) and length. The River Subarnarekha is a rain fed river originating near Nagri village (2301810211 N, 8501110411 E) in the Ranchi district, runs through several major cities and towns such as Ranchi, Muri, Jamshedpur, Ghatshila, Adityapur etc covering a distance about 400 km.

It finally joins the Bay of Bengal at Kirtania Port(2103311811 N, 8702313211 E) in Odisha. Before falling in to the Bay of Bengal the River flows through Ranchi, Saraikela and East Singhbhum district of Jharkhand, West Midnapur district of West Bengal and Balasore district of Odisha. Of its total length 269 km are in Jharkhand, 64 km in West Bengal and 62 km in Odisha. The Subarnarekha basin covers an area 19,300 km2. This area is nearly the 0.6% of the total national river basin area and yields 0.4% of the country's total surface water resources. The climate of the study area is temperate. Annual rainfall is 1,200-1,400 mm. This area is subject to the southwest monsoon and receives heavy rain (about 80%) during June-September (monsoon season). Its important tributaries include Kanchi, Karkari, Kharkai and Sankh rivers.



The water samples were grouped under following categories :

S1 = Subarnarekha at Domohani
S2 = Subarnarekha at Mango Bridge
S3 = Subarnarekha near Baridih

Sampling and Analysis

Water samples were collected every month, from January 2015 to December 2015 from three different stations as mentioned below. In each site, three replicates were collected and subsequently mixed in situ. Water samples were collected in pre-conditioned acid-washed high-density polyethylene (HDPE) containers. The samples were filtered through pre-washed 0.45μmMillipore nitrocellulose filters. The initial portion of the filtration was discarded to clean the membrane, and the following ones destined for metal determination were acidified to pH < 2 using suprapure nitric acid and then stored refrigerated in pre-cleaned HDPE bottles until analysis (Radojevic and Bashkin 1999).

The water samples were analysed in the CSIR-NML Jamshedpur using standard methods (APHA 2005). The pH and Dissolved Oxygen of water samples were measured immediately after sampling at the field itself. Samples were subjected to filtration before chemical analysis. The determination of TDS was done by gravimetric process while the total hardness was carried out by EDTA complexometric titration method (APHA 2005).The Winkler's alkali iodide-azide method was followed for the estimation of DO and BOD. Nitrate was determined colorimetric procedure (APHA 2005).

Heavy Metal Pollution Index

The HPI represent the total quality of water with respect to heavy metals. The HPI is based on weighted arithmetic quality mean method and developed in two steps. First by establishing a rating scale for each selected parameter giving weightage and second by selecting the pollution parameter on which the index is to be based. The rating system is an arbitrary value between 0 to 1 and its selection depends upon the importance of individual quality considerations in a comparative way or it can be assessed by making values inversely proportional to the recommended standard for the corresponding parameter (Horton 1965; Mohan et al. 1996). In computing the HPI, Prasad and Bose (2001) considered unit weightage (Wi) as a value inversely proportional to the recommended standard (Si) of the corresponding parameter as proposed by Reddy (1995).

The drinking water standards for India (IS 2012)were used for the metals for the calculation of Wi, with the exception of Co and V for which IS (2012) does not provide a standard. Instead, the standards for Co by USEPA (USEPA 2002) and for V by Gerke et al. (2010) were used for the calculations. The HPI model (Mohan et al. 1996) is given by Eq. (1)

$$HPI = \frac{\sum_{i=1}^{n} WiQi}{\sum_{i=1}^{n} Wi} \quad ...(1)$$

where Qi is the sub-index of the ith parameter. Wi is the unit weightage of the ith parameter and n is the number of parameters considered.

The sub-index (Qi) of the parameter is calculated by Eq. (2)

$$Qi = \sum_{i=1}^{n} \frac{\{Mi(-)li\}}{(Si-li)} \times 100 \quad ...(2)$$

where Mi is the monitored value of heavy metal of ith parameter, Ii is the ideal value of the ith parameter and Si is the standard value of the ith parameter. The sign (?) indicates numerical difference of the two values, ignoring the algebraic sign. The critical pollution index of HPI value for drinking water as given by Prasad and Bose (2001) is 100. However, a modified scale using three classes has been used in the present study after Edet and Offiong (2002). The classes have been demarcated as low, medium and high for HPI values <15, 15-30 and >30, respectively.

RESULTS AND DISCUSSION

The parameters, their weightings, their classification and the corresponding numerical ranges are given in Tables 1 and 2 respectively.

Table 1 : NSF WQI Parameter and Weights

Parameters	WQI Weight
Dissolved Oxygen	0.17
pH	0.12
BOD5	0.1
Nitrates	0.1
Total Phosphates	0.1
Temperature Change	0.1
Turbidity	0.08
Total Solids	0.08

Table 2 : WQI Value Ranges (From Mitchell and Stapp, 1995)

Classification	WQI Range
Very Bad	0-25
Bad	26-50
Medium	51-70
Good	71-90
Excellent	91-100

Table 3 : Physiochemical Parameters in Subarnarekha River

Parameters	S1= Subarnarekha at Domohani			S2= Subarnarekha near Mango Bridge			S3 = Subarnarekha near Baridih		
	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
P^H	7.3	8.0	7.57	7.1	7.7	7.49	6.9	7.5	7.30
Turbidity	2.4	520	103.57	1.4	490	128.5	28.6	560	156.0
Total Solids	143	650.6	279.1	130	195	147.9	149.5	754	389.45
DO	2.0	8.9	6.06	4.8	7.0	6.00	0.0	7.6	3.23
BOD	0.4	39.6	4.48	0.3	2.2	1.09	0.4	59.8	17.35
Total Phosphate	0.01	0.16	0.05	0.01	0.14	0.06	0.02	0.24	0.06
Nitrate	0.36	1.94	0.80	0.12	0.83	0.43	0.32	1.38	0.51
WQI	49	78	70	68	78	73	40	73	56

Table 4 : Monthly Water Quality Index at Domohani in Subarnarekha River

Parameters	Jan 2015	Feb 2015	Mar 2015	Apr 2015	May 2015	June 2015	July 2015	Aug 2015	Sep 2015	Oct 2015	Nov 2015	Dec 2015
P^H	7.3	7.6	7.4	7.3	7.3	7.6	7.8	7.7	8.0	7.9	7.5	7.5
Turbidity	8.2	2.4	2.8	3.2	2.7	32.4	122.6	520	320	180	36.2	12.4
Total Solids	214.5	279.5	318.5	650.5	474.5	487.5	143	111.2	143	169	169	188.5
DO	7.0	6.2	3.2	5.8	7.0	2.0	6.0	5.8	6.8	6.2	7.9	8.9
BOD	2.0	3.0	0.4	0.4	2.0	39.6	1.8	0.6	1.2	0.4	0.8	1.6
Total Phosphate	0.01	0.16	0.02	0.04	0.01	0.04	0.08	0.01	0.06	0.12	0.02	0.01
Nitrate	0.84	1.94	0.78	0.92	1.10	0.46	0.52	0.52	0.38	0.36	0.82	0.98
WQI	74	71	68	71	73	49	68	69	70	68	76	78
Classification	Good	Good	Med	Good	Good	Bad	Med	Med	Good	Med	Good	Good

Table 5 : Monthly Water Quality Index Near Mango Bridge in Subarnarekha River

Parameters	Jan 2015	Feb 2015	Mar 2015	Apr 2015	May 2015	June 2015	July 2015	Aug 2015	Sep 2015	Oct 2015	Nov 2015	Dec 2015
P^H	7.3	7.5	7.6	7.4	7.3	7.7	7.7	7.5	7.5	7.7	7.6	7.1
Turbidity	8.6	2.8	1.4	1.8	1.6	34.6	180	360	490	360	82	18.6
Total Solids	156	162.5	175.5	156	169	162.5	149.5	136.7	130	130	175.5	195
DO	7.2	6.4	6.4	6.2	4.8	5.4	6.8	4.8	6.0	7.0	5.0	6.0
BOD	0.6	0.8	1.0	2.0	0.6	2.2	1.0	0.8	2.0	0.4	0.8	1.2
Total Phosphate	0.12	0.14	0.08	0.06	0.04	0.01	0.02	0.01	0.04	0.08	0.06	0.01
Nitrate	0.76	0.64	0.46	0.32	0.28	0.28	0.32	0.24	0.12	0.18	0.78	0.83
WQI	78	76	78	76	73	69	73	68	70	75	69	73
Classification	Good	Good	Good	Good	Good	Med	Good	Med	Good	Good	Med	Good

Table 6 : Monthly Water Quality Index Near Baridih in Subarnarekha River

Parameters	Jan 2015	Feb 2015	Mar 2015	Apr 2015	May 2015	June 2015	July 2015	Aug 2015	Sep 2015	Oct 2015	Nov 2015	Dec
P^H	6.9	7.4	7.5	7.2	7.4	7.4	7.5	7.4	7.0	7.7	7.0	7.2
Turbidity	28.6	36.1	47.2	30.2	29.4	152	280	560	362	260	48.6	38.2
Total Solids	169	520	754	520	175.5	650	520	559	253.5	149.5	208	195
DO	6.0	4.0	0.0	0.0	1.2	0.0	2.8	0.0	3.0	6.6	7.6	7.6
BOD	1.8	1.6	0.4	20.0	0.4	59.8	19.9	60.0	40.0	0.8	2.0	1.6
Total Phosphate	0.14	0.08	0.06	0.06	0.01	0.02	0.02	0.01	0.06	0.04	0.08	0.08
Nitrate	0.68	0.52	0.46	0.42	0.51	0.32	0.47	0.68	0.12	0.43	0.80	0.71
WQI	69	59	53	44	61	40	44	40	47	71	71	73
Classification	Med	Med	Med	Bad	Med	Bad	Bad	Bad	Bad	Good	Good	Good

Table 7 : Average Concentration of Heavy Metals in Surface water (µg/l) of River Subarnarekha (Each Value in average of five Samples)

Location	Cu			Pb			Ni			Zn			Cr			Co			Sr		
	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C
Study Area 1	18.0	17.4	17.2	ND	ND	ND	2.2	2.8	2.02	18.2	14.2	12.8	1.90	1.84	1.78	0.96	0.88	0.76	35	34	33.8
Study Area 2	18.8	17.8	17.4	ND	ND	ND	1.98	1.81	1.46	18.8	17.0	16.0	2.10	1.92	1.88	1.08	0.90	0.82	36.2	34	32
Study Area 3	18.0	18.0	17.8	ND	ND	ND	3.82	2.98	2.46	20.6	18.6	14.8	2.04	2.00	1.80	1.02	0.92	0.80	37.8	34.6	29.8

A= April' 15, B= July'15, C= Oct'15, N D = Not Detected

Table 8 : Average Concentration of Heavy Metals in Sediment sample (µg/g) of River Subarnarekha (Each Value in average of five Samples)

Location	Cu			Pb			Ni			Zn			Cr			Co			Sr			Cd			Fe		
	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C
Study Area 1	88	82	78.0	86	74	86	42	38	40	884	776.2	668	70.2	68.2	66.4	12.6	11.4	10.2	32.0	28.8	27.8	1.02	0.84	0.88	24 22 50	22 47 26	20 24 32
Study Area 2	86	84	78.0	88	78	79	44	39	34	798	782	704	80.6	78.4	66.6	13.0	11.2	10.0	30.0	27.6	25.4	0.88	0.74	0.72	23 21 40	23 01 90	20 01 20
Study Area 3	89	85	78.5	84	72	70	40	36.4	31.2	845	792	720	82.0	78.0	68.0	12.8	10.5	9.8	31.8	27.8	25.6	1.08	0.88	0.78	24 61 21	23 24 10	20 10 40

A= April' 15, B= July'15, C= Oct'15, N D = Not Detected

Table 9 : HPI values of surface water of the Subarnarekha River for the different locations

Code	Sampling Site			
S1	Domohani	21.47	8.83	9.60
S2	Near Mango Bridge	22.93	9.96	5.93
S3	Near Baridih	26.37	9.51	11.21

CONCLUSION

High values of TDS during rainy seasons may be due to massive soil erosion. The poor water quality of Subarnarekha River near Baridih is due to the improper treatment of the effluents from Jamshedpur steel plant. The prime duty of the educated public should be to spread awareness in the rural as well as the urban areas. City drains connecting the safety tanks should not be allowed to directly fall in to the river. Proper treatment of the solid wastes should be made especially in urban areas. Deforestation should be strictly checked to control soil erosion due to which the TDs and Turbidity increases significantly during monsoon. Above all a long term action plan and online monitoring is a must to ensure the river water quality (Mitchell et al; 1995)

Concentrations of dissolved metals (Cu, Pb, Ni, Zn, Cr, Co, Sr, Cd and Fe) in the surface water of the Subarnarekha River demonstrated great seasonality. Irrespective of the locations, the elemental concentrations were lower in rainy monsoon season as compared to the other seasons due to pronounced dilution effect. When compared to drinking water guidelines established by WHO, India and the USEPA, much greater attention should be paid to Cu, Fe, Ni and Se though the concentrations were below the critical values in the monsoon season for some elements. The higher values of metals in the rivers imply additional inputs from unusual geochemical enrichment, which in turn may be attributed to the geological sources coupled with anthropogenic inputs from the catchments. The same is depicted in the calculated HPI also. The HPI ranged from 3.55 to 388.9 with an average of 32.27, falling in the high class. High HPI were observed at few locations near to industries, mining and the estuary. All the other locations fall under low to medium classes of HPI. Thus, it is reasonably justified to conclude that the augmented concentrations of metals in water of the Subarnarekha River is greatly influenced by direct discharge of industrial, urban and mining.

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