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Full Length Research Paper

Distribution of Heavy Metals in River Chambal and its Tributaries

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Heavy metals are major pollutants in river water because of industrial and municipal waste discharges into the environment without proper treatment. To a small extent these heavy metals find their way into human bodies via food, drinking water and air. These metallic chemical elements are toxic or poisonous at low concentration. However, at higher concentration they can lead to poisoning as a result of bio-accumulation in the human body. The study was designed to establish the distributions of heavy metals into the river Chambal and its tributaries. Thirty six water samples of the study area were analysed for As, Cr, Cu, Cd, Hg. Fe, Pb, Ni and Zn by Atomic Absorption Spectrophotometer (AAS). The metal concentrations in the river water ranges as As (0.19-7.15µg/L), Cd (0.01 – 3.0 µg/L), Cr (0.07 – 22.86 µg/L), Cu (0.21 – 42.49 µg/L), Hg (0.01 – 0.68 µg/L), Pb (0.07 – 9.37 µg/L), and Ni (0.25 - 9.76 µg/L), Zn (0.008 – 0.099 mg/L) and Fe (0.020 – 0.30 mg/L. The analysed data revealed that, toxic metals content among all the samples were distributed in a decreasing sequence of Fe>Zn>Cu> Cr>Ni>Pb>As>Cd>Hg. Iron, zinc metals were found to be the most abundant metals in the river Chambal and its tributaries. All the metals are within the acceptable limit of BIS.

Keywords: River Water quality, Heavy metals, AAS.

INTRODUCTION

Heavy metals are significant environmental pollutants, and their toxicity is a problem of increasing significance for ecological, evolutionary, nutritional and environmental reasons. The term "heavy metals" refers to any metallic element that has a relatively high density and is toxic or poisonous even at low concentration (Lenntech Water Treatment and Air Purification 2004). "Heavy metals" in a general collective term, which applies to the group of

metals and metalloids with atomic density greater than 4 g/cm³, or 5 times or more, greater than water (Hawkes 1997). However, chemical properties of the heavy metals are the most influencing factors compared to their density. Heavy metals include lead (Pb), cadmium (Cd), nickel (Ni), cobalt (Co), iron (Fe), zinc (Zn), chromium (Cr), iron (Fe), arsenic (As), silver (Ag) and the platinum group elements.

Heavy metals have been referred to as common pollutants, which are widely distributed in the pristine river catchments originating from natural sources and processes as chemical weathering, soil erosion, fall out of aerosols from marine, volcanic or arid soils sources (Gaillardet et al 2003). However, the level of these metals in the environment has increased tremendously as a result of human inputs and activities (Merian 1991). For some metals, natural and anthropogenic inputs are of the same order (for example Hg and Cd), whereas for others (for example Pb) inputs due to human activities dwarf natural inputs (Clark 2001). Heavy metals discharged into a river system by natural or anthropogenic sources during their transport are distributed between the aqueous phase and sediments. Heavy metals are of high ecological significance since they are not removed from water as a result of self purification, but accumulate in reservoirs and enter the food chain (Loska and Wiechula 2003).

Aquatic ecosystem is the ultimate recipient of almost everything, including heavy metals. Pollution of heavy metals in the aquatic environment is a growing problem worldwide and currently it has reached an alarming rate. There are various sources of heavy metals; some originate from anthropogenic activities like draining of sewerage, dumping of Hospital wastes and recreational activities. Conversely, metals also occur in small amounts naturally and may enter into an aquatic system through leaching of rocks, airborne dust, forest fires and vegetation (Fernandez and Olalla, 2000). As heavy metals cannot be degraded, they are continuously being deposited and incorporated in water, sediment and aquatic organisms (Linnik and Zubenko, 2000), thus causing heavy metal pollution in water bodies. In view of the hazardous nature of metal ions, an attempt has been made to study the distribution of heavy metal in the River Chambal and its tributaries.

RIVER SYSTEM

River Chambal

boundary between Madhya Pradesh and Uttar Pradesh for 117 km and continues in north-easterly direction up to village Pinhat. It then gradually turns right and flows in south-easterly direction to enter in Uttar Pradesh, north west of village Chakar Nagar. After flowing for 46 km in Uttar Pradesh, the river outfalls into Yamuna southeast of village Sehon in Etawah District of Uttar Pradesh. Topographically, out of total area of 1,39,468 sq km of the basin, about 3083 sq km around the origin of the river can be classified as hilly and rest as plains. There are three (03) water quality stations at Tal, Dholpur, and Udi on River Chambal.

Tributaries of Chambal River:

Kali Sindh

It originated in the northern slopes of Vindhya Hills. Flowing in the M.P., it enters in the Rajasthan near Bindha village in Jhalwara District. After flowing 145 km in Rajasthan its joins Chambal River near Nonera village of Kota District. The catchment area of the Kalisindh River is 7944km². There is one (01) water guality station at Barod on River Kali Sindh.

River are Lhasi, Berni, Bethli, Andheri, Retri, Dubraj, Bilas and Kunu. There are two water quality stations at A.B. Road Xing and Khatoli on River Parwati.



Banas River

The Banas River originates in the Khamnor hills of the Aravali range (about 5km from Kumbhalgarh) and flows along its entire length through Rajasthan. Banas is a major tributary of the Chambal River, the two rivers meeting near village Rameshwar in Khandar Block in Sawai Madhopur District. The total length of the river is about 512 km and the catchment area is 45,833 km². The main tributaries of the Banas River are Berach and Menali on the right bank and Kothari, Khari, Dai, Dheel, Sohadara, Morel and Kalisil on the

left bank. The Banas River itself has many big tributaries. The Berach River originates in the hills northeast of Udaipur city. It flows northeast for about 157 km from Udaipur, Chittorgarh and Bhilwara district before joining Banas near Bigod village in Mandalgarh Tehsil of Bhilwara District. The catchment area of the river is 7502 km², which lies between $70^{0}25'$ and $75^{0}02'$ east longitudes and $24^{0}29'$ and $25^{0}14'$ north latitudes. The Berach flows in a hilly region up to Badgaon reservoir and then through plains. This river receives flow from Ayar, Wagli Wagon, Gambhiri and Orai Rivers. There are one water quality stations in Tonk with River Banas.

S. No.	Name of WQ Site	Name of River /Tributary/ Sub Tributary/	Catchment Area (sq km)	Latitude	Longitude	District	State
1	Tal	Chambal	4270	23°43'03"	75°21'14"	Ratlam	Madhya Pradesh
2	Dholpur	Chambal	138123	26°39'24''	77°54'00''	Dholpur	Rajasthan
3	Udi	Chambal	139972	26°42'16''	80°10'23''	Etawah	Uttar Pradesh
4	Barod	Chambal/ Kalisindh	24713	25°23'00"	76°20'02"	Kota	Rajasthan
5	Aklera	Chambal/Kalisindh/ Parwan	6050	24°25'47"	76°36'14"	Jhalawar	Rajasthan
6	Sangod	Chambal/Parwan	9288	24°58'09"	76°17'32"	Kota	Rajasthan
7	Khatoli	Chambal/Parwati	15148	25°40'57"	76°28'58"	Kota	Rajasthan
8	A.B.Road Crossing	Chambal/Parwati	5669	24°22'00"	77°05'56"	Guna	Madhya Pradesh
9	Tonk	Chambal/Banas	39614	26°12'32"	75°47'00"	Tonk	Rajasthan

Table 1: Hydrological characteristics of the Chambal River and its tributaries

Central Water Commission, 2012

SAMPLING

Grab samples were collected from the Chambal river and its tributaries (Kalisindh, Parwan, Parwati and Banas) at a depth of about 0.3 m from all the sampling locations. The sample bottles were soaked in 10% HNO3 for 24hr and rinsed several times with double distilled water (DW) prior to use. Water samples (500ml) were collected and immediately acidified with 2ml ultra pure nitric acid (1:1 or 50ml concentrated HNO₃ + 50 ml DW) and 2ml HCl for arsenic to lower pH to <2. The samples thus preserved were stored at 4°C in sampling kits and brought to the lab for metal analysis. In the lab water samples were filtered through 0.45 µm membrane filter. Samples were collected in the months of during September 2011, February 2012, June 2012, October, 2012, March 2013 and August 2013. All chemicals and reagents used were of analytical grade and were purchased from Merck, India. Standard solutions of metals were obtained from Merck, Germany. Deionized water was used throughout the study. All glassware and other

containers were thoroughly cleaned and finally rinsed with deionized water several times prior to use. Trace metal analysis was carried out using Agilent 240 FS Atomic Absorption Spectrometer (AAS) following standard methods given in APHA, 2012.

Drinking Water Standards

In view of the direct consumption of water by humans, the domestic water supply is considered to be most important use of water and drinking usage has been given priority on utilization of water resource in the National Water Policy. In India, agencies like the Bureau of Indian Standards (BIS) and Indian Council of Medical Research (ICMR) have formulated drinking water standards. The World Health Organization (WHO) has also initiated drinking water standards, which are considered international standards. According to BIS 10500, 2012 the Requirement (Acceptable Limit) and **P**ermissible Limit in the Absence of Alternative Source is given in Table 2.

Sr.	Toxic metal	Requirement (Acceptable Limit)		Permissible Limit in the Absence of Alternative Source		
		(mg/L)	(µg/L)	(mg/L)	(µg/L)	
1	Total arsenic as As	0.01	10	0.05	50	
2	Cadmium as Cd	0.003	3	No relaxation		
3	Total Chromium as Cr	0.05	50	No relaxation		
4	Copper as Cu	0.05	50	1.5	1500	
5	Iron as Fe	0.3	300	No relaxation		
6	Lead as Pb	0.01	10	No relaxation		
7	Mercury as Hg	0.001	1	No relaxation		
8	Nickel as Ni	0.02	20	No relaxation		
9	Zinc as Zn	5	5000	15	15000	

Table 2: Drinking Water Standards for Trace & Toxic metals (BIS-10500-2012)

RESULT AND DISCUSSION

Heavy metals or trace elements are among the most harmful of the elemental pollutants. Some like Pb, Sn, Hg, Zn and Cu are toxic to the system (CWC, 2014; Bhatia, 2006). Trace metals include essential elements like Fe as well as toxic metals like Cd and Hg (Pandey and Madhuri 2014). Most of these have strong affinity for sulphur and disrupt enzyme function by forming bonds with sulphydryl groups in enzymes (CWC, 2014). Heavy metals are persistent and easily enter a food chain and accumulate until they reach toxic levels (Abah et al., 2013). These may eventually kill fish, birds and mammals (Abah et al., 2013). Many countries in the world have experienced menace of metal pollution in water and large number of people has been affected and causes of this pollution have been well documented (Samanidou and Papadoyannis, 1992; Newchurch & Kahwa, 1984; Voutsa, et al., 1995; Valová et al., 2010; Sharma et al., 1992; Tao et al., 2014; Song, et al., 2013; Tariq et al., 1994; Chukwujindu et al., 2012; Nirmala et al., 1991). However, the main sources of metal toxicity in surface water have been thought to be natural occurrence and subsequent degradation of the environment (Jessica and Andrew, 2011). Heavy metal distribution in River Chambal River and tributaries during September 2011, February 2012, June 2012, October, 2012, March 2013 and August 2013 is shown in table 3.

S. No.	Metals	Chambal	Banas	Kalisindh	Parwati	Parwan
1	Arsenic (µg/L)	0.64 - 7.15	0.38 - 6.04	0.19 - 5.36	0.31 - 3.68	0.27 -1.66
2	Cadmium (µg/L)	0.01 - 3.00	0.02 - 0.61	0.19 - 0.97	0.03 - 0.62	0.03 - 2.03
3	Chromium (µg/L)	0.07 - 22.86	0.23 - 4.56	1.16 - 7.05	0.32 - 6.07	0.39 - 4.95
4	Copper (µg/L)	0.74 - 42.49	0.21 - 8.90	0.90 - 8.73	0.38 - 14.82	0.43 - 13.12
5	Nickel (µg/L)	0.25 - 9.76	0.56 - 3.37	3.10 - 5.43	0.87 - 4.96	1.69 - 4.39
6	Lead (µg/L)	0.21 - 9.37	0.17 - 1.93	0.11 - 2.75	0.07 - 2.58	0.13 - 4.65
7	Mercury (µg/L)	0.08 - 0.26	0.01 - 0.28	0.01 - 0.48	0.01 - 0.19	0.13 - 0.68
8	Zinc (mg/L)	0.013 - 0.099	0.012 - 0.089	0.016 - 0.090	0.008 - 0.086	0.011 - 0.095
9	Iron (mg/L)	0.020 - 0.300	0.054 - 0.102	0.052 - 0.183	0.051 - 0.142	0.051 - 0.063

Table: 3- Heavy metals distribution in River Chambal and its tributaries

Arsenic

Arsenic (As) is a ubiquitous element that is comparatively rare, but widely distributed in the atmosphere, soils and rocks, natural waters and organisms. It is mobilized in the environment through a combination of natural processes such as weathering reactions, biological activity and volcanic emissions as well as through a range of anthropogenic activities (Walter et al., 1995; Kinniburgh, D. G. & Smedley, P. L. 2001; Kapaj, et al., 2006). Most environmental arsenic problems are the result of mobilization under natural conditions, but man has had an important impact through mining activity, combustion of fossil fuels, the use of arsenical pesticides, herbicides and crop desiccants and the use of arsenic as an additive to livestock feed, particularly for poultry (Welch 2003; Karthikeyan and Hirata 2003). Although the use of arsenical products such as pesticides and herbicides has decreased significantly in the last few decades, their use for

wood preservation is still common. The impact on the environment of the use of arsenical compounds, at least locally, will remain for some years (Faust et al., 1983; Nadeem, and Shafiq, 2007)

BIS has recommended 0.01 mg/l (10µg/L) as acceptable concentration of arsenic in drinking water. Total 34 numbers of water samples from 10 water quality monitoring stations were collected and analyzed for arsenic content in Chambal River and its tributaries in the period September 2011 to August 2013. The arsenic concentration varies from 0.19 to 7.15 µg/L. Maximum arsenic concentration (7.15µg/L) was observed at Dholpur water quality monitoring station on Chambal River during October 2012. In the study area, all the River water quality stations are reported to have arsenic concentration well within the acceptable limits of Bureau of Indian Standards (BIS) and no toxicity of arsenic in the River waters is observed during the study period.



Figure: 2 – Arsenic level in Chambal River and its tributaries

Copper

Copper is an essential element in human metabolism, and it is well-known that deficiency results in a variety of clinical disorders, including nutritional anaemia in infants (Massie and Aiello, 1984) BIS, 10500, 2012 has recommended a acceptable limit of 0.05 mg/l (50µg/l) of copper in drinking water; this concentration limit can be extended to 1.5 mg/l (1500 µg/l) of copper in case no alternative source of water with desirable concentration is available. The intake of large doses of copper has resulted in adverse health effects (EPA 1987; Stern et al., 2007). Copper and its compounds are widely distributed in nature, and copper is found frequently in surface water and in some groundwater. Copper concentration of the Chambal River and its tributaries was found between 0.21 - 42.49µg/L. The maximum concentration (42.49 µg/L) was found in Dholpur (Chambal River) and minimum (0.21 µg/L) at Tonk (Banas River) water quality station. In the study area all the water quality stations having copper concentration are within the acceptable limits of Bureau of Indian Standard (BIS).

Cadmium

Cadmium is a rare natural element which is widely distributed in the earth's crust in very small amount. It is uniformly distributed in the Earth's crust, where it is generally estimated to be present at an average concentration of between 0.15 and 0.2 mg/kg. Cadmium may be present in the aquatic environment at relatively low levels as inorganic complexes such as carbonates, hydroxides, chlorides or sulphates, or as organic complexes with humic acids (Hiatt, and Huff, 1975). Even in polluted rivers the cadmium levels in aqueous phase may be significantly low and even sometimes below detection limit. A maximum acceptable concentration for cadmium in drinking water has been established on the basis of health considerations. BIS proposed the maximum desirable limit of cadmium is 0.003 mg/l or 3µg/l and no relaxation maximum permissible limit in absence of another source. The concentration of cadmium in unpolluted fresh waters is generally less than 0.001 mg/L. Surface waters containing in excess of a few micrograms of cadmium per liter have probably been contaminated by industrial wastes from metallurgical plants, plating works, plants manufacturing cadmium pigments, textile operations, cadmium-stabilized plastics, or nickel–cadmium batteries, or by effluents from sewage treatment plants (Rani et al., 2014). Data reveal that cadmium concentration varies from $0.010 - 3.00 \mu g/L$. The highest cadmium concentration ($3.00\mu g/L$) was observed in the Dholpur water quality monitoring station on Chambal River during June 2012.

Chromium

Chromium can exist in di to hexavalent forms but is present in the environment mainly in the trivalent or hexavalent state. Trivalent chromium (Cr⁺³) is the most common naturally occurring state; hexavalent chromium (Cr⁺⁶) present in the environment are generally the result of industrial and domestic emissions. A maximum acceptable concentration of 0.05 mg/L (50µg/L) for chromium in drinking water has been established on the basis of health considerations. Trivalent chromium, the most common naturally occurring state of chromium, is not considered to be toxic (Jacobs et al., 2005; Saha et al., 2011) Toxic effects of chromium in man are attributed primarily to this hexavalent form (MNHWC, 1978.) BIS (Bureau of Indian Standard), 10500; 2012 have recommended acceptable limit of 0.05 mg /l or 50 µg/l of chromium in drinking water. Data reveals that chromium concentration varies from 0.070 (Dholpur) - 22.86 (Udi). Chambal and its tributaries have maximum 22.86 µg/L concentration observed at Dholpur water quality station during September, 2011. Table 3 is showing the chromium concentration in river Chambal, Kalisindh, Parwan, Parwati and Banas.





Lead

Lead is the one of the most common of the heavy elements. It has therefore been used extensively since Roman times and, as a result, has become widely distributed throughout the environment (Greenwood, N.N. and Earnshaw, A. 1984). The acceptable limit (AL) for lead in drinking water is 0.010 mg/L (10µg/L). Above the acceptable limit lead is a cumulative general poison, with fetuses, infants, children up to six years of age and pregnant women (because of their fetuses) being the most susceptible to adverse health effects (CWC, 2014). Lead can severely affect the central nervous system. Overt signs of acute intoxication include dullness. restlessness, irritability, poor attention span. headaches, muscle tremor, hallucinations and loss of memory (Lawrence, et al., 2009). Signs of chronic lead toxicity, including tiredness, sleeplessness, irritability, headaches, joint pain and gastrointestinal symptoms, may appear in adults (ATSDR, 1999). After one or two years of exposure, muscle weakness, gastrointestinal symptoms, lower scores on psychometric tests, disturbances in mood and symptoms of peripheral neuropathy were observed in occupationally exposed populations (Baker, et. al., 1984). Bureau of Indian Standard (10500, 2012) had recommended an acceptable limit of lead is 0.01 mg/l or 10µg/l in drinking water. Lead concentration was maximum (9.37 µg/L) at Udi water quality station on Chambal River during August, 2013.

Nickel

Nickel is a nutritionally essential trace metal for at least several animal species, micro-organisms and plants, and therefore either deficiency or toxicity symptoms can occur when, respectively, too little or too much Ni is taken up (Cempel and Nikel, 2006) ... According to BIS-10500 (2012) the acceptable limit of nickel in drinking water is 20 µg/L. The average abundance of nickel in the earth's crust is 1.2 mg/L; in the soils it is 2.5 mg/L; in streams it is 1 µg/L, and in groundwater it is <0.1 mg/L. Nickel is obtained chiefly from pyrrhotite and garnierite. It is suspected to be an essential trace element for some plants and animals. Udi water quality station was reported to have the highest nickel concentration 9.76 µg/L during March, 2013. All twenty eight water samples from 10 water quality monitoring stations are observed to have nickel concentrations within the acceptable limits in drinking water during the study period. Chambal, Chambal, Kalisindh, Parwan, Parwati, Banas and Shipra river are within the acceptable limit in respect to with Nickel.

Mercury

Mercury is a heavy metal that has significant impacts on human health (USDHHS, 1999). Mercury comes in three forms- metallic, inorganic, and organic - each with its own degree of toxicity and particular exposure pathways. Mercury is a metal found naturally in the environment but human activities have greatly increased its atmospheric concentration, accounting for approximately 75 percent of worldwide emissions. Anthropogenic sources of mercury in the environment include incinerators (municipal waste), coal-burning facilities (electrical generation), industrial processes (older methods for producing chlorine and caustic soda), and some consumer products (e.g., batteries, fluorescent light, thermometers)(Andrew and Dan Becker, 2010) The form of mercury of most concern from a water quality perspective is Hg²⁺ because it dissolves quickly in water and is consequently the form most often found in aquatic ecosystems (Geneviève, and James, 2006)..

BIS have recommended a maximum permissible desirable limit of 1 μ g/L of mercury in drinking water. Analytical data reveals that all the water samples, mercury concentrations are within the acceptable limit of 1 μ g/L. The mercury concentration varies from 0.010 (Tonk, Barod, Khatoli WQ stations) – 0.68 μ g/L (Aklera). Chambal and its tributaries have maximum 0.68 μ g/L concentration observed at Aklera during August, 2013.

Iron

Iron is the fourth most abundant element in the earth's crust and the most abundant heavy metal; it is present in the environment mainly as Fe^{+2} or Fe^{+3} . Iron isit an essential element in human nutrition, it is an integral component of cytochromes, porphyrins and metalloenzymes. The ingestion of large quantities of iron results in hemochromatosis. It is a condition in which normal regulatory mechanisms do not operate effectively which leads to tissue damage as a result of the accumulation of iron. Tissue damage has occurred, however, in association with excessive intake of iron from alcoholic beverages in some cases of alcoholism (Mesías et al., 2013; CWC, 2014). Iron is generally present in surface waters as salts containing Fe (III) when the pH is above 7. According to BIS the acceptable limit of Iron is 0.3 mg/L (300µg/L). The occurrence of iron in river water ranges 0.020 - 3.00 mg/L. All the thirty six water quality samples are within the acceptable limit prescribed by BIS. Iron concentration was maximum (3.00 mg/L) at Dholpur water quality station on Chambal River during September, 2011.

Zinc

Zinc is an essential element for all living things, including man. Zinc-containing proteins and enzymes are involved in every aspect of metabolism, including the replication and translation of genetic material (Galdes and Vallee, 1983). BIS has recommended 5mg/l acceptable concentration of zinc in drinking water, which can be extended to 15 mg/l in case no alternative source of water is available. If water have zinc concentration of more than 5 mg/l are not suitable for drinking purposes. Zinc concentration varies from 0.010 - 0.099 mg/L. High zinc level is found at Tal water quality site during October, 2012. In the study area all the water quality stations having zinc concentration are well within the acceptable and permissible limits of Bureau of Indian Standard (BIS) and there is no toxicity of Zn in the river water. Zinc is an essential element for human nutrition. The daily requirement is between 4 and 10 mg depending on age and sex, but pregnant women and new mothers may require up to 16 mg/day. Food constitutes the most important source of zinc.

CONCLUSION

The metal concentrations in the river water ranges as As (0.19-7.15 μ g/L), Cd (0.01 – 3.0 μ g/L), Cr (0.07 –

22.86 µg/L), Cu (0.21 - 42.49 µg/L), Hg (0.01 - 0.68 μ g/L), Pb (0.07 – 9.37 μ g/L), and Ni (0.25 - 9.76 μ g/L), Zn (0.008 - 0.099 mg/L) and Fe (0.020 - 0.30 mg/L. The analyzed data revealed that, toxic metals content among all the samples were distributed in a decreasing sequence Fe>Zn>Cu> of Cr>Ni>Pb>As>Cd>Hg. Iron, zinc metals are in the most dominate metals in river Chambal and its tributaries. The Chambal river and tributaries (Kalisindh, Parwan, Parwati and Banas) water has found to be within the desirable (Acceptable) limit prescribed for the water by BIS in respect of heavy metal. The concentration of iron is the most dominating metal in river water.



Figure 4: Box and Whisker Diagram for heavy metals



Figure 5 – Distribution of heavy metals (in µg/L) in River Chambal and it's tributaries (September, 2011)



Figure 6 – Distribution of heavy metals (in µg/L) in River Chambal and it's tributaries (August, 2013)

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