factory discharge Ni in their effluents. Other sources of contamination include electrical equipment, household appliances, batteries and the dumping of municipal sewage (Dean *et al.*, 1972). Occupational and environmental exposure to Cr and Cd has been previously linked to a wide array of inflammatory and degenerative conditions and cancer. Cadmium is a by-product of Zinc production and is one of the most toxic heavy metals. The potential for Cadmium to harm human health depends upon the form present and the amount taken (Bernard, 2008). The intake of Cd over a long period of time leads to its bio-accumulation in the kidney and liver for years and results in severe kidney and liver damage. It is employed in several industrial processes such as protective coatings (electroplating) for metals like iron, preparation of Cd-Ni batteries, control rods and shields within nuclear reactors and television phosphors. Chromium is a notorious environmental pollutant used in several anthropogenic activities. It is a transition metal which is present in the hexavalent Cr (VI) and trivalent Cr (III) forms (Dey and Paul, 2013). Hexavalent chromium toxicity is more severe due to its high permeability to bio-membranes. Ingestion of large amounts of chromium (VI) also has severe detrimental health effects, It can lead to severe respiratory, cardiovascular, gastrointestinal, hepatic and renal damage and potentially death (Bagchi *et al*, 2002). The presence of Cr in the Yamuna river is attributed to electroplating industries situated near the banks of the river.

The values of pH, Total dissolved solids (TDS), Total suspended solids (TSS), Biological oxygen demand (BOD),Chemical oxygen demand (COD) and total coliform are indicators of the levels of microorganisms present and quality of the water body. BOD is a measure of the amount of oxygen that bacteria will consume while decomposing organic matter under aerobic conditions while COD does not differentiate between the biologically available and inert organic matter (Lenore *et al*, 2005; Malik *et al*, 2014).

In the present study, the physico-chemical parameters like pH, TDS, TSS, BOD, COD and total coliform have been examined from the samples collected from the four stations viz., i)Ganges at Kanpur and Varanasi, ii) Yamuna at Delhi and iii) Sabarmati at Ahmedabad. In view of the hazardous nature of metal ions, an attempt has also been made to study the pollution potential of Pb, Cu, Zn, Cr, Cd and Ni at the above mentioned stations.

2. Materials and Methods

2.1 Sampling of river water

The water samples for analysis were collected from midstream at 15 cm depth from the Ganges river at Kanpur (Nanarao Ghat) and Varanasi (Dashashwamedh Ghat), Yamuna river at Delhi (Nizamuddin Bridge) and Sabarmati river at Ahmedabad (Sabarmati Ashram).The sample bottles were then soaked in 10 percent HNO_3 for 24 h and rinsed thoroughly with double distilled water prior to use. The water samples were then preserved with concentrated HNO_3 to bring down the pH to <2.0. They were then stored at 4°C and brought to the laboratory for metal analysis (Ali and Jain, 2001).

2.2 Physico-chemical analysis of river water

The water was processed immediately post collection, in order to ensure that the water profile is not affected by storage. The various physico-chemical parameters like pH, TDS, TSS, BOD and COD were estimated using pH meters and titrimetric methods (APHA, 2005) respectively. The total coliforms present in the water were also estimated by dilution method to estimate the most probable number (MPN) of coliform bacteria in 100 ml of culture (APHA, 20th edition, 1998).

2.3 Heavy metal analysis of river water

The analysis of the toxic metals present in the water samples were carried out using Perkin Elmer Atomic Absorption Spectrometer (Model 3110). The operational conditions were adjusted to obtain optimal determination. The quantification of metals was based upon calibration curves of standard solutions of metals (Jain and Ali, 2001).

3. Results

3.1. Analysis of physico-chemical parameters

Water samples were collected from four stations of the three major rivers, namely Ganges (Kanpur and Varanasi), Yamuna (Delhi) and Sabarmati (Ahmedabad), and were analyzed for various physico-chemical parameters (Table 1). The pH of the water samples were found to vary between the acceptable range of 7.38 (Sabarmati, Ahmedabad) and 7.72 (Yamuna, Delhi) (Fig. 1). The total TDS found in the samples ranged between 235 mg/L (Ganges, Kanpur)to 642 mg/L(Yamuna,Delhi) respectively, which though well within the permissible limits, is quite high. The total TSS was found to range between 12 mg/L (Ganges, Varanasi) and 230 mg/L (Yamuna, Delhi). The BOD levels were from 4.6 mg/L (Sabarmati at Ahmedabad) to 29mg/L (Yamuna, Delhi), while the COD levels were found to vary from 19.7 mg/L (Ganges, Varanasi) and 110 mg/L (Yamuna, Delhi) (Fig. 2). The total coliform count was found to be the least at 62342 MPN/100 ml (Ganges, Varanasi) and the maximum of 11786556 MPN/100 ml (Yamuna, Delhi) (Fig. 3), which was much higher than the accepted levels.

Table 1: The Physicochemical parameters of water viz., pH, TDS, TSS, BOD, COD and Coliform organism were determined

LOCATION	pH	Total Dissolved Solids TDS (mg/L)	Total Suspended solids TSS (mg/L)	Biochemical Oxygen Demand (BOD) 20 ^{0}C mg/L)	Chemical Oxygen Demand (COD) (mg/L)	Coliform Organism (MPN/100 ml)
Ganga (Kanpur- Nanarao Ghat)	7.4	235	22	6.7	19.7	131000
Ganga (Varanasi- Dashashwamedh Ghat)	7.56	320	12	7.4	21.5	62342
Yamuna (Delhi- Nizammudin Bridge)	7.72	642	230	29	110	11786556
Sabarmati (Ahmedabad-Sabarmati	7.38	245	16	4.6	31	590000

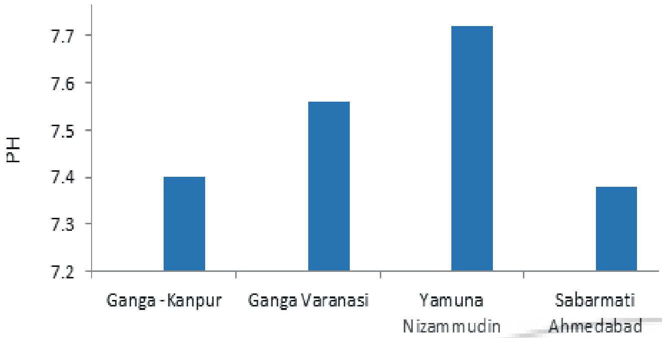


Figure 1: pH analysis of water samples collected from four different stations across India viz., Ganges at Kanpur and Varanasi, Yamuna River at Delhi and Sabarmati at Ahmedabad

3.2. Analysis of heavy metal levels

Water samples collected from the four stations located on the rivers Ganges, Yamuna and Sabarmati were analyzed for the levels of heavy metals present in them (Table 2). In the present study the heavy metals Pb, Cu, Zn, Cr, Cd and Ni were analyzed and observed for their toxicity.

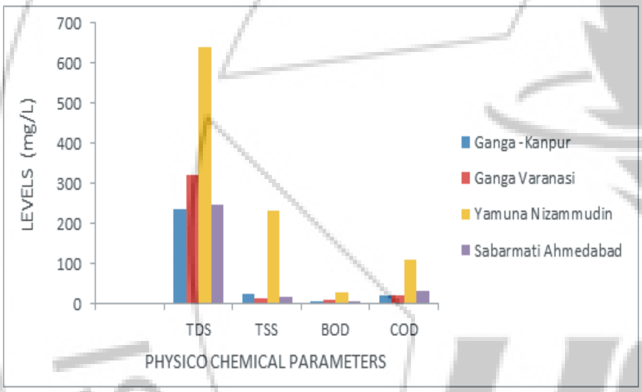
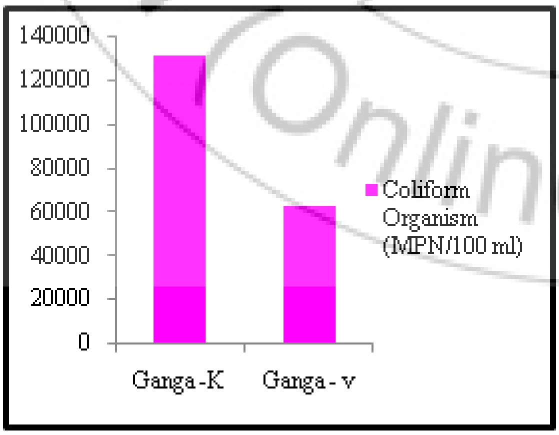
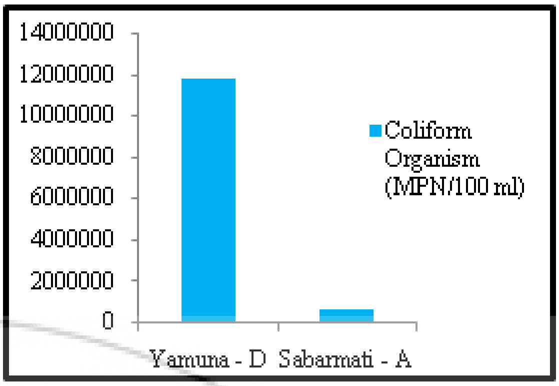


Figure 2: Comparative analysis of the physico-chemical parameter soft water samples collected from four different stations. Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) were estimated using titrimetric methods (APHA, 2005). The values of BOD and COD are indicators of the levels of microorganisms present in a water body.



A



B

Figure 3 A & B: Analysis of the Coliformin the collected water samples. The maximum numbers of coliforms were detected in the Yamuna river in Delhi at Nizammudin Bridge. Indicating a high microbial load. The lowest numbers of coliforms were detected in Ganga at Kanpur and Varanasi.

Our results suggest that the concentrations of metal ions vary significantly depending upon the nature of the effluent discharged into the rivers. The level of the toxic heavy metals (mg/L) reported by ICMR, CPCB, WHO and EPA have been graphically represented (Fig. 4). The levels of lead was found to range between 0.01 mg/L (Ganges, Kanpur) and 0.030 mg/L (Yamuna, Delhi), which is within the permissible limits (Table 2). Zinc levels were found to range between 0.15 mg/L (Ganges, Kanpur) and 0.133 mg/L (Yamuna, Delhi) and were well within the acceptable levels. The levels of copper which ranged between 0.02 mg/L (Ganges, Kanpur) and 0.06 mg/L (Yamuna, Delhi) were also within the permissible limits (Fig. 5). Of the four stations, the lowest level of Cadmium was found to be 0.043 mg/L (Ganges,Varanasi) and the highest was0.061mg/L (Yamuna, Delhi) (Fig. 5). Thus, the levels of these metals are in permissible limits except for Chromium ranging from 0.02 to 0.08 mg/ L, which is above the toxicity level in Yamuna at Nizamuddin.

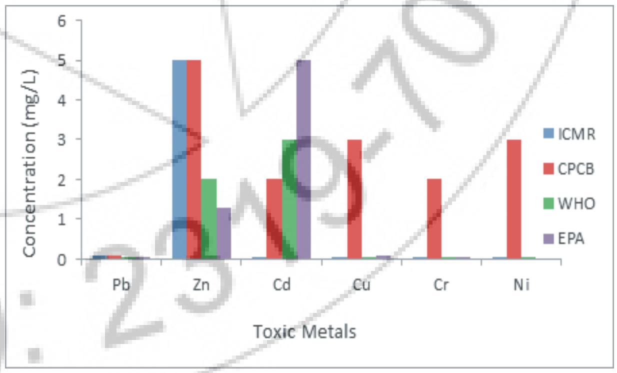
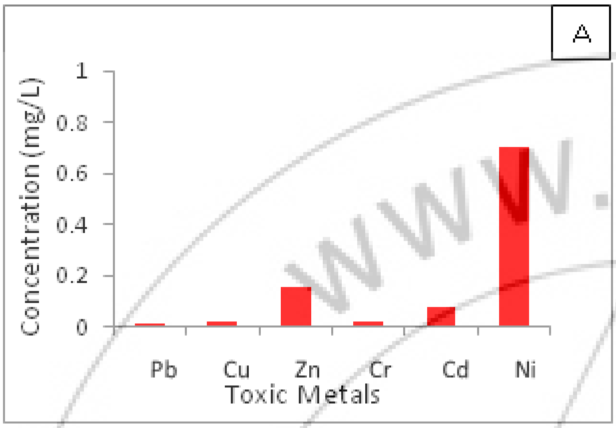
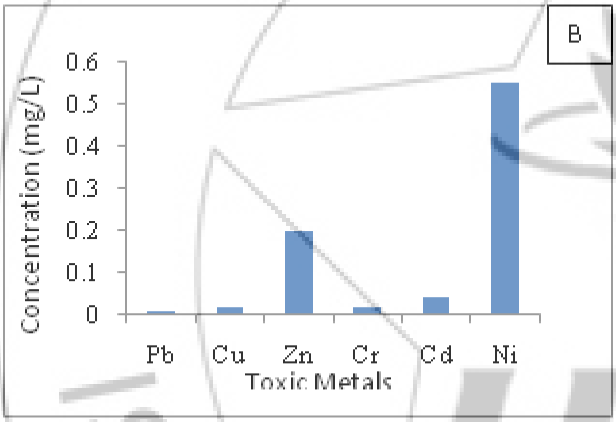


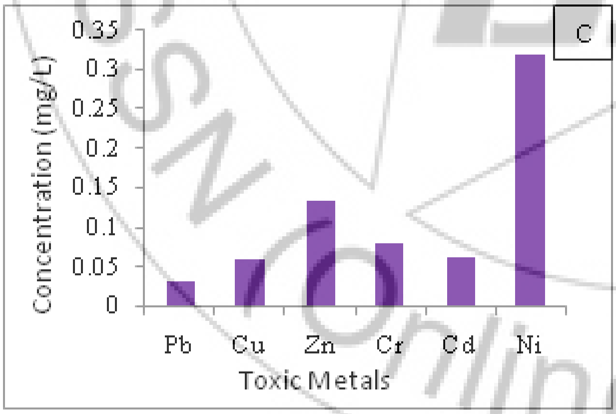
Figure 4: Prescribed limits of metals viz., Lead, Zinc, Cadmium, Copper, Chromium, Nickel reported by ICMR (Indian Council of Medical Research), CPCB (Central Pollution Control Board), WHO (World Health Organization) and EPA (Environmental Pollution Agency)

Table 2: The determination of toxic heavy metals was done in the collected samples from different places

Station	Lead (Pb) (mg/L)	Copper (Cu) (mg/L)	Zinc(Zn) (mg/L)	Chromium(Cr +6) (mg/L)	Cadmium (Cd) (mg/L)	Nickel (Ni) (mg/L)
Ganga (Kanpur- Nanarao Ghat)	0.01	0.02	0.15	0.02	0.075	0.70
Ganga (Varanasi-Dashashwamedh Ghat)	0.01	0.02	0.2	0.02	0.043	0.55
Yamuna (Delhi-Nizammudin Bridge)	0.030	0.06	0.133	0.08	0.061	0.32
Sabarmati (Ahmedabad-Sabarmati Ashram)	0.02	0.05	1.2	0.02	0.059	0.46







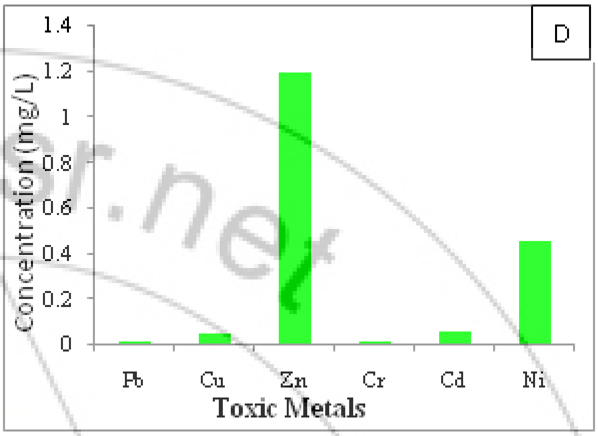


Figure 5: Heavy metal concentrations in the water samples collected from the different stations were determined using Elmer Atomic Absorption Spectrometer (AAS). Significant levels of Zn, Cr and Ni were observed. The four stations included in study are: A-Ganga (Kanpur- Nanarao Ghat); B-Ganga (Varanasi-Dashashwamedh Ghat); C-Yamuna (Delhi-Nizammudin Bridge); D- Sabarmati (Ahmedabad-Sabarmati Ashram).

4. Discussion

The exposure to toxic metals pose a serious human health hazard based on ubiquitous environmental presence, the extent of exposure, and the toxicity and disease states associated with it (Ray *et al*, 2014). It has been known that heavy metal ions such as Pb, Cu, Zn, Cd, Cr and Cd when present at an elevated level may enter our food chain through the vegetables grown on the banks of the river and accumulate in different parts of the body. This eventually causes reduced growth and impaired metabolism. Studies have shown that metal binding to the cell nucleus causes promutagenic damage by the production of reactive oxygen species. This leads to metal-mediated carcinogenicity and acute toxicity (Kasprzak, 1995; Cunningham, 1997).

Our study of water samples collected from the four different stations indicate high levels of Chromium at Yamuna River in Delhi (0.08mg/L). This value is much higher than the toxic levels recommended by the ICMR (0.05mg/L) and WHO (50µg/L). Chromium exposure has severe deleterious effect on chromosomal DNA and causes mutations in it. It is also responsible for the oxidative damage of proteins and the generation of free radicals. These free radicals act as carcinogens and lead to the formation of tumors (Dayan and Paine, 2001). Though the levels of Lead and Cadmium was found to be well within the acceptable range as per the health agencies, these metals are known to bio-accumulate in the system and attain toxic levels over a period of time. This would lead to severe health problems eventually.

Previous work has shown that when the heavy metals Ni, Cr & Cu are mixed in 1:1:1 ratio they show a synergistic toxic effect (Agarwal and Saxena, 2011). The sample analysis from the four chosen stations in this study indicate that approximately the same ratio, thereby indicating severe toxicity to the aquatic life and consequently to human beings as a result of bio-magnification.

The water samples collected from the four stations were analyzed with respect to the quality of the water indicator and oxygen consuming substances (pH, BOD and COD). The pH value is an indicator of the quality of water. The slight increase in pH of the river water (pH 7.72) at Yamuna river in comparison with the other three stations indicate the presence of carbonates of calcium and magnesium (Begum *et al*, 2009).Our study shows that the Yamuna river has the unhealthiest levels of microorganisms which renders it unfit for human use. Municipal sewage disposal into the river can be the primary source of a high BOD, TSS and TDS. This in turn leads to high amount of coliform bacteria, which pose a severe hazard to human health. The discharge of various chemical effluents by the industries located around the river would lead to the high COD levels, further rendering it unfit for human use. Through our study, we thus show that the quality of our river water is steadily deteriorating and needs immediate attention.

5. Future Prospects

Through our study we have shown that three of the important rivers of India have a heavy metal load of varying concentrations. We would now like to extend this study to other major rivers of India, viz. Brahmaputra, Cauvery, Narmada, Tapti, Mahanadi, Krishna and Indus. This would give us a comprehensive view of the current situation of pollution levels in the river systems of the country. We would also like to extend this study to the aquatic life in the rivers in order to estimate the extent of biomagnifications occurring. The flora and fauna occurring on the banks of the rivers can also be analyzed for their content of heavy metals. Such a study would thus enable us obtain an insight into the extent of metal pollution of the rivers in India and the biomagnifications and bioaccumulation arising due to it.

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