

Effect of Heavy Metals on the Water Quality of River Tons and River Asan in Doon Valley, Uttarakhand, India

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Abstract: With the rapid development in agriculture, mining, urbanization and industrialization activities, the river water contamination with hazardous wastes and waste water is becoming a common phenomenon. Nowadays, many industries have developed in Uttarakhand state viz. pharmaceutical, textiles, toy making, coloring etc. They disposed the waste directly or indirectly into the river water, which have degraded the quality of river water. The pollution of aquatic ecosystem by heavy metals has assumed serious proportions due to their toxicity and accumulative behavior. In order to know the effect of heavy metals on the water quality, the present study was conducted on River Tons and River Asan in Doon Valley Uttarakhand for a period of one year. The investigation suggested that the heavy metals were found in minimum concentration in both the rivers however the analysis of physicochemical parameters showed that the water of River Asan was highly polluted due to anthropogenic activities and industrial effluents than River Tons. The metals like Co, Cd, Zn, Cr, Ni and Fe were analyzed in which Zn and Fe was found in maximum concentration in both the rivers. The heavy metals showed the negatively correlation with DO in both the rivers however positive correlation was found between heavy metals.

Key words: Heavy Metals • Water Quality • Toxicity • River Tons • River Asan

INTRODUCTION

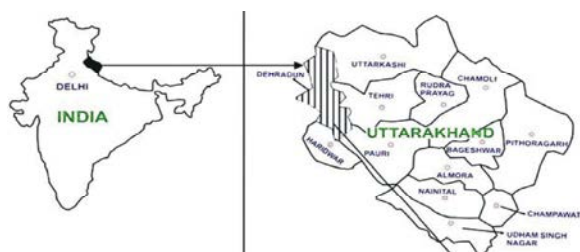
Water is the most precious resource essential to sustain the life on earth. Rapid industrialization and urban development results in inclusion of variety of pollutants into rivers including heavy metals of geological origin and their entry into river bodies by weathering, erosion and due to anthropogenic activities. Anthropogenic activities like mining, disposal of treated and untreated toxic waste and metal chelates from different industries resulted in deterioration of water quality rendering serious environmental problems [1, 2]. During recent years, the pollution of riverine system by heavy metals has attracted a lot of attention of the scientific community. Unlike organic pollutants, natural processes of decomposition do not remove heavy metals. On the contrary, they may be enriched by organisms and can be converted to organic

complexes, which may be even more toxic [3]. Metals are introduced into the aquatic system as a result of weathering of soil and rocks, from volcanic eruptions and from a variety of human activities involving mining, processing and use of metals and/or substances containing metal contaminants [4]. Trace metals entering natural water become part of the water sediment system and their distribution processes are controlled by a dynamic set of physico-chemical interactions and equilibria. The River Tons in Dehradun Uttarakhand India is one of the most important tributary of River Yamuna and flows south west. Its source lies in the 20,270 ft. (6,315 m) high in Banderpooch Mountain and is one of the most major perennial Indian Himalayan Rivers. In fact it carries more water than the Yamuna itself, which meets it below Kalsi near Dehradun. The River Asan is another tributary of River Yamuna flowing North West of Doon

Valley and later joins the River Yamuna. A number of researchers like [1, 5, 6] have made a study on such aspects in different rivers of India and abroad. The main aim of the study was to assess the effect of heavy metals on the water quality of River Tons and River Asan in Doon valley Uttarakhand India.

MATERIALS AND METHODS

Study Area and Collection of Samples: The present study was carried out on monthly basis for a period of one year from August 2010- July 2011. Three sampling stations namely Tapkeshwar Temple (S1), Garhi Cant. (S2), Selaqoi (S3) were selected on River Tons and three sampling stations were chosen on River Asan which include Chanderbani (S4), Asarori (S5) and Confluence point (S6). Water samples were collected early in the morning in sterilized sampling bottles and were analyzed for 18 important physicochemical parameters and trace heavy metals. Few physicochemical parameters like Temperature (°C), pH and Dissolved Oxygen (mg/l) were performed on spot and other parameters like Total Alkalinity (mg/l), Total Hardness (mg/l), Calcium (mg/l), Magnesium (mg/l), BOD (mg/l), Phosphate (mg/l), Nitrate (mg/l), Sodium (mg/l), potassium (mg/l), Cobalt (mg/l), Cadmium (mg/l), Zinc (mg/l), Chromium (mg/l), Nickel (mg/l) and Iron (mg/l) were analyzed under standard laboratory conditions in accordance with APHA [7], Trivedy and Goel [8] and Khanna and Bhutiani [9]. The data was also analyzed by statistical approaches like Standard deviation (SD), Analysis of Variance (ANOVA) and Pearson Correlation coefficient (r).



Map Showing Study area

RESULTS AND DISCUSSION

Physicochemical Attributes of River Tons and River Asan: Table 1 and 2 depicted the average values of physicochemical characteristics of River Tons and River Asan in Dehradun. Temperature is one of the most important parameters to indicate the status of any water body. In the present study the maximum temperature was

Table 1: Mean ± SD values of physicochemical parameters in River Tons

Parameters/ Sites	River Tons		
	S1	S2	S3
Temperature °C	18.33±2.42	18.25±2.41	19.75±2.37
pH	8.18±159.68	8.32±0.14	7.5±0.19
Total alkalinity mg/l	468.33±68.65	367.09±179.80	133.16±4.93
Total Hardness mg/l	252.33±19.52	260.66±22.18	135.25±21.76
Calcium mg/l	53.81±7.18	53.81±5.72	49.92±8.30
Magnesium mg/l	49.85±4.02	49.85±5.86	20.85±3.95
DO mg/l	9.51±0.82	9.26±0.55	8.59±0.79
BOD mg/l	2.82±0.50	2.75±0.40	3.76±0.50
Phosphates mg/l	1.08±0.31	0.969±0.11	1.470±0.25
Nitrates mg/l	0.809±0.26	0.965±0.38	0.691±0.09
Sodium mg/l	0.510±0.12	0.604±0.12	0.590±0.09
Potassium mg/l	0.437±0.07	0.368±0.07	0.476±0.08

P = 0.647, Significant at 0.05 confidence level

Table 2: Mean ± SD values of physicochemical parameters in River Asan

Parameters/ Sites	River Asan		
	S4	S5	S6
Temperature °C	19.66±2.05	19.65±1.77	18.0±3.33
pH	7.4±0.18	7.5±0.14	7.4±0.30
Total alkalinity mg/l	253.5±38.09	267.0±39.06	155.75±18.31
Total Hardness mg/l	192.33±17.31	156.6±8.93	153.91±10.30
Calcium mg/l	61.78±7.60	53.39±7.69	44.19±5.39
Magnesium mg/l	31.84±2.77	25.19±2.78	26.76±2.23
DO mg/l	8.45±0.89	8.29±0.66	9.37±0.20
BOD mg/l	4.08±0.57	3.76±0.48	2.65±0.15
Phosphates mg/l	1.45±0.32	1.33±0.33	0.584±0.19
Nitrates mg/l	0.840±0.32	1.38±0.09	0.537±0.12
Sodium mg/l	0.660±0.13	0.575±0.08	0.564±0.10
Potassium mg/l	0.554±0.12	0.487±0.08	0.523±0.09

P = 0.900, Significant at 0.05 confidence level

found at S3 (19.75±2.37°C) and minimum at S2 (18.25±2.41°C) in River Tons whereas in River Asan maximum temperature was found at S4 (19.66±2.05°C) and minimum at S6 (18.0±3.33°C). In River Tons pH values ranged from 7.5±0.19 to 8.32±0.14 where as in River Asan pH ranged from 7.4±0.18 to 7.5±0.14. The higher pH recorded in River Tons may be attributed to higher alkaline nature of water. The pH was found negatively correlated with temperature in River Tons ($r = -0.994$, $p > 0.05$) and showed positive relation with temperature in River Asan ($r = 0.495$, $p < 0.05$). In River Tons and Asan Total alkalinity was recorded in highest possible concentration ranging from 133.16±4.93 mg/l to 468.33±68.65 mg/l and 155.75±18.31 mg/l to 267.0±39.06 mg/l. The alkaline pH and high alkalinity of waters might be due to the use of detergents by neighboring population for washing of clothes, vehicles and utensils. A wash off from area having calcite and dolomite minerals

could also partly contribute to alkalinity [10]. Higher alkalinity indicated the potential susceptibility of these water bodies for eutrophication. Water body with alkalinity values above 100 mg/l is considered nutritionally rich. Spence [11] and on the basis of this observation the river tons and Asan may be considered as eutrophic and indicated high pollution load. Total Alkalinity was also found to be significantly positively correlated with pH in both the rivers ($r = 0.896$, $p > 0.05$ and $r = 0.593$, $p < 0.05$). Total hardness was recorded highest in both the rivers with highest value found at S5 (260.66 ± 22.18 mg/l) and S7 (192.33 ± 17.31 mg/l). Higher values of Hardness may be attributed to higher concentration of calcium and magnesium which were also found higher in both the rivers. Both the calcium and magnesium showed a significant positive relation with Total Hardness in both the rivers. The DO content varied from 8.59 ± 0.79 mg/l to 9.51 ± 0.82 mg/l in River Tons and 8.29 ± 0.66 mg/l to 9.37 ± 0.20 mg/l. The DO was recorded mostly in low concentration throughout the year and does not showed any clear trend with respect to different stations. It was also an indication of poor quality of river water and an increasing load of pollution on both the rivers. In aquatic systems, oxygenation is the result of an imbalance between the process of photosynthesis, degradation of organic matter, re-aeration [12] and physicochemical properties of water [13]. DO was recorded in low values in months of summer and high in months of winter and monsoon. Low dissolved oxygen during summer might also be due to anticipated higher microbial activities. Decomposition of organic matter might be an important factor in consumption of dissolved oxygen, as more vigorous deposition could be likely during warm weather, which also witnessed increased inflow of Pilgrims and tourists in the region [14]. The re-oxygenation of waters during monsoon might be occurring due to circulation and mixing by inflow after monsoon rains [15]. DO was also found negatively correlated with temperature in both the rivers ($r = -0.951$, $p > 0.05$ and $r = -0.999$, $p > 0.05$). BOD values in both the rivers ranged from 2.75 ± 0.40 mg/l to 3.76 ± 0.50 mg/l and 2.65 ± 0.15 mg/l to 4.08 ± 0.57 mg/l. The concentration of BOD varies from month to month and season to season in both the rivers however the concentration of BOD was found relatively high throughout the year. The higher BOD might be attributed to seasonal effect at high temperature. The rate of biological processes going on in the River Tons and Asan is reduced hence decreasing the degradation of oxygen consuming waste material. BOD also showed a negative relation with DO in both

the rivers ($r = -0.947$, $p > 0.05$ and $r = -0.939$, $p > 0.05$) and a positive correlation was recorded between BOD and Temperature in both the rivers ($r = 0.999$, $p > 0.05$ and $r = 0.978$, $p > 0.05$). In the present study the concentration of phosphate in River Tons was found highest at S3 (1.470 ± 0.25 mg/l) and minimum at S2 (0.969 ± 0.11 mg/l) whereas in River Asan maximum concentration of phosphate was recorded at S3 (1.45 ± 0.32 mg/l) and minimum at S6 (0.584 ± 0.19 mg/l). However the concentration of phosphate exhibited almost similar pattern of variation during the study. The phosphate in water may be attributed to runoff from feedlot or heavily fertilized fields may import phosphorous into the rivers. The presence of phosphate may be due to decomposition of plant materials releasing nutrients in the water beds and increasing the nutrient load of the aquatic systems. Similar observations were made earlier by Ayyappan and Gupta [16]. The values of nitrate does not showed much variation from S1 to S6 in both the rivers throughout the year and highest was recorded at S2 and S4 and minimum at S3 and S6 In both the rivers. Nitrate is thermodynamically the most stable form of combined inorganic nitrogen in well-oxygenated waters [17]. Variations in nitrate and its reduced inorganic compounds are predominantly the results of biologically activated reactions [18]. The overall monthly mean values of Sodium and Potassium were relatively lower in River Tons and Asan and does not showed any great variation at different sites and seasons (Figures 1-6). The River Tons at S1, S2 and S3 was polluted to a great extent because of the pollution from anthropogenic, commercial and industrial sources. The S1 is the main residential area in Dehradun city and anthropogenic activities dominate the site. At S2 the famous Tapkeshwar Mahadev temple is located and hundreds of pilgrims visit the temple per day. Apart from washing with detergents, pilgrims offer milk, curd, ghee, flowers, coins, idols, ashes of departed ones, body hairs and other religious materials into the water. Many a times such offerings are brought in polythene carry bags. In the absence of a proper disposable system, the polythene bags are dropped in the water or near the sides of the water body. These polythene bags and other non-biodegradable materials remain either floating on the water surface or cover the river bed substratum which is hazardous to aquatic life. The S3 is an industrial as well as residential and commercial area. The effluents and waste water from drains are discharged into the river. The River Asan at S4 and S5 is highly polluted due to domestic sewage. Throughout the year fecal matter, leaves, flowers,

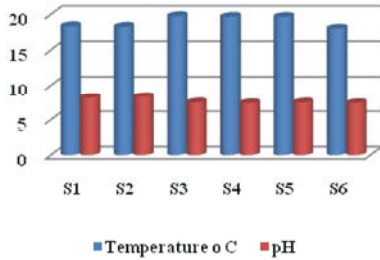


Fig. 1:

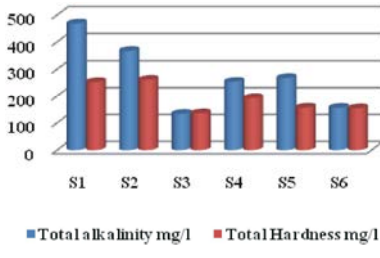


Fig. 2:

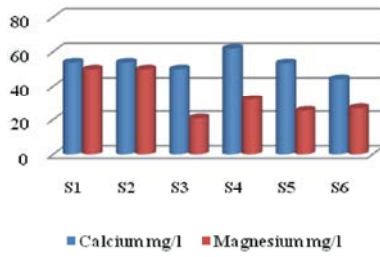


Fig. 3:

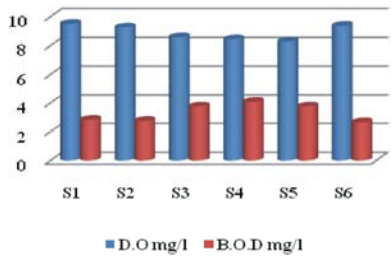


Fig. 4:

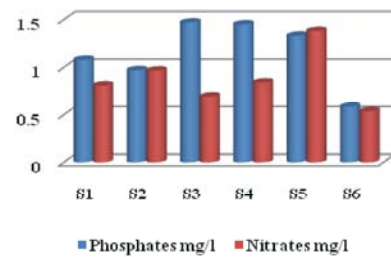


Fig. 5:

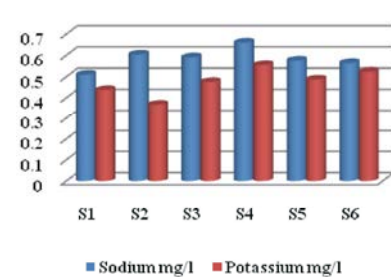


Fig. 6:

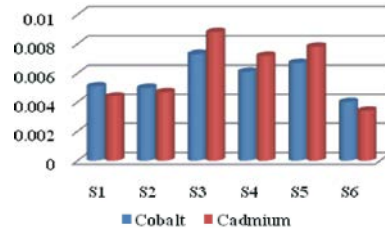


Fig. 7:

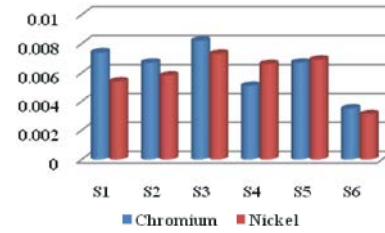


Fig. 8:

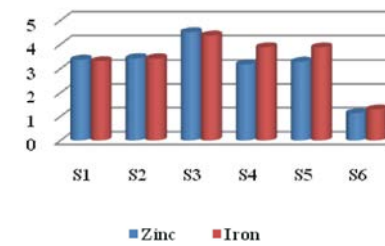


Fig. 9:

Figs. 1-9: Showing graphical representation of data collected on Physicochemical parameters and heavy metals (mg/l) at sampling sites in both Rivers Tons and Asan

seasonal drainage, wooden parts, waste clothes, food material, ashes, laundry discharges etc can be visible and observed in this river.

Heavy Metal Concentration in River Tons and River Asan: Average variation of the heavy metals (Co, Cd, Zn, Cr, Ni and Fe,) of River Tons and Asan river are shown in Tables 3 and 4 and depicted graphically from Figures 7-9. The measured concentration of metals levels showed considerable difference associated with the season and month. Zinc concentration was recorded highest in the study period. Higher values for these metals may be because of the precipitation and discharges of surface water into the rivers. For these elements, the acidification status of the soil in the drainage areas is by far the most important factor regulating the transport process into the rivers [19]. Maximum concentration of iron was recorded in the present study throughout the year, because Fe has more solubility at acidic pH, due to this reason large quantities of iron are leached out from the neighboring

Table 3: Average \pm SD heavy metals concentration (mg/l) in River Tons

Parameters/ Sites	River Tons			Avg. \pm SD
	S1	S2	S1	
Cobalt	0.0051	0.0050	0.0073	0.0058 \pm 0.0013
Cadmium	0.0044	0.0047	0.0088	0.005967 \pm 0.002458
Zinc	3.3751	3.4282	4.5113	3.771533 \pm 0.641207
Chromium	0.0074	0.0067	0.0082	0.007433 \pm 0.000751
Nickel	0.0054	0.0058	0.0073	0.006167 \pm 0.001002
Iron	3.3145	3.4218	4.3729	3.703067 \pm 0.582568

P = 0.935, Significant at 0.05 confidence level

Table 4: Average \pm SD heavy metals concentration (mg/l) in River Asan

Parameters/Sites	River Asan			Avg. \pm S.D
	S4	S5	S6	
Cobalt	0.0061	0.0067	0.0040	0.0056 \pm 0.001418
Cadmium	0.0072	0.0078	0.0034	0.006133 \pm 0.002386
Zinc	3.1807	3.2964	1.1381	2.5384 \pm 1.214074
Chromium	0.0051	0.0067	0.0035	0.0051 \pm 0.0016
Nickel	0.0066	0.0069	0.0031	0.005533 \pm 0.002113
Iron	3.8821	3.8765	1.2964	3.018333 \pm 1.491241

P = 0.610, Significant at 0.05 confidence level

Table 5: Pearson correlation coefficient between physicochemical parameters and trace heavy metals in River Tons

	Tempe- rature	pH	Total Alkalinity	Total Hardness	Calcium	Magnesium	DO	BOD	Phosphate	Nitrate	Sodium	Potassium	Cobalt	Cadmium	Zinc	Chromium	Nickel	Iron
Temperature	1																	
pH	-0.994	1																
Total Alkalinity	-0.941	0.896	1															
Total Hardness	-0.999	0.995	0.936	1														
Calcium	-0.999	0.987	0.955	0.998	1													
Magnesium	-0.999	0.987	0.955	0.998	0.999	1												
DO	-0.951	0.911	0.999	0.948	0.964	0.965	1											
BOD	0.999	-0.995	-0.936	-0.999	-0.998	-0.998	-0.947	1										
Phosphate	0.986	-0.999	-0.872	-0.988	-0.978	-0.978	-0.888	0.988	1									
Nitrate	-0.849	0.903	0.619	0.856	0.8234	0.823	0.645	-0.857	-0.925	1								
Sodium	0.331	-0.223	-0.632	-0.320	-0.376	-0.376	-0.606	0.317	0.172	0.216	1							
Potassium	0.805	-0.867	-0.556	-0.812	-0.776	-0.776	-0.583	0.813	0.892	-0.997	-0.293	1						
Cobalt	0.999	-0.993	-0.944	-0.999	-0.999	-0.999	-0.954	0.999	0.985	-0.845	0.339	0.799	1					
Cadmium	0.994	-0.976	-0.972	-0.993	-0.998	-0.998	-0.979	0.992	0.963	-0.787	0.431	0.736	0.995	1				
Zinc	0.996	-0.980	-0.967	-0.995	-0.999	-0.999	-0.975	0.994	0.968	-0.799	0.413	0.749	0.997	0.999	1			
Chromium	0.906	-0.948	-0.708	-0.911	-0.885	-0.885	-0.731	0.911	0.963	-0.993	-0.099	0.981	0.902	0.854	0.864	1		
Nickel	0.969	-0.935	-0.995	-0.966	-0.980	-0.980	-0.998	0.965	0.916	-0.693	0.553	0.634	0.971	0.990	0.987	0.774	1	
Iron	0.999	-0.968	-0.979	-0.989	-0.996	-0.996	-0.985	0.988	0.954	-0.768	0.459	0.715	0.991	0.999	0.998	0.838	0.994	1

Table 6: Pearson correlation coefficient between physicochemical parameters and trace heavy metals in River Asan

	Tempe- rature	pH	Total Alkalinity	Total Hardness	Calcium	Magnesium	DO	BOD	Phosphate	Nitrate	Sodium	Potassium	Cobalt	Cadmium	Zinc	Chromium	Nickel	Iron
Temperature	1																	
pH	0.495	1																
Total Alkalinity	0.993	0.593	1															
Total Hardness	0.558	-0.445	0.457	1														
Calcium	0.881	0.026	0.821	0.884	1													
Magnesium	0.297	-0.683	0.183	0.958	0.712	1												
DO	-0.999	-0.614	-0.999	-0.430	-0.81	-0.157	1											
BOD	0.978	0.303	0.947	0.718	0.96	0.488	-0.939	1										
Phosphate	0.992	0.385	0.971	0.655	0.933	0.411	-0.965	0.996	1									
Nitrate	0.771	0.934	0.840	-0.100	0.38	-0.379	-0.854	0.622	0.688	1								
Sodium	0.592	-0.407	0.494	0.999	0.902	0.945	-0.471	0.747	0.687	-0.056	1							
Potassium	-0.04	-0.887	-0.154	0.808	0.439	0.943	0.179	0.171	0.085	-0.665	0.782	1						
Cobalt	0.976	0.671	0.995	0.365	0.758	0.082	-0.997	0.91	0.942	0.891	0.403	-0.253	1					
Cadmium	0.991	0.604	0.999	0.444	0.812	0.168	-0.999	0.942	0.968	0.848	0.481	-0.168	0.996	1				
Zinc	0.999	0.540	0.998	0.513	0.855	0.245	-0.996	0.966	0.985	0.804	0.548	-0.091	0.986	0.997	1			
Chromium	0.863	0.866	0.916	0.063	0.523	-0.226	-0.926	0.740	0.795	0.987	0.104	-0.537	0.952	0.922	0.889	1		
Nickel	0.997	0.560	0.999	0.493	0.843	0.222	-0.998	0.959	0.980	0.817	0.529	-0.114	0.99	0.998	0.999	0.899	1	
Iron	0.999	0.498	0.994	0.555	0.88	0.293	-0.999	0.977	0.992	0.773	0.589	-0.041	0.977	0.992	0.999	0.865	0.997	1

soils through acidic water (acid mine drainage) [20]. It is also one of the most abundant elements of rocks and soils. The inter conversion of iron and manganese both in their reduced and oxidized forms have a significant bearing on the water chemistry. With the intensity of precipitation of their hydroxides, phosphates may also get co precipitated. Excess sulphides can also be precipitated as ferrous sulphide [21]. Water bodies generally have higher concentration of iron at the bottom sediments due to the prevailing reducing conditions [22]. As regards the effect of season on heavy metal concentration in the water of both the rivers, concentrations of metals like Co, Cd, Cr, Zn, Fe and Ni were maximum during summer, while minimum concentrations were observed during winter season. This trend could be attributed to the evaporation of water from lakes during summer and subsequent dilution due to precipitation and run-off from the catchment area during rainy season [23]. The Co, Cd, Cr and Ni were found in possible lesser amounts and had not any great effect on the water quality of both rivers.

Simple correlation coefficients (r) computed between physicochemical properties and concentrations of different heavy metals in River Tons and Asan are presented in Table 5 and 6. The concentrations of Co, Cd, Cr, Ni, Fe and Zn in River Tons were significantly and positively correlated with Temperature, BOD and Phosphate and negatively correlated with pH, Total Alkalinity, Total hardness and DO at $p=0.01$. The concentrations of Co, Cd, Cr, Ni, Fe and Zn in River Asan were significantly and negatively correlated with DO and positively correlated with all other physicochemical parameters at $p=0.01$. The relationships between the concentrations of different metals in waters indicated the state of dynamic equilibrium through which these metals that contribute directly or indirectly to ambient water in the aquatic ecosystem [24, 25]. A significant and positive correlation between concentrations of Co, Cd, Cr, Ni, Fe and Zn with this chemical pool indicated the easy establishment of equilibrium in respect of these metals. This kind of behavior is attributed to the affinity of these elements to form sparingly soluble carbonate salts, which might release these metals under aquatic environment [26, 27]. Discharge of heavy metals with industrial effluent and distilleries have increased the concentration of heavy metals like Fe and Zn in the waters of river Tons and Asan. Inadequate urban sanitary infrastructure, lack of formulation of plans and effective implementation of necessary pollution control measures are making the situation worse. Due to rapid industrialization and flow of urban population in past few years is suspected to deterioration of water quality of ecologically rich

Himalayan State of India namely Uttarakhand. The domestic waste from each building along with the effluent of small scale industries is disposed off into the open drains and gutters which ultimately enter into the rivers. Both the rivers are the important tributaries of River Yamuna and the entry of these metals and other pollutants from both the rivers into the Yamuna could degrade the water quality of River Yamuna directly and indirectly.

CONCLUSION

The present study revealed that the River Tons and Asan are on the brink of pollution and are seriously getting polluted by the discharges from industries clustered on the bank of both the studied rivers. The sediment load with trace metals in the river area has been increased as compared to that reported 5 years back. Though trace metals were not found in highest amounts except Zn and Fe but an effect on water quality was observed. The concentrations of heavy metals and other water quality parameters undergo seasonal and monthly changes and the values of most parameters were generally higher. The problem of heavy metal contamination was not serious in the water of these natural waters. The concentrations of heavy metals in waters were also related to different physicochemical properties of waters. The water being moderately hard supported medium productivity. Nevertheless, the increasing concentration of heavy metals is degrading the quality of water. There is a possibility of bioaccumulation of metals in fish. Hence, effluents should be thoroughly treated before letting them into rivers. It is therefore suggested that, restorative measures should be taken for reducing the heavy metal levels in rivers as they are of great socio-economic importance. Further studies are needed on the analysis of water for other priority pollutants and monitoring the area of influence in River Tons and Asan in Dehradun Uttarakhand.

ACKNOWLEDGEMENTS

The DST (Department of Science and Technology, Ministry of Science and Technology New Delhi) is highly acknowledged for the financial assistance in the form of project under Women Scientist Scheme (WOS-A).

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