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Elemental Profiling with Reference to Metal Index to Study Pollutant Load in Northern River of India

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

Present light was to determine elemental load in Sirsa river ecosystem to know the concentration of toxicants in this Sutlej river's tributary that act as a gutter for industrial effluents of Baddi region. The inductively coupled plasma mass spectroscopy was used to detect concentration of elements in the department of biochemical engineering and biotechnology at IIT Delhi and the collected data was further analyzed statistically using one way ANOVA at ($p \leq 0.05$) followed by post hoc Duncan's test to predict degree of variations and comparative profile in Table 1. The application of metal index was also performed to estimate water quality and co-related it with health hazards. Variations in concentration of elements was reported near common effluent treatment plant on pollutant Nallah (S_2) in deceasing order read as Mg>Na>Ca>B>Zn>Cu>Mn>Fe>Mo>Al>Tl>Se in ppb. The concentration of elements reported at S_1, S_2, S_3 were within permissible limit of WHO and Bureau of

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Indian Standards, except the value of Boron, Magnesium and Thallium were exceeded these guidelines constantly at site S_2 of study area.The metal index values at S_1, S_2 and S_3 were 1.55, 5.80 and 2.57 respectively. The site S_2 was affected strongly due to presence of elemental dust and un-treated waste water discharged by chemical industrial units of Baddi region. This site (S_2) was nearer to common effluent treatment plant on the bank of Sirsa river and found to be unsuitable at all with more value of metal index. It was also viewed to adopt such scale indices to estimate drinking water quality with respect to concentration of elements after equal interval of time; as there may be seasonal change in the load of debris due to rate of pollutants dumping in the riverine ecosystem which is directly proportional to the content of elements. The load of pollutants in water system was underlined to know the impact of inorganic waste discharges on water quality of river in this region of Himachal Pradesh along industrial belt.

Keywords: Elements; indexing; pollutants; profiling; health; water quality.

1. INTRODUCTION

Indian riverine water system is complex in hydrology and ecology in the northern part under Himalayan zone. The river pathways have no origin as well as no ending without any area boundary; only showing geochemical cycle in nature. The role played by rivers in the development of a country needs, no elaboration as water system was life line of people since time immortal. The majority of works have been done on the ecology of lakes, reservoirs (Gobindsagar) and rivers as well as hill streams, but river tributaries in the foot hill ecotone are always ignored or these were only surveyed as a part of government planning [1]. This foothill area of Sirsa river was consist of various zones (lotic as well as lentic habitats) showing change in biotic and abiotic regime [2]. An attempt was made on elemental aspects especially the load of toxicants and their impact on Sirsa river water as these substance in an aquatic ecosystem visually remain in dissolve form and move to the substratum or will enter into the food chain as a final repository [3]. The toxicant substances were tend to be transfer through food chain and lead to inhibit metabolism of both plants and animals in the long run due to bioaccumulation of elements [4,5]. This type of bioaccumulation of one element inevitably affects the other; their non-degradation has resulted in resistivity in life support system for short span, it repairs itself and reverts to its original state if possible. However, if the deterioration continues at the same pace, the whole system is thrown out of gear [6]. It was essential to explore water resources on scientific lines to full extent so that their physico-chemical state with respect to inorganic pollutants provide a baseline data in the near future [5,7]. Therefore, it has become important to study immediate effects of pollutants on the water quality of rivers of India.

1.1 Study Area

Studies was on one of the major tributary (river Sirsa) of river Sutlej which is adjacent to foot's of Kausauli hill and lies at 426 metre above sea level in between 30º 57′N; 76º22′E. The selected sites act as dumping gutters to various pollutants indirectly and directly. The effluents of Baddi industry which were common in origin include products such as medicine, distillery, beverages, textile dyeing, cement, electronics, pulp and paper mill, cosmetics, metal components, battery, raw chemical store etc. In study area, there 3 sampling site (S_1, S_2, and S_3) as shown in Fig. 1 with their descriptions below:

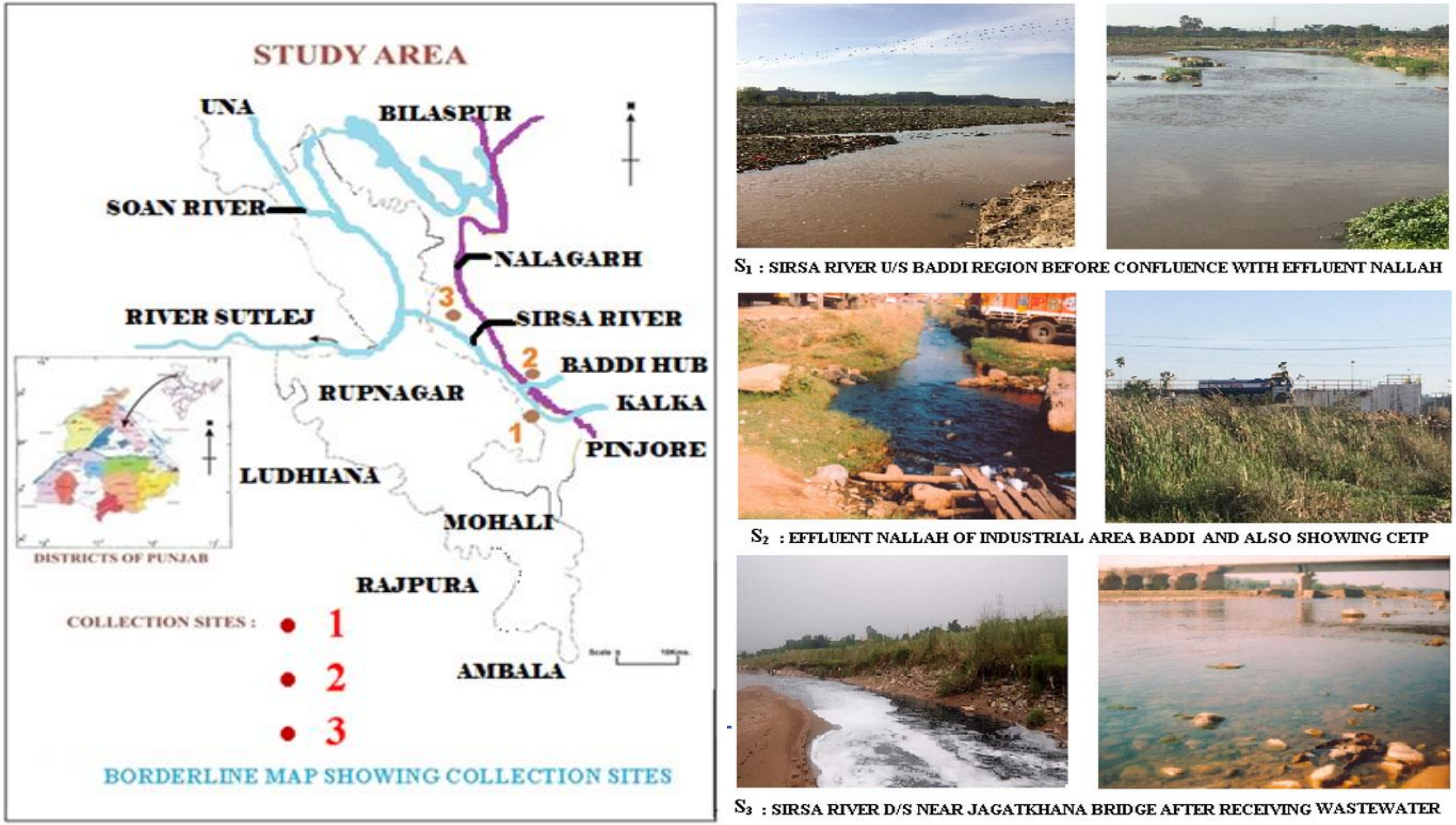
S_1: River Sirsa upstream of Baddi area (Lotic Zone) in Foothill.

S_2: Pollutant Nallah of Baddi industry near CETP but not linked to it.

S_3: Located on river Sirsa downstream toward river Sutlej at Jagatkhana bridge.

2. MATERIALS AND METHODS

The water samples were collected quarterly in pre-rinsed with 10% nitric acid high grade new polyethylene bottles (0.5 L) by using grab sampling method from midstream of Sirsa river (0.3 m in depth) and well mixed point on effluent nallah of Baddi, then added Conc. nitric acid (1 ml in each un-filter water sample at site) to avoid precipitation of elements and kept at 4°C to prevent evaporation. Whatman filter paper number 1 was used to filter each water sample (20 ml) in a vial of borosilicate glass and to prevent precipitation of elements (1ml in each filterate) nitric acid (3%) was added again. Inductively Coupled Plasma Mass Spectroscopy was used to detect concentration of Elements in the department of bio-



S_1 : SIRSA RIVER U/S BADDI REGION BEFORE CONFLUENCE WITH EFFLUENT NALLAH

S_2 : EFFLUENT NALLAH OF INDUSTRIAL AREA BADDI AND ALSO SHOWING CETP

S_3 : SIRSA RIVER D/S NEAR JAGATKHANA BRIDGE AFTER RECEIVING WASTEWATER

Fig. 1. Showing map and photographs of the water collection sites (S_1, S_2 and S_3)

engineering and biotechnology (ICPMS Facility Lab) at IIT Delhi. The collected data was analyzed statistically using one way ANOVA at ($p \leq 0.05$) followed by post hoc Duncan's test and SPSS 16.0 USA software was used. Element profiles were shown in Table 1 as Mean ± S.D. of sites (S_1, S_2 and S_3). The calculation of metal index to determine complete water quality status with reference to addition of metal load [8] and variations in concentration of elements was reported in parts per billion.

3. RESULTS AND DISCUSSION

The profile study of various elements revealed a history of metal load in the catchment area of Sirsa river with more variations in the concentration of pollutants at site S_2 as shown in Table 1.The concentration of elements reported at S_1, S_2, S_3 were within permissible limits of World Health Organization and Bureau of Indian Standards [9,10] except the value of Boron, Magnesium and Thallium were exceeded these guidelines constantly at site S_2 of study area may be concurrent with the findings of Singh et al. [11]. The Boron concentration at S_2 was 2156 ppb, at S_1 was 1093 ppb and at S_3 was 1367 ppb. The difference was noted as per permissible limit of WHO and BIS for drinking water supply and found to be not significant ($p \leq 0.05$) statistically for this river water body. The exposure of boron as a borate ion includes laundry detergent, pesticides, facial creams, cleaners, plant foods and household cleaners. It is important to monitor such a pollutant (B) in surface water and ground water as it cannot be destroyed in the environment, only changes its form. The use of boron compounds in production of thermal shock resistant borosilicate glass and fiberglass have been increased in these days [12]. The concentration of Sodium at S_2 was 13969 ppb, at S_1 was 1403 ppb and at S_3 was 2132 ppb, the differences or (variations reported: S_1vs S_3) were not statistically significant ($p \leq 0.05$) between S_1 and S_3 for all the elements as shown in Table 1 may be due to presence of more inorganic salts, TDS, leaching and the use sodium ion batteries instead of lithium ion batteries in electric vehicles [13].

Aluminium content viewed to be coming with food as well as drinking water and found to be accumulated in CNS because of its ubiquitous nature. The concentration of Aluminium at S_1 was 1.62 ppb, at S_3 was 3.25 ppb and at S_2 was 5.37 ppb. It was not significant ($p \leq 0.05$) for the riverine water system. Aluminium is also accessible as foils, kitchen utensils, aero-plane parts, window frames, beer kegs and cans to human population may cause intoxication [14]. The concentration of Manganese at S_3 was 17.25 ppb, at S_1 was 0.66 ppb and at S_2 was 18.17 ppb. It was found to be not statistically significant (S_1vs S_2vs S_3) may be due to surface run off waste water into river. It may be concurrent with the findings of Friedman et al. [15] where, the mean concentration of Manganese in drinking tap water was exceeded (2.3 µg/L) in Holliston (US) town in a few sample and may be co-related with adverse problem especially in children.

The concentration of calcium at S_3 was 1064 ppb, at S_1 was 810 ppb and at S_2 was 2246 ppb. The result was very significant (S_1vs S_2 and S_2vs S_3) for calcium study. The value of Calcium and Magnesium was in the range of 78–155 mgL^{-1} and 28–54 mgL^{-1} respectively in the ground water [16]. Magnesium is essential for maintenance of normal cell functions in various biochemical pathways [17]. The concentration of Magnesium at S_3 was 8126 ppb, at S_1 was 11634 ppb, at S_2 was 31315 ppb and was not found to be significant (S_1vs S_3 with P value 0.80) may be due to more release of pharma pollutants.

The concentration of Iron at S_3 was 3.52 ppb, at S_1 was 0.13 ppb, at S_2 was 17.84 ppb; the differences were not statistically significant for the water body. The similar high value of Iron was 3820 ppb in ground water and in surface water was 6294 ppb [18]. The concentration of Copper at S_3 was 1.02 ppb, at S_1 was 0.71 ppb, at S_2 was 35.09 ppb; the differences were not statistically significant ($p \leq 0.05$) for discharge waste water contaminated with copper and can be related with study of Manne et al. [19] where, Copper ranged (0.009 to 0.823 mg/L) in water; stored in copper containers and will increase with time duration.

The Umeda river in Japan contain 48–159 mg Zinc per Kg of sediments in surface water and can be related with industrialization; but no threat to biota [20]. The concentration of Zinc was 6.58 ppb at S_3, 0.62 ppb at S_1 and 38.75 ppb at S_2. The content of Zinc was lower at S_3 and S_1 than S_2 may be due to presence of toxicants in pollutant nallah and can be co-related with high content of Zinc in Sirsa river water [21]. The concentration of Selenium at S_3 was 0.05 ppb, at S_1 was 0.05 ppb, at S_2 was 0.10 ppb; the reported result was not significant as there was no variation at sampling site (S_1 and S_3) may be less presence of Selenium ions in pollutants.

Present work was in co-occurrence with the work of Karaj et al. [22] on Selenium content (0.01 to 35.6 μg L^{-1}) and found that water was not suitable for the purpose of irrigation of crops.

The concentration of Thallium at S_3 was 1.48 ppb, at S_1 was 0.00 ppb and at S_2 was 3.34 ppb. The variation was significant between (S_1vs S_2) but it was found to be varied at sites (S_1vs S_3 and S_2vs S_3) and can be co-related with study on heavy metals [23] in Nairobi area of Kenya as per ascending order of (Tl <Cd <Hg <Ni <Cr <Pb) elemental concentration ranged between 0.0001 to 0.015 ppm with more value of Hg and Tl according to limit of US EPA [24]. The concentration of Molybdenum at S_3 was 2.5 ppb, at S_1 was 1.2 ppb, at S_2 was 5.87 ppb, the variations reported was not significant statistically for study sites as (S_1vs S_3 and S_2vs S_3) but it was found to be within P value at (S_1vs S_2) may be due to self-purification of water as well as surface run-off discharges (washing of unloaded tracks in Sirsa river) from industrial based river basin in this zone [2]. It was co-incidence with the reported work of Heijerick et al. [25] on riverine Molybdenum (1-90 nmol per Kg of sediment) in river Mahi of western India. In addition to above, the concentration of lead in fish tissue and water of river Panjkora was 2.028 mg/kg and 0.060 mg/L respectively as per [26] to detect related cancer risk. The similar work of Dixit et al. [27] on the aspects of ecology and related human health problems or risks was underlined to study the effect of four pharmaceuticals on algae, daphnia and fishes of Sirsa river basin with overall ecological risk factor found to be (CTZ > CIP > ECP > NOR) in order to uncertain water conditions in Baddi area and its management practices. These characteristics of elemental profiling has reflected common source of pollution and their impact on water quality assessment to sustain aquatic resources.

3.1 Elemental Load and Metal Index

River Sirsa in Baddi area is a lifeline of people for water resources as a perennial tributary of river Sutlej in Northern part of India. This river basin also act as a dumping site hereby for industrial pollutants even near the common effluent treatment plant, the conditions were under scan at the edge of river bank. The baseline estimation of inorganic elements of daily use or non-use with their acceptable limit will be the need of current research output as an essential part of environmental policies [3]. The present study include profiling of selected elements to generate database to assess their ecological role in riverine water study at the cost of metal monitoring approach or indices in the near future.

The hydro-biological study includes physico-chemical analysis, bio-monitoring as well as pollution indices such as Metal Index (MI) to estimate the effect of addition of elements or heavy metals on the overall quality of river water. The higher concentration of elements in comparison to permissible limit of World Health Organization and Bureau of Indian Standards [9, 10] classifies water quality for various purposes. The metal index (MI) was suggested by Tamasi et al. [8] and can be expressed:

$$\mathrm{MI} = \sum_{i=1}^{N} \frac{C_i}{(MAC)_i}$$

Where, C_i is the reported concentration of elements in sample, MAC is the permissible limit or concentration allowed in maximum as per standards of concerned Nation. To find relationship among the concentration of elements at sites S_1, S_2 and S_3; the statistical analysis of data collected was performed by using one way Analysis of Variance at ($p \leq 0.05$) followed by post hoc Duncan's test to predict the degree of variations.

The metal index values at S_1, S_2 and S_3 were 1.55, 5.80 and 2.57 respectively as depicted in Table 2. The site S_2 was affected strongly due to presence of elemental load and un-treated waste water discharges by chemical industrial units of Baddi region. This site (S_2) was nearer to CETP on the bank of Sirsa river and found to be unsuitable at all with more value of metal index. The calculated MI for Boron was very high at S_2 (2.15) as compared with other elements (Fe, Mo, Al, Tl, Se, Na, Mg, Ca, B, Zn, Cu, Mn) under investigation. Result was similar with the findings of Raj et al. [28] on river Sutlej flowing in the trans-zone region with high concentration of metals (Cd, Ni, Cr, As).

The index applied in the light of Elemental load in Sirsa river water indicated that the value of calculated Metal Index was found to be more for Boron (1.09-2.15), Magnesium (0.38-1.04) and Thallium (0-1.67) in the present study and can be co-related with the work of Mohamed et al. [29] on Ismailia canal tributary of river Nile, which was polluted due to discharge of industrial effluents. It was also related with studies of Bhardwaj et al. [21] on HPI (999) and MI (13.68) in BBN industrial belt for metal load and noted very poor category of water running into Sirsa riverine ecosystem.

Table 1. The concentrations of elements reported at S_1, S_2, S_3 and their permissible limit as specified by WHO (2022) and BIS (2012)

S No.	**Elements**	**S_1 (Lotic Zone)** (MEAN ± SD) **ppb**	**S_2 (Pollutant Nallah)** (MEAN ± SD) **ppb**	**S_3 (Lentic Zone)** (MEAN ± SD) **ppb**	**Permissible limits WHO (2022)**	**Permissible limits BIS (2012)**	**Significance level ($p \leq 0.05$)**		
					ppb	**ppb**	**S_1vs S_2**	**S_1vs S_3**	**S_2vs S_3**
1	**B**	1093 ± 97	2156 ± 72	1367 ± 89	NA	1000	0.07	0.79	0.19
2	**Na**	1403 ± 80	13969 ± 757	2132 ± 96	20000	NA	0.00*	0.88	0.00*
3	**Mg**	11634 ± 79	31315 ± 190	8126 ± 394	30000	NA	0.01*	0.80	0.00*
4	**Al**	1.62 ± 0.25	05.37 ± 0.22	3.25 ± 0.5	50	200	0.61	0.91	0.85
5	**Ca**	810 ± 35	2246 ± 65	1064 ± 79	NA	200000	0.00*	0.57	0.00*
6	**Mn**	0.66 ± 0.03	18.17 ± 1.67	17.25 ± 01.96	100	300	0.35	0.39	0.97
7	**Fe**	0.13 ± 0.05	17.84 ± 2.18	03.52 ± 0.09	300	300	0.27	0.94	0.41
8	**Cu**	0.71 ± 0.04	35.09 ± 02.74	01.02 ± 0.21	1300	1500	0.41	1.05	0.41
9	**Zn**	0.62 ± 0.005	38.75 ± 03.22	6.58 ± 00.90	3000	15000	0.02*	0.86	0.05*
10	**Se**	0.05 ± 0.002	0.10 ± 0.001	0.05 ± 0.001	50	10	0.61	0.99	0.64
11	**Tl**	0.00 ± 0.00	03.34 ± 0.64	01.48 ± 0.38	2	NA	0.01*	0.25	0.15
12	**Mo**	01.20 ± 0.32	05.87 ± 0.12	02.50 ± 0.08	70	70	0.02*	0.67	0.11

The collected data was analyzed statistically by one way ANOVA at ($p \leq 0.05$) followed by post hoc Duncan's test.
*Element profiles were shown in Table 1 as Mean ± S.D. of sites (S_1, S_2 and S_3) and Significance level was denoted by**

Table 2. The metal index was calculated for sites (S_1, S_2 and S_3) and compared it with locations vulnerable to industrial pollution with reference to class of water quality

Sites	**Element wise (METAL INDEX)**													**Studies on Metal Index**	**Class**	**References**
	B	**Na**	**Mg**	**Al**	**Ca**	**Mn**	**Fe**	**Cu**	**Zn**	**Se**	**Tl**	**Mo**				
S_1 (Lotic Zone)	1.09	.07	.38	0	0	0	0	0	0	0	0	.01		1.55	III	Present study
S_2 (Effluent Nallah)	2.15	.69	1.04	.02	.01	.06	.05	.02	0	.01	1.67	.08		5.80	V	Present study
S_3 (Lentic Zone)	1.36	.10	.27	.01	0	.05	.01	0	0	0	.74	.03		2.57	IV	Present study
River Yamuna	**Heavy Metal Studied**													3.44	IV	[31]
	Fe	Cu	Zn	Ni	-	Cr	Pb			-	Cd		-			
River Sirsa	Cr	Fe	Cd	Ni	-	Mn	Pb	Zn		Cu	As	-	-	13.68	VI	[21]
Peenya Industrial Area	Fe	-	-	Cu	Ni	Cd	-	-		Pb	-	Cr	-	25.68	VI	[41]
River Hasdeo	Cd	Fe	Cr	Cu		Mn	Pb	Ni		Zn	-	-	-	25.47	VI	[36]
River Halda	Hg	Fe	Mn	Cu	Pb	Cd	Zn	Cr		Ca	As	Co	-	0.038	I	[39]
River Sirwan	Zn	Al	Fe	Cd	Cr	Pb	Ni	-		-	Fe	-	-	5.7	V	[40]
River Ghaggar	Pb	Ni	Cd	-		Fe	-	-		-	-	Al	-	29.54	VI	[38]
River Bhima	Pb		Mn		Ni	Zn		Cd		Cu		Cr		3	IV	[37]

The Sirsa river water was affected lightly to strongly with reference to metal pollution as per classification of Caeiro et al. [30] and element profile study co-relation persistency also suggested that source of such water pollution was common in origin emanating from pharmaceutical industrial units. Further, it was similar with other findings such as river Yamuna at Agra with high value of MI (3.44-23.15) reported by Bhardwaj et al. [31]; river Danro in Garhwa was found to be more contaminated with lead as per metal indices (HPI) used by Majumdar et al. [32]; river Hindon was contaminated with more Iron and Copper due to electroplating units assessed by Mishra et al. [33]; river Ganga showed seasonal changes in the value of HPI as reported by Matta et al. [34]; najafgarh drain and shahdara drain were found to be potential outlet for heavy metal pollution (HPI was 1491.15) near river Yamuna reported by Bhardwaj et al. [31]; the same result was reported by Reza et al. [35] on HPI (36.19-32.37) while worked on riverine ecosystem. It was also reported to estimate that the critical limit of this present application of metal index relied only on the use of water in and around Sirsa river basin co-occurrence with the findings of Rajkumar et al. [7] on ground water of BBN area in reference to metal index (10.31 to 46.87) and its suitability. An attempt to narrow the gap between habitat and metallic pollutants in river water and wastewater was underline to control related health issues. Further, metal index approach on fish diversity and fisheries in the lap of foot hill has still dark and doom fate due to lack of incomplete elemental profile at the trophic status.

4. CONCLUSION

The change in the concentration of Elemental load in river water is directly proportional to aquatic alterations occurring at trophic level. It was due to the presence of toxicant substances which acts as nutrients for the process of eutrophication through bio-magnification and bioaccumulation. It was an intriguing fact that the town of Baddi is biggest in Asia as Industrial Hub (3120 factories) with more rapid growth in pharmaceutical sector (above700 pharma units) may be due to presence of easily available raw materials, man power and climatic conditions. The input resources and output factors (including industrial effluents) must be governed in such directions to optimise a balance between biotic and abiotic regime of Sirsa river basin. The health of water bodies was rare consideration in developing country due to economy loss and management failure at the end of natural calamities. Indian riverine ecosystem has become gutter for discharge of pollutants. The nature of material released in the environment include organic and inorganic compounds for geochemical recycling. The impact of flow of such elements in various trophic level has emerged in multiple domain of cutting edge research (new indices) and technology.

FUTURE SCOPE

Further scope of present study is, to restore the water quality of riverine tributaries for sustainable development of aquatic resources to the cater needs of local public and can be explore more on scientific lines in the area of elemental load and their toxicity.

DISCLAIMER (ARTIFICIAL INTELLIGENCE)

Author(s) hereby declare that NO generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc) and text-to-image generators have been used during writing or editing of manuscripts.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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