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Persistence of Heavy Metals in River Sirsa Around Industrial Hub Baddi, India.

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Abstract

The Indian riverine system has become dumping site for toxic industrial pollutants. For assessing the flow of pollutants at various trophic levels, it is primarily important to do elemental profiling first so as to detect their load in Sirsa tributary of river Sutlej flowing through foothills of Shivalik in Himachal Pradesh, around the industrial hub Baddi, Solan. The study area includes three observation sites (S_1, S_2, and S_3) on river Sirsa and drainage system of Baddi industrial units; the Effluent Nallah as demarcated in figure1. Heavy metal concentrations in water samples were detected using inductively coupled plasma mass spectroscopy of elements (Ti, V, Cr, Co, Ni, As, Li, Cd, Cs, Pt, Pb, Hg) as these were found to be very common in effluents of chemical, cement, textile dyeing, electronics and pharmaceutical industries. Statistical analysis showed that the concentrations (ppb) of elements found to be within permissible limits of WHO at sites under study for seven metals (Hg, Li, Ti, V, Co, Cs, Pt) but it was higher for five toxic heavy metals (Cr, Ni, Pb, As, Cd) at S_2 only, streamlined in order Cr >Ni > Pb> As >Cd >Hg >Li >Ti >V >Co > Cs > Pt. It may be due to improper installation of common effluent treatment plant (CETP) on the bank of river Sirsa or due to leakage by tanker carrying waste water from various industrial set ups as these units were not directly linked to CETP. These sites were committed to act as ultimate gutter to receive all types of industrial pollutants as part of mismanagement. The load of Arsenic and Lead is increasing in lotic region and its impact on aquatic ecosystem at trophic level can be explored to combat toxicant pollution.

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Introduction

The river system is complex in nature as it receives freshwater discharges through land drainage and effluents from industries, thus the limnology of river body is unique and dynamic in lentic and lotic regions. Industrial wastewater may contain specific

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toxicants which are non-biodegradable substances that act as irreversible metabolic inhibitors of both aquatic and terrestrial ecosystems. They also changes the status of river water body from oligotrophic to eutrophic as these effluents are rich in nutrients. The potent accumulation of these toxic elements in various organs of freshwater creatures ultimately endanger the aquatic biota in the long run. These organisms also act as bio-indicators of pollution, depending upon the limit of their tolerance to metals and thus, the ecological regime of the aquatic ecosystem determines its overall health. The present study aims to reflect the toxicity load on river Sirsa flowing in the vicinity of Asia's biggest pharmaceutical hub near Sirsa tributary.

Study Area

The present study is on Sirsa river which is adjacent to Baddi town and lies between 30º 57'N, 76º22'E at 426 m above sea level. It acts as an ultimate recipient of various pollutants directly or indirectly. These wastewaters were being generated from various industries such as pulp and paper mill, textile dyeing, chemical, beverages, distillery, battery, electronics, medicine, metal components, cement, etc. The study area includes three observation sites (S1, S2, and S3) on river Sirsa and drainage system of industrial units; the effluent Nallah as demarcated in figure1and 2. Brief description of the collection sites are given below:

S_1: River Sirsa upstream of Baddi area but 4 km downstream of Barotiwala.

S_2: It is on Effluent Nallah of Baddi industrial hub after CETP but before confluence with river Sirsa.

S_3: Situated downstream on Sirsa river near Jagatkhana Bridge, where it receives wastewaters from Baddi Industrial hub.

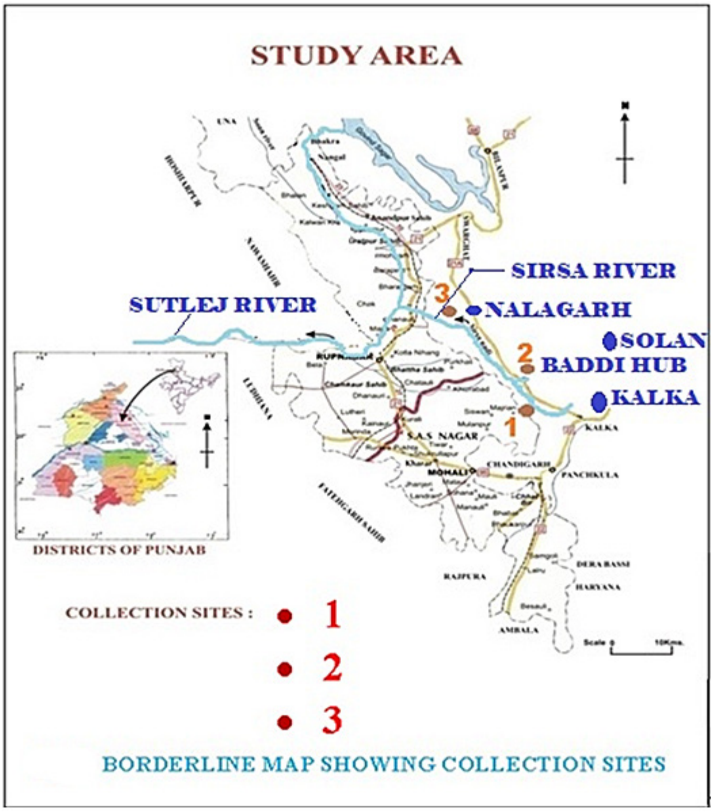

Fig. 1: Borderline Map Showing Collection sites

Fig. 2: Location of collection sites depicted as S1, S2 and S3

Material and Methods

The water samples were collected in 0.5 L high-grade polyethylene bottles previously rinsed with 10% nitric acid and acidified by adding 1 ml of Conc. nitric acid to avoid precipitation of heavy metals and stored at 4◦C to prevent evaporation.[1] Each water sample (20 ml) was filtered with Whatman filter paper number 1. The site specific filtrate was collected in borosil vials and 3% nitric acid (1ml) was added to it. Further, final detection of heavy metals concentrations in water samples were performed by central research facility laboratory at Indian Institute of Technology, Delhi using inductively coupled plasma mass spectroscopy as it is one of the revolutionary and effective technique for determination of a range of metals and several non-metals at concentrations below one part per trillion. Statistical analysis of data was done by using one-way Analysis of Variance followed by post hoc Duncan's test ($P \leq 0.05$ was considered significant). Results were expressed as Mean ± S.E. at three independent sites and shown in Table 1. The collected data were analyzed using the statistical software package, SPSS 16.0 (SPSS, USA).

Results and Discussion

The mean comparison of concentrations of toxic elements at selected sites; S_1, S_2 and S_3 of study area are depicted in Table 1. The degree of variation in the values of heavy metals concentration at three selected sites was observed in the Sirsa river water body through the entire year of study period. It was similar with the work of Sehgal *et al*., (2012)[1] on river Yamuna. Further, it was reported that concentrations of Cr, Ni, Pb, As, Cd were found to be statistically significant (p≤0.05) and were above the permissible limits of WHO at S_2 only, but the values of Hg, Li, Ti, V, Co, Cs, Pt were not statistically significant as shown in the Table 1 and Fig.3 below.

Table. 1: The Concentrations of Heavy Metals reported at S_1, S_2 & S_3 and their Permissible Limits in ppb as specified by WHO (2004), US EPA (2002) and BIS (1993).

S No.	Elements	S_1 (SEM) n=4	S_2 (SEM) n=4	S_3 (SEM) n=4	Permissible limits WHO (2004)	Permissible limits US EPA (2002)	Permissible limits BIS (1993)
					Ppb	Ppb	ppb
1	Ti	0.12± 0.01	1.38 ±0.22	0.95 ±0.03	100	100	NA
2	V	0.3±0.05	1.37±0.02	0.16±0.01	100	100	200
3	Cr	1.42±0.07	63.18± 1.02*	15.45±1.03	50	100	50
4	Co	0.11±.03	0.3±0.01	0.67±.007	100	100	NA
5	Ni	1.22±0.04	23.72±0.97*	7.54±0.11	20	100	3000
6	As	0.40±0.02	11.69±0.85 *	4.2±0.03	10	50	50
7	Li	0.28±0.01	1.42±0.01	0.64 ±0.16	NA	2500	NA
8	Cd	0.08±0.02	4.23±0.06*	1.14±0.09	3	5	10
9	Cs	0.13±0.05	0.04±.01	0.008±0.003	100	100	NA
10	Pt	1.12±0.03	32.2±0.001	11.52±0.06	100	100	NA
11	Pb	0.14±.09	13.40±0.75*	6.23±.08	10	15	100
12	Hg	0.001±.0	1.64±0.1	1.21±0.06	2	2	2

Statistical comparisons: The data was analyzed by ANOVA (Analysis of Variance) followed by post Hoc Duncan's test. Values are expressed as SEM (Mean ± Standard Error Mean) at significant level (p≤0.05) and represented by symbol*)

The leakage of Titanium dioxide in the water body as a food grade nanoparticles was reported to disturb the ecosystem health.[2] The mean concentration of Ti at S_3 was 0.95 ppb, at S_1 was 0.12 ppb and at S_2 was 1.38 ppb. S3 and S_1 have lower mean value than S_2. It may be due to the disposal of more food colouring agents near effluents nallah. Vanadium is an emerging contaminant to be reported in wastewater and act as a potential toxicant to animals and human beings.[3] The mean concentration of V at S3 was 0.16 ppb, at S_1 was 0.3 ppb and at S_2 was 1.37 ppb, the source of which may be the discharge of waste water from ore smelting industrial units.

Chromium in hexavalent form is considered as a potent poison in the wastes of batteries, tannery, electroplating, pharmaceutical hub and adversely effects aquatic environment.[4] The mean concentration of Cr at S_3 was 15.45 ppb, at S_1 was 1.42 ppb, at S_2 was 63.18 ppb and the difference reported was statistically significant (p≤0.05) for river water at S_2 as compared with S_1 and S_3 because there is no proper waste landing site near CETP area. In the process of bioremediation micro-organisms act as potential bio-indicators to combat chromium toxicity, but it was challenging part to use proper selection techniques for it.[5] in the area of contamination. The present mean concentration of Co at S_3 was 0.67 ppb, at S_1 was 0.11 ppb and the value of Co at S_2 (0.30 ppb) was less as compared to S_3, this could be attributed to lower disposal of Co at the site of effluent Nallah.

The presence of Nickel was reported in industrial wastewater discharge and it also changes biochemical properties of food crops, can be used for recycling of nutrients.[6] to maintain the ecological balance in the long run. The mean concentration of Ni at S_3 was 7.54 ppb, at S_1 was 1.22 ppb and at S2 was 23.72 ppb. The values reported at site S_2 were significantly higher ($p \le 0.05$) than S1 and S_3. The impact of Ni on micro-crustaceans present in river Saigon was reported to show chronic toxicity.[7], in the present study also Ni level was higher than normal range at S_2 site, which may be due to washing of pharma chemical carrier trucks and dismantling of battery parts in open landfills area. The drinking water is the largest source of arsenic poisoning worldwide and it also affects directly and indirectly human health.8The mean concentration of As at S3 is 4.2 ppb, at S_1 was 0.40 ppb and at S_2 was 11.69 ppb. The difference was statistically significant ($p \le 0.05$) for Sirsa river and higher at S_2 which may be explained as the dissolution of minerals as well as ores in industrial effluents and was found in concurrence with variations reported to induce arsenic related disorders.[9]

Lithium was reported in some rivers of United States in low concentration; also related with present study on Li, the concentration of Li at S_3 was 0.64 ppb, at S_1 was 0.28 ppb and at S_2 was 1.42 ppb; well within permissible limits of US EPA.[10], as well as co-related with global results on Li survey to optimise its impact on ecosystem and city dweller.[11] The disposal of Ni-Cd based batteries, dis-coloured and discarded electronic raw materials guttered into landfills ultimately leached down into water body was reported to cause serious health problems. The mean concentration of Cd at S_3 was 1.14 ppb, at S_1 was 0.08 ppb and at S_2 was 4.23 ppb; it was ($p \le 0.05$) found to be significant statistically as highlighted in Table 1 because Effluent Nallah receives more e-waste water indirectly and can be related with the similar reason for high concentration of Cd in underground water of western Uttar Pradesh area.[12]

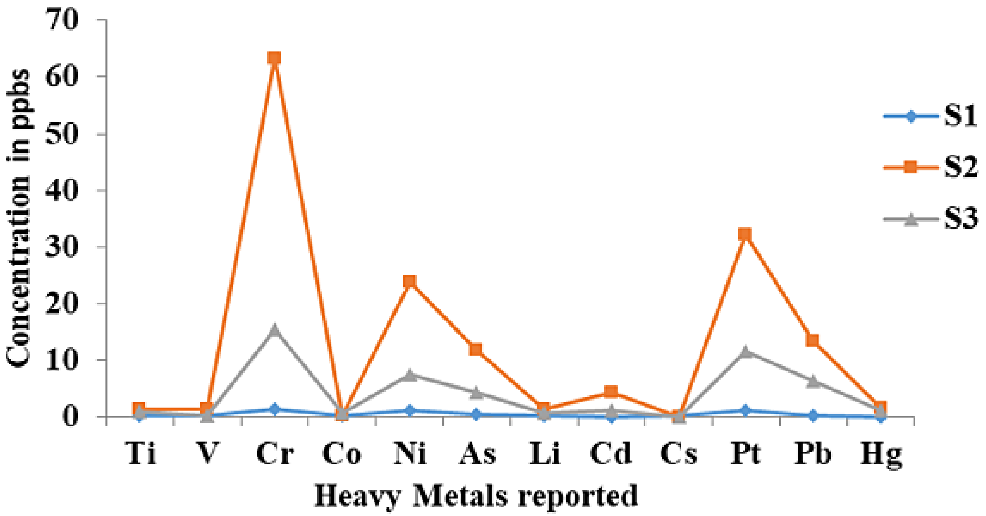

Fig. 3: Graph Showing Concentration of Heavy metals at S_1, S_2 and S_3

The waste water of pharmaceutical industry reported to show deleterious effect on living organisms due to the use of platinum in manufacture of cytostatic drugs.[13] The mean concentration of Pt at S_3 was 11.52 ppb, at S_1 was 1.12 ppb and at S_2 was higher (32.3 ppb) which may be due to agricultural surface run-off or pharmaceutical residues. The similar results were reported in Fukushima city water of Japan contaminated with Cesium as pollutant.[14] and it was also reported to show some effects of low dose of radioactive Cs on animals.[15] The impact of platinum on reproduction inhibition also reported to be high in South Africa near Hex River's vicinity.[16] The most hazardous heavy metal toxicant is Lead which affects oxidative reactions of body to induce haemolytic anemia, affects neurotransmitter level and may also resulted in organ damage.[17] The mean concentration of Pb at S_3 was 6.23 ppb, at S_1 was 0.14 ppb and at S_2 was 13.40 ppb. The reported variation was statistically significant ($p<0.05$) for Sirsa river water at S_2 which may be due to discharge of waste water from industrial units near CETP and plumbing fittings (soldering and due to use of PVC pipes), also found to in concurrence with variation of Lead in ground water system of India.[18] The wastewaters are being generated from various industries such as pulp and paper mill, textile dyeing, chemical, beverages, distillery, battery, electronics, medicine, metal components, and cement etc. in Baddi region, the mean concentration of Hg at S_3 was 1.21 ppb, at S_1 was 0.001 ppb, at S_2 was 1.64 ppb. It may be noted that the open discharge of pharma based effluents in the vicinity of river Sirsa has resulted in mercury pollution related with findings of overdose effects of it on riverine system.[19]

The concentrations of toxic elements at S_2 were in the order: Cr >Ni > Pb> As >Cd >Hg >Li >Ti >V >Co > Cs > Pt respectively, while at S_3, in the order: Cr > Ni > Pb > As >Hg >Cd >Co >Li > Pt >Ti >V > Cs. According to the WHO standard for drinking water the mean values obtained at upstream effluent nallah were found to be in the order: Cr > Ni > As > Ti > V > Li > Pb > Cs > Pt > Co > Cd > Hg in this study. The concentrations of elements found to be within permissible limits of WHO at sites under study for seven metals (Hg, Li, Ti, V, Co, Cs, Pt) but it was higher for five toxic heavy metals (Cr, Ni, Pb, As, Cd) at S_2 only (Fig.3), which may be due to improper installation of common effluent treatment plant on the bank of river Sirsa or due to leakage by tanker carrying waste water from various industrial set ups as these units were not directly linked to CETP. It was also observed that washing of trucks in its vicinity directly pour residual chemical substances into river water and soil in the shoreline area. The present study on heavy metal pollution is strongly in correlation with earlier work as the concentration of Ni and Pb was found to be higher in this industrial belt.[22] and also due to sodicity hazard with high KR value, the water of Sirsa river was reported to be unfit for irrigation.[23] so these sites were committed to act as ultimate gutter to receive all types of industrial pollutants.

In addition, the issue of remedial action against failure of authorities in Himachal Pradesh, in preventing pollution of rivers Balad, Sirsa and Sutlej in Baddi industrial area of Solan was underlined recently. It was found that discharge of toxic industrial pollutants due to leakage from Common Effluent Treatment Plant and discharge of toxic waste as activated pharmaceutical ingredient residues from pharma industries which cannot be treated by CETP and even by ETPs were causing water pollution. This situation is due to lack of finalised draft of standards to be implemented as per state local authority, but regulatory mechanism is such an important issue cannot remain in abeyance for indefinite period. So, it is necessary to address the grievances related to the discharge of untreated or partially treated toxic waste by pharmaceutical industries into water body, which may pose serious damage to environment and public health.

Conclusion

In view of sustainability of aquatic ecosystem, the present area under study lies in foot hills between lentic and lotic habitat needs to be restored as per ecological parameters. The ruthless discharges in to river Sirsa be monitored on scientific lines regularly so that the flow of toxic pollutants at trophic level can be assessed in near future. The elemental analysis in this direction is of prime importance to calculate concentration load of each heavy metal present in the waste water and Sirsa river water to draw a clear line of demarcation for further research and policy implementations. The concrete outcome of the work undertaken is that the high levels of carcinogenic lead and arsenic in Sutlej river's tributary water, flowing down stream towards Ropar district of Punjab, is decreasing the potability of water for various purposes. Hence, the wide array of river restoration programmes are still in dark and doom for sustainability of aquatic ecosystem.

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Conflict of Interest
There is no conflict of interest for this manuscript.

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