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Ion Chromatographic analysis of heavy metals from a glacial fed cold water Himalayan stream, Bhaderwah, J&K, India

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Abstract

Monitoring of heavy metals *viz.*, Copper, Nickel, Zinc, Cobalt and Manganese has been done from 25 stations selected along Neeru stream and its tributaries for two years i.e., Jan 2014- Dec 2015. Ultra trace level analysis have been done on Ion Chromatograph by using Metro Sep C4 150 mm column taking 1.75 mM Oxalic acid and 2 mM Ascorbic acid as eluent and 0.15 mM PAR, 0.4 mM ammonia (25%) and 80 mM nitric acid as post column reagent with UV Visible detection. The observed values of Copper, Nickel, Zinc, Cobalt and Manganese at different sampling stations were found to be in the range BDL-0.199, BDL-0.258, 0.001-0.078, BDL-0.074 and BDL-2.050 ppm, respectively. All the analysed metals were found within the permissible limits except Nickel and Manganese at some stations.

Key Words: ***Heavy metals, Ion chromatography, Permissible limits, Tributaries***

Introduction

Heavy metals are essential elements required for the well being of plants and animals in extremely small amount for proper functioning of biological systems and their deficiency or excess could lead to a number of disorders (Bharti *et al*., 2014). Heavy metals entering the ecosystem in higher concentrations from natural and anthropogenic sources may lead to geo-accumulation, bioaccumulation and biomagnifications. These metals may accumulate to a very high toxic level and cause severe impact on the aquatic organisms without any visible indication (Gupta *et al*., 2009). Therefore, monitoring of environmental concentration of heavy metals is essentially required to have the useful information on the health of a particular ecosystem.

In recent decades accumulation of heavy metals in aquatic systems has received a great attention all over the world and several studies have been carried out on the heavy metals of various lotic water bodies from the state and out of the state (Dhar *et al*., 1989; Kakati and Bhattacharyya, 1990; Madhystha *et al*., 1996; Dwivedi and Tewari, 1997; Naik *et al*., 2000; Ramesh *et al*., 2000; Sinha, 2004; Gaur *et al*.,2005; Gupta *et al*., 2009; Huang *et al*., 2009; Suthar *et al*., 2009; Fotedar *et al*., 2010; Pandey *et al*., 2010; Sekabira *et al*., 2010; Zakir *et al*., 2012; Bharti *et al*., 2014; Obaje *et al*., 2015 and Paudyal *et al*., 2016). However, the detailed study in this regard has not been done on the glacial fed Himalayan cold water streams. Therefore, present study is undertaken to assess the status of heavy metals in the glacial fed Neeru stream.

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Material and Method

Study area

The present study has been carried on Neeru stream which is an important left bank glacial fed perennial tributary of the river Chenab that originates from Kaplash Kund (4200 m a.s.l.) and equally contributed by Ashapati glacier. It drains the Neeru watershed and finally joins the river Chenab at Pul Doda (850 m a.s.l.) in the Bhaderwah Tehsil of District Doda of Jammu and Kashmir (Figure 1). During downstream journey, it experience great climatic variation from temperate snow laden mountains in the upper reaches of Kaplash Kund and Ashapati glacier to almost dry subtropical climate at Pul Doda. The valley also has a unique and diverse ecosystem with rich diversity and density of both flora and fauna.

Sampling Stations

For monitoring the water quality with respect to selected heavy metals, water samples have been

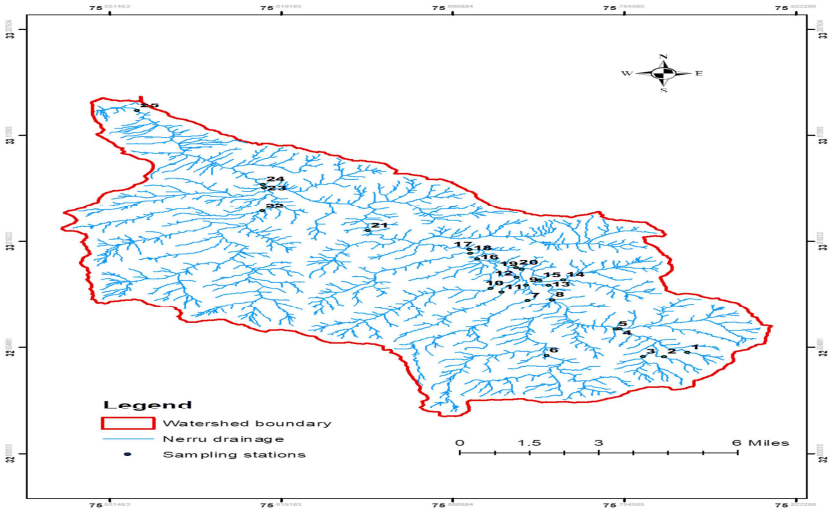

Figure 1: Map of the study area showing watershed boundary, drainage and different sampling stations.

Table 1: Details of the different sampling stations.

S. No.	Station Name	Station Code	Geo-Coordinates	Altitude (in meters)
1.	Thanallah I	ST-1a	32^0 55' 13.3" N 75^0 46' 46.6" E	2240
2.	Thanallah II	ST-1b	32^0 54' 59.8" N 75^0 46' 13.5" E	2184
3.	Thanallah III	ST-1c	32^0 54' 59.9" N 75^0 45' 43.4" E	2156
4.	Bheja I	ST-1d	32^0 56' 28.5" N 75^0 45' 10.5" E	1823
5.	Bheja II	T-1	32^0 56' 27.6" N 75^0 45' 04.7" E	1815
6.	Thanthera	MC-1	32^0 55' 03.0" N 75^0 43' 26.5" E	2163
7.	Puneja	T-2a	32^0 58' 01.2" N 75^0 42' 59.4" E	1733
8.	Dareja	MC-2	32^0 58' 03.2" N 75^0 43' 34.4" E	1683
9.	Dharampura	T-2b	32^0 58' 49.4" N 75^0 42' 57.4" E	1638
10.	Launcher Morh	ST-3a	32^0 58' 39.7" N 75^0 42' 07.1" E	1682
11.	Hallayan	ST-3b	32^0 58' 27.5" N 75^0 42' 22.6" E	1700
12.	College link Road	T-3	32^0 59' 15.1" N 75^0 42' 44.0" E	1572
13.	Gupt Ganga	MC-3	32^0 58' 49.5" N 75^0 43' 29.2" E	1628
14.	Atalgarh	T-4	32^0 59' 06.6" N 75^0 43' 50.1" E	1636
15.	Renda	MC-4	32^0 59' 05.2" N 75^0 43' 16.2" E	1553
16.	Domail	MC-6	33^0 00' 13.3" N 75^0 41' 47.6" E	1467
17.	Amira Nagar	MC-7	33^0 00' 43.1" N 75^0 41' 37.2" E	1423
18.	Hanga Nallah	T-5	33^0 00' 30.8" N 75^0 41' 37.9" E	1480
19.	Sarol Bagh I	T-2c	32^0 59' 40.3" N 75^0 42' 51.0" E	1521
20.	Sarol Bagh II	MC-5	32^0 59' 45.3" N 75^0 42' 43.2" E	1510
21.	Dhrudu	MC-8	33^0 01' 43.4" N 75^0 39' 12.3" E	1334
22.	Mallothi	T-6a	33^0 02' 46.9" N 75^0 36' 42.3" E	1357
23.	Bhalla I	T-6b	33^0 04' 02.3" N 75^0 36' 45.1" E	1202
24.	Bhalla II	MC-9	33^0 04' 12.9" N 75^0 36' 43.3" E	1185
25.	Galgander	MC-10	33^0 08' 07.5" N 75^0 33' 44.4" E	863

ST= Sub tributary,T= Tributary,MC= Main Channel/Stream

Table 2: Average monthly variation of heavy metal concentrations at different stations

Months / Heavy metals	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
	Station 1											
Copper (ppm)	0.002	BDL	BDL	0.001	0.035	0.002	0.007	0.004	0.004	0.003	0.002	0.001
Nickel (ppm)	BDL	BDL	BDL	0.003	BDL	BDL	0.004	0.001	0.003	0.001	0.002	0.027
Zinc (ppm)	0.012	0.011	0.015	0.016	0.020	0.017	0.013	0.012	0.012	0.009	0.009	0.070
Cobalt (ppm)	0.002	0.001	BDL	BDL	0.008	0.001	0.001	0.004	0.004	0.002	0.003	0.017
Manganese (ppm)	0.184	0.138	0.092	BDL	BDL	BDL	BDL	BDL	BDL	0.188	0.376	0.539
	Station 2											
Copper (ppm)	0.002	0.003	BDL	0.014	0.012	BDL	0.009	BDL	BDL	BDL	0.001	0.049
Nickel (ppm)	0.008	0.003	BDL	0.019	0.012	0.004	0.009	0.001	BDL	BDL	0.002	0.045
Zinc (ppm)	0.027	0.031	0.033	0.031	0.023	0.021	0.013	0.008	0.008	0.007	0.005	0.022
Cobalt (ppm)	0.008	BDL	BDL	0.011	0.010	0.001	0.003	BDL	BDL	0.001	0.001	0.007
Manganese (ppm)	0.501	0.261	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.626	0.750	0.529
	Station 3											
Copper (ppm)	BDL	BDL	BDL	0.002	BDL	BDL	0.002	BDL	BDL	BDL	0.005	0.009
Nickel (ppm)	0.001	BDL	0.001	0.016	0.002	0.003	0.002	BDL	0.001	BDL	BDL	0.018
Zinc (ppm)	0.014	0.013	0.013	0.013	0.0095	0.008	0.011	0.007	0.005	0.004	0.0025	0.005
Cobalt (ppm)	0.004	BDL	BDL	0.001	BDL	BDL	BDL	BDL	BDL	BDL	0.001	0.014
Manganese (ppm)	0.990	0.667	0.333	0.167	BDL	BDL	BDL	0.461	0.344	0.227	0.316	0.231
	Station 4											
Copper (ppm)	BDL	BDL	BDL	0.001	BDL	BDL	BDL	BDL	BDL	BDL	0.001	0.005
Nickel (ppm)	BDL	BDL	BDL	BDL	0.00	BDL	BDL	BDL	BDL	BDL	0.005	0.005
Zinc (ppm)	0.006	0.005	0.005	0.005	0.005	0.006	0.009	0.008	0.007	0.005	0.005	0.005
Cobalt (ppm)	0.001	BDL	BDL	BDL	BDL	0.001	BDL	0.001	0.001	BDL	0.005	0.003
Manganese (ppm)	0.699	0.524	0.349	BDL	BDL	BDL	BDL	0.302	0.326	1.003	1.153	1.418
	Station 5											
Copper (ppm)	0.001	0.002	0.002	0.002	BDL	0.004	0.004	0.003	0.002	0.001	0.003	0.199
Nickel (ppm)	0.002	0.005	BDL	BDL	BDL	BDL	0.004	BDL	0.003	0.004	0.002	0.258
Zinc (ppm)	0.006	0.005	0.005	0.005	0.006	0.005	0.006	0.005	0.005	0.006	0.007	0.033
Cobalt (ppm)	BDL	BDL	BDL	0.002	BDL	BDL	BDL	BDL	BDL	0.001	0.002	0.011
Manganese (ppm)	0.568	0.293	0.147	0.073	BDL	BDL	BDL	0.124	0.295	0.803	0.549	1.612
	Station 6											
Copper (ppm)	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.075
Nickel (ppm)	0.01	BDL	BDL	0.012	BDL	0.001	BDL	BDL	BDL	BDL	0.099	0.018
Zinc (ppm)	0.003	0.003	0.006	0.002	0.006	0.002	0.004	0.003	0.002	0.001	0.002	0.003
Cobalt (ppm)	0.002	BDL	BDL	0.003	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.009

Manganese (ppm)	0.516	0.258	BDL	0.516	BDL	BDL	BDL	0.267	0.724	0.802	0.880	1.347
	Station 7											
Copper (ppm)	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.006
Nickel (ppm)	0.011	BDL	BDL	0.026	BDL	0.001	BDL	BDL	BDL	BDL	BDL	0.035
Zinc (ppm)	0.002	0.003	0.004	0.004	0.006	0.004	0.005	0.006	0.007	0.007	0.008	0.008
Cobalt (ppm)	BDL	BDL	BDL	0.004	BDL	BDL	BDL	BDL	0.001	0.001	0.002	0.009
Manganese (ppm)	1.346	0.524	BDL	BDL	BDL	BDL	BDL	BDL	0.477	0.747	1.216	1.530
	Station 8											
Copper (ppm)	BDL	BDL	BDL	0.001	BDL	0.024	BDL	BDL	BDL	BDL	BDL	0.004
Nickel (ppm)	BDL	BDL	BDL	0.007	0.001	BDL	BDL	0.002	0.001	0.002	0.006	0.042
Zinc (ppm)	0.005	0.004	0.003	0.003	0.075	0.003	0.005	0.003	0.002	0.003	0.003	0.003
Cobalt (ppm)	0.002	BDL	BDL	0.001	BDL	BDL	BDL	BDL	BDL	BDL	0.002	0.008
Manganese (ppm)	1.156	0.399	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.580	1.191	1.702
	Station 9											
Copper (ppm)	0.001	0.003	BDL	0.002	BDL	BDL	BDL	0.002	0.002	0.001	BDL	0.001
Nickel (ppm)	BDL	BDL	BDL	0.003	BDL	BDL	BDL	0.001	0.003	0.001	BDL	0.053
Zinc (ppm)	0.009	0.006	0.006	0.004	0.046	0.002	0.002	0.004	0.004	0.005	0.005	0.067
Cobalt (ppm)	BDL	BDL	BDL	BDL	BDL	BDL	0.002	0.006	0.007	0.002	0.003	0.015
Manganese (ppm)	0.838	0.583	0.456	0.329	BDL	BDL	BDL	0.179	0.747	0.834	1.206	1.460
	Station 10											
Copper (ppm)	BDL	BDL	BDL	0.006	BDL	0.003	0.005	BDL	BDL	BDL	BDL	BDL
Nickel (ppm)	BDL	BDL	BDL	0.010	BDL	BDL	0.005	BDL	BDL	BDL	BDL	0.044
Zinc (ppm)	0.006	0.005	0.004	0.006	0.013	0.001	0.002	0.002	0.003	0.002	0.001	0.007
Cobalt (ppm)	BDL	BDL	BDL	0.001	0.007	BDL	0.001	BDL	BDL	BDL	0.001	0.007
Manganese (ppm)	1.608	0.804	0.402	BDL	BDL	BDL	BDL	0.349	0.577	0.663	0.786	1.620
	Station 11											
Copper (ppm)	BDL	BDL	BDL	0.003	0.019	BDL	0.025	BDL	BDL	BDL	BDL	0.027
Nickel (ppm)	BDL	BDL	BDL	BDL	BDL	BDL	0.025	0.009	BDL	0.003	0.005	0.010
Zinc (ppm)	0.005	0.006	0.006	0.008	0.031	0.018	0.022	0.013	0.006	0.004	0.003	0.031
Cobalt (ppm)	BDL	BDL	BDL	BDL	BDL	0.001	0.008	0.001	BDL	BDL	0.002	0.007
Manganese (ppm)	1.640	0.956	0.883	0.783	0.252	0.032	0.362	0.624	0.817	1.200	1.438	1.841
	Station 12											
Copper (ppm)	0.001	0.002	0.004	0.003	BDL	BDL	BDL	0.006	0.001	0.007	BDL	0.013
Nickel (ppm)	BDL	BDL	BDL	0.009	BDL	BDL	BDL	0.005	0.002	0.009	0.028	0.024
Zinc (ppm)	0.003	0.003	0.003	0.003	0.016	0.010	0.007	0.025	0.043	0.060	0.078	0.012
Cobalt (ppm)	0.001	0.001	BDL	0.002	BDL	BDL	BDL	0.007	0.005	0.01	0.074	0.004
Manganese (ppm)	0.972	0.850	0.729	0.569	0.347	0. 141	0.093	0.192	0.699	1.262	1.581	2.050

	Station 13											
Copper (ppm)	BDL	BDL	BDL	BDL	BDL	BDL	0.001	0.003	BDL	0.004	0.001	0.011
Nickel (ppm)	0.002	0.006	BDL	0.011	0.002	0.003	0.002	0.005	0.003	0.002	0.003	0.042
Zinc (ppm)	0.005	0.008	0.004	0.027	0.006	0.005	0.010	0.013	0.013	0.013	0.013	0.004
Cobalt (ppm)	0.001	BDL	BDL	0.012	BDL	BDL	0.002	BDL	BDL	BDL	0.003	0.01
Manganese (ppm)	1.218	0.552	0.486	0.669	BDL	BDL	BDL	0.390	0.779	1.059	1.169	1.579
	Station 14											
Copper (ppm)	0.001	BDL	BDL	BDL	BDL	0.003	0.006	BDL	BDL	BDL	BDL	BDL
Nickel (ppm)	0.002	BDL	BDL	0.014	BDL	BDL	0.004	BDL	BDL	BDL	BDL	0.041
Zinc (ppm)	0.005	0.003	0.004	0.008	0.005	0.003	0.007	0.007	0.008	0.008	0.009	0.054
Cobalt (ppm)	0.001	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.003	0.025
Manganese (ppm)	0.721	0.335	0.259	0.090	BDL	0.029	0.090	0.316	0.378	0.606	0.792	0.762
	Station 15											
Copper (ppm)	BDL	BDL	BDL	0.002	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Nickel (ppm)	BDL	BDL	0.005	BDL	BDL	0.003	BDL	BDL	BDL	BDL	0.006	0.04
Zinc (ppm)	0.003	0.022	0.011	0.004	0.006	0.012	0.005	0.006	0.009	0.010	0.015	0.029
Cobalt (ppm)	BDL	BDL	BDL	BDL	BDL	0.003	0.001	BDL	0.001	0.002	0.004	0.005
Manganese (ppm)	0.732	0.244	0.239	0.222	BDL	0.010	0.028	0.124	1.398	1.102	1.316	1.671
	Station 16											
Copper (ppm)	BDL	BDL	BDL	0.038	BDL	BDL	BDL	BDL	BDL	BDL	0.007	0.002
Nickel (ppm)	0.03	BDL	0.002	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.001	0.008
Zinc (ppm)	0.027	0.022	0.018	0.002	0.003	0.006	0.004	0.004	0.005	0.009	0.009	0.019
Cobalt (ppm)	0.014	BDL	0.003	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.002	0.007
Manganese (ppm)	1.266	0.613	0.707	0.241	BDL	0.661	0.163	0.179	0.761	1.044	1.149	1.474
	Station 17											
Copper (ppm)	BDL	BDL	BDL	0.001	BDL	BDL	0.003	BDL	BDL	BDL	BDL	0.005
Nickel (ppm)	0.007	BDL	0.001	0.004	BDL	BDL	0.003	BDL	BDL	BDL	0.001	0.007
Zinc (ppm)	0.013	0.010	0.010	0.007	0.005	0.004	0.002	0.003	0.004	0.005	0.007	0.008
Cobalt (ppm)	0.003	BDL	BDL	0.001	BDL	BDL	BDL	BDL	BDL	BDL	0.003	0.016
Manganese (ppm)	1.219	1.048	0.171	0.074	BDL	BDL	0.067	0.638	0.803	0.961	1.561	1.764
	Station 18											
Copper (ppm)	BDL	BDL	BDL	BDL	BDL	BDL	0.004	BDL	BDL	BDL	BDL	0.016
Nickel (ppm)	0.002	BDL	BDL	BDL	BDL	BDL	0.004	BDL	BDL	BDL	0.001	0.021
Zinc (ppm)	0.007	0.007	0.008	0.005	0.009	0.003	0.002	0.003	0.005	0.008	0.007	0.003
Cobalt (ppm)	0.004	BDL	BDL	BDL	0.002	BDL	BDL	BDL	BDL	0.001	0.004	0.007
Manganese (ppm)	1.262	1.131	0.697	BDL	BDL	BDL	0.211	1.808	0.454	0.938	1.373	1.517
	Station 19											
Copper (ppm)	0.001	0.002	BDL	BDL	BDL	0.003	0.004	0.002	0.003	0.002	0.001	BDL
Nickel (ppm)	BDL	BDL	0.001	0.082	BDL	BDL	0.004	0.003	0.001	0.003	0.001	0.001
Zinc (ppm)	0.004	0.006	0.006	0.017	0.007	0.003	0.002	0.006	0.005	0.006	0.008	0.003
Cobalt (ppm)	0.014	BDL	BDL	0.004	BDL	BDL	BDL	0.001	0.005	0.005	0.001	0.002

Manganese (ppm)	1.331	0.891	0.611	0.471	BDL	BDL	BDL	0.450	0.629	1.083	1.538	1.604
	Station 20											
Copper (ppm)	BDL	BDL	BDL	BDL	0.023	BDL	BDL	BDL	BDL	BDL	0.019	0.006
Nickel (ppm)	BDL	0.004	BDL	BDL	0.032	BDL	BDL	BDL	BDL	BDL	0.005	BDL
Zinc (ppm)	0.005	0.008	0.005	0.009	0.026	0.017	0.002	0.006	0.008	0.006	0.004	0.006
Cobalt (ppm)	0.003	BDL	BDL	0.002	0.009	BDL	BDL	BDL	BDL	BDL	BDL	0.002
Manganese (ppm)	1.647	0.988	0.238	0.119	BDL	BDL	0.351	0.477	1.053	1.241	1.394	1.840
	Station 21											
Copper (ppm)	BDL	BDL	BDL	0.002	BDL	BDL	0.041	BDL	BDL	BDL	BDL	0.005
Nickel (ppm)	BDL	BDL	0.002	0.003	BDL	BDL	0.041	BDL	0.005	BDL	0.002	BDL
Zinc (ppm)	0.010	0.013	0.005	0.006	0.014	0.019	0.023	0.010	0.007	0.008	0.004	0.004
Cobalt (ppm)	0.003	BDL	BDL	0.002	BDL	BDL	0.014	0.001	BDL	BDL	BDL	0.002
Manganese (ppm)	1.669	1.572	1.286	0.643	BDL	BDL	BDL	0.316	1.044	1.489	1.578	1.860
	Station 22											
Copper (ppm)	0.001	BDL	0.001	BDL	BDL	0.004	0.006	BDL	BDL	BDL	BDL	0.003
Nickel (ppm)	0.002	BDL	BDL	0.042	BDL	0.007	0.006	BDL	BDL	BDL	BDL	0.003
Zinc (ppm)	0.006	0.008	0.004	0.004	0.010	0.008	0.012	0.006	0.006	0.004	0.005	0.006
Cobalt (ppm)	BDL	0.001	BDL	0.001	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.001
Manganese (ppm)	1.694	0.664	0.332	0.166	BDL	0.191	0.289	0.723	0.929	1.258	1.587	1.636
	Station 23											
Copper (ppm)	BDL	0.001	BDL	BDL	BDL	BDL	0.007	0.003	0.005	0.002	0.001	0.002
Nickel (ppm)	BDL	BDL	BDL	BDL	BDL	BDL	0.007	BDL	BDL	BDL	0.002	0.002
Zinc (ppm)	0.007	0.007	0.005	0.004	0.005	0.003	0.008	0.006	0.007	0.004	0.005	0.002
Cobalt (ppm)	0.001	BDL	BDL	0.001	BDL	0.001	BDL	BDL	BDL	0.001	BDL	0.001
Manganese (ppm)	1.980	0.985	0.790	0.293	BDL	BDL	BDL	0.344	0.696	1.097	1.347	1.562
	Station 24											
Copper (ppm)	BDL	BDL	BDL	BDL	BDL	BDL	0.005	BDL	BDL	BDL	0.005	BDL
Nickel (ppm)	BDL	BDL	BDL	BDL	BDL	BDL	0.005	0.003	0.003	0.001	0.003	0.001
Zinc (ppm)	0.009	0.008	0.007	0.004	0.005	0.003	0.004	0.004	0.002	0.003	0.004	0.005
Cobalt (ppm)	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.004
Manganese (ppm)	1.258	0.851	0.526	0.063	BDL	BDL	BDL	0.244	0.686	1.128	1.269	1.511
	Station 25											
Copper (ppm)	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.003	0.001
Nickel (ppm)	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.003	0.001
Zinc (ppm)	0.004	0.004	0.004	0.002	0.007	0.004	0.003	0.004	0.003	0.002	0.002	0.005
Cobalt (ppm)	0.002	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.001	0.004
Manganese (ppm)	1.494	1.004	0.522	0.443	BDL	BDL	BDL	0.392	0.447	0.869	1.090	1.310

BDL- below detection limits

All values of the given parameters are average of two years (Jan 2014- Dec 2015)

collected for 2 years (Jan 2014- Dec 2015) on monthly basis from different 25 stations which were identified all along the Neeru stream and its tributaries (Table 1). For recording the coordinates and altitude of different monitoring stations Garmin, Montana 680 (GPS) has been used. For each tributary, sampling was done from two points viz., 200 metres before its confluence with the main stream and 200 meters after the confluence, to monitor the effect of that particular micro watershed on water quality of the stream.

Methodology

i) Chemicals and Reagents

Eluent: 1.75 millimolar (mM) oxalic acid and 2 mM ascorbic acid solution was prepared using ultrapure water (Metrohm, Application Work AW IN6-0975 IC -122009).

PCR reagent: Post column reagent was prepared using 0.15 mM PAR (4-(2-Pyridylazo) resorcinol), 0.4 mM ammonia (25%) and 80 mM nitric acid.

Standards: heavy metal IC standards for Copper, Nickel, Zinc, Cobalt and Manganese of 1000 mg/l manufactured by Sigma-Aldrich (Fluka) were used for system calibration.

Ultrapure water: Ultrapure water was prepared using Millipore (DirectQ-3 with pump).

ii) Instrument

Metrohm Ion Chromatograph system (model 850 professional) integrated with Compact Autosampler (model 863) through a computer system has been used for analysis.

iii) Analysis

Samples were prepared using 1:10 dilution factor (i.e., one ml of sample was raised to 10ml using ultrapure water) to avoid saturation of the column in case of polluted samples. Properly marked sample vials were arranged in the Auto sampler for analysis. Information about the sample identification and position was entered in the determination series in the workplace of the MagIC Net software of the IC system. 0.9 mL/min of flow rate and 8.55 MPa pressure was maintained in Metrosep C4, column. Loop size of 20 µL was used for sample injection. UV detector capable of trace level analysis was used at 520 nm absorbance during the analysis. Calibration of the system was done using 1 ppm, 2 ppm and 5 ppm concentrations of heavy metal IC standards of Cu, Ni, Zn, Co and Mn. After scheduled recording time of 15 minutes results were obtained in the Database of MagIC Net software. The results were reprocessed using 1 ppm standard to phase out any errors in the retention time and percentage window for analyte under consideration.

Table 3: BIS drinking water acceptable and permissible limits for analysed heavy metals

S.No.	Water Quality Parameter	BIS	
		Acceptable Limit	Permissible Limit
1.	Copper (mg/l)	0.05	1.5
2.	Nickel (mg/l)	0.02	No relaxation
3.	Zinc (mg/l)	5.0	15
4.	Cobalt (mg/l)	*	*
5.	Manganese (mg/l)	0.1	0.3

* Acceptable and permissible limits for Cobalt not available.

Table 4: Correlation analysis of heavy metals among all sampling stations.

Heavy metals	Cu (ppm)	Ni (ppm)	Zn (ppm)	Co (ppm)	Mn (ppm)
Cu (ppm)	1				
Ni (ppm)	**0.65***	1			
Zn (ppm)	**0.91***	**0.72***	1		
Co (ppm)	**0.77***	**0.66***	**0.79***	1	
Mn (ppm)	0.08	0.47	0.40	0.45	1

*Statistically significant positive relationships, $p < 0.05$.

Result and Discussion

Average data of two years (Jan 2014- Dec 2015) on monthly variation of heavy metals for different stations on the Neeru stream and its tributaries is represented in the Table 2. Acceptable and permissible limits of various analysed heavy metals as per BIS have been listed in the Table 3. Perusal of table 2 revealed that the values of Copper (Cu), Nickel (Ni), Zinc (Zn), Cobalt (Co) and Manganese (Mn) were in the range of BDL-0.199, BDL-0.258, 0.001-0.078, BDL-0.074 and BDL-2.050 ppm, respectively. Values of Zn were found to be within acceptable and permissible limits as per the Bureau of Indian Standards (BIS) for drinking waters (2012). Concentration of Cu were observed to be above acceptable limits at station 5 and 6 in December while in rest of the period and stations its value remained within permissible limits or below detection level. However, concentrations of Nickel exceeds above acceptable and permissible limits at 16 stations (stations 1, 4, 6 to 15, 18 to 21) mostly during the month of December while in some of the stations during the months of April, May, July and November. The concentration of Manganese exceeded the limits in almost all the stations during January-February and September to December when there is low flow condition. Acceptable and permissible limits of Co have not been given in BIS drinking water specifications. In the present study, atmospheric deposition as source of heavy metals in Neeru water as suggested by Pandey *et al*., (2010) has been ruled out because of absence of industrial establishments in the study area. Therefore, the most probable source of heavy metals in the stream water is parent soil /rock weathering in the catchment area. Ramesh *et al*., (2000); Fotedar *et al*., (2010); Obaje *et al*., (2015) and Paudyal *et al*., (2016) has also suggested the geological origin of heavy metals in the stream water. Watershed of River Chenab has been reported to have rich pockets of Fe, Ni and Mn in the rocks- phyllites and slates (Wadia, 1970; Fotedar *et al*., 2010). Abundance of Phyllites and slates in the Neeru watershed, which is a part of Chenab watershed, might have contributed for the higher concentrations of Ni and Mn in the Neeru stream. During the present investigation, majority of the sampling stations with higher concentrations of the Ni has been observed to be located in and around Bhaderwah town. Thus, anthropogenic contribution for the higher concentration of Ni cannot be ruled out, which however need further investigations. Higher concentration of Nickel and Manganese has also been reported in river Chenab by Fotedar *et al*., (2010). Among studied heavy metals there is no considerable monthly as well as seasonal variations except for Manganese which exhibited maximum average values for all stations during December while minimum values has been recorded in the month of June. Seasonally, the higher concentrations have been observed during winters whereas lower concentrations have been recorded during summers. Correlation analysis revealed that there is significant positive relationship between Copper and Nickel, $r(10) = 0.65$; Copper and Zinc, $r(10) = 0.91$; Copper and Cobalt, $r(10) = 0.77$; Nickel and Zinc, $r(10) = 0.72$; Nickel and Cobalt, $r(10) = 0.66$ and Zinc and Cobalt, $r(10) = 0.79$ at $p < 0.05$ at all stations (Table 4). This suggests that each pair of metals exhibiting significant positive relationship have similar source or chemical process (Sekabira *et al*., 2010).

Conclusion

Analysed metals *viz.,* Copper, Zinc and Cobalt were within the permissible limits of BIS whereas values of Nickel at some stations and Manganese at most of the stations have been found to be above permissible limits of BIS. Higher concentrations of Nickel and Manganese are attributed to the rich pockets of nickel and Manganese in the phyllite and slate present in the catchment area.

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