Physical Fractionation of Trace Metals in Surface Sediments of the Pandoh Lake, Lesser Himalaya, India

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ABSTRACT

The seasonal variation during monsoon (August, 2004), winter (January, 2005) and summer (May, 2005) in concentration and distribution of the trace metals (Cd, Co, Cu, Fe, Mn, Ni, Pb, and Zn) were investigated in surface sediments and in different grain size fractions of the Pandoh Lake located in the Lesser Himalayan region, Mandi district of Himachal Pradesh State of India. The seasonal variations were attributed to the influence of biological activities, geological/mineralogical changes and anthropogenic activities. The cadmium, Co and Zn were high in bunch of <63 µm size fractions while Cu, Fe, Mn, Ni, and Pb were significantly higher in all the grain size fractions (> 250 µm to <63 µm) in all the seasons, suggest the operation of complex biogeochemical processes operating in the study area. The enrichment factor (EF) for surface sediments revealed that Cd and Co emerged as a pollution threat to the existing biodiversity of the Pandoh Lake. The seasonal trends of I_{geo} value for the Pandoh Lake surface sediments also showed that Cd and Co are metal pollutants in the Pandoh Lake with geoaccumulation rating of 4 and 1, respectively, in the monsoon season.

INTRODUCTION

Mountains as "Water Towers" play an important role for the surrounding lowlands. In recent years, high mountain lakes in Himalayan region are highly polluted due to increasing anthropogenic pressure mainly modern agriculture practices, infrastructure developments, tourism and urbanization, and growth of mountain cities (Anshumali and Ramanathan, 2007). These man made activities ultimately affect the pristine natural water bodies. Worldwide, more than 700 million people live in mountain areas, of these, 625 million are in developing countries (Anshumali, 2006). They are directly and/or indirectly overusing mountain ecosystems. Consequently, they have negative effects on the environment especially on water resources. This study on metals distribution is one step to understand the ongoing natural and human processes and their impact on the biogeochemistry of this high altitude lake structure and function.

STUDY AREA

Pandoh Lake is a beautiful rectangular shaped high altitude lake surrounded by Shivalik Mountains located at about 21 km from Mandi district (Fig. 1). It is situated an

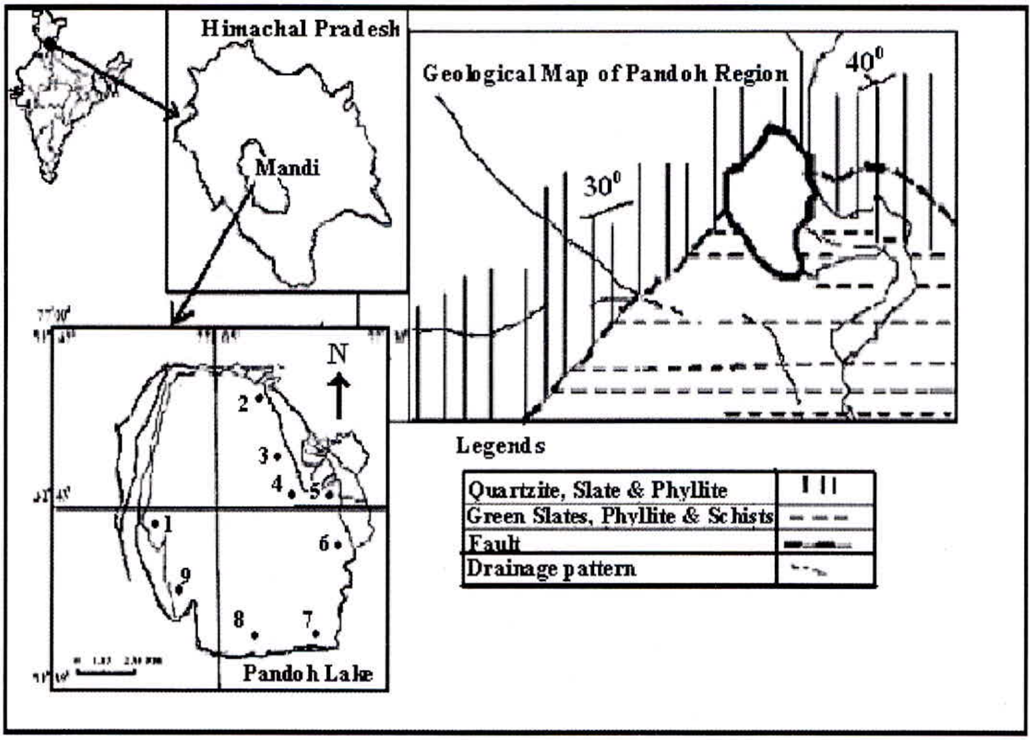

Fig. 1 (a) Pandoh Lake with surface sediment sampling sites. (b) Geological Map showing drainage and lithology around Pandoh Lake.

elevation of 899 m and bound by 30°40' N latitude and 77°50' E longitude. The lake follows a strait and broad course between three steep hill slopes. The sources of water to the lake are watershed, atmospheric inputs and base flow. The maximum length of Pandoh is 2134 m and its maximum width is 457 m. Its average depth is 15.58 m. The catchment's area is 134 hectare. For the generation of hydroelectric power an earth-rock fill dam has constructed. The weather condition of the Pandoh region is given in Table 1. The Pandoh Lake lies entirely in the rock of Chail series (Fig 1), which consists of mainly phyllites and slates. In catchment's region, interbedded Chail phyllites and quartzite are exposed. The phyllites are grayish white to dark grey in colour with suspect magnetite. The Pandoh-Larji syncline of Auden and a wide belt of granite are emplaced in the folded Chail series (Auden, 1934). The Chail series is dissected by number of sub parallel faults Bnaik, Lindi Khad, Bobri. In view of the structural complexity of the area and the overall tectonic and seismic character of the Himalayas, the region has been included in the seismic zoning map of India that put the Mandi district in a "Very High Risk Zone-V" (Mathur, 2002). This region comprises of sub-montane, hills and tarai soils. These soils occurring in this region are formed from parent rocks such as sandstones, gray micaceous sandstones and shales of sub-Himalayan region. These soils are loam to silty loam and medium to high in organic matter and poor in available nutrients (Kaushal et al., 1978). The most abundant mineral identified in the study area is quartz (26-57%); secondary minerals identified are kaolinite, biotite, goethite and calcite and to some extent gypsum (Anshumali, 2006).

Table 1 : Average daily rainfall (mm), temperature (^{0}C) and relative humidity (%) in the study area.

Parameters	June 2004	July 2004	Aug 2004	Sep 2004	Oct 2004	Nov 2004	Dec 2004	Jan 2005	Feb 2005	Mar 2005	Apr 2005	May 2005
Season	Summer	Monsoon				Winter				Summer		
Rain fall	4.5	6.5	9.8	2.0	3.2	0	0.5	2.1	3.6	1.4	0.2	0.9
Temp Min	20.2	20.5	19.6	17.8	11.7	6.3	3.4	2.9	5.2	9.9	14.9	17.8
Temp Max	22.4	22.6	22	19.7	13.2	8.6	5.3	4.0	6.1	11.7	16.7	19.6
% Humidity	79.7	83.5	88.2	82.5	81.2	79.2	80.0	83.3	78.3	79.8	72.5	73.0

MATERIALS AND METHODS

The field observations of the Pandoh Lake were undertaken in 2004-2005. Surface sediment samples were taken in August-2004 (monsoon), January-2005 (winter) and May-2005 (summer). The sampling sites are shown in Fig. 1. Nine grab surface sediments samples (top 2 cm) were collected from water-sediment interface in each season. These samples were collected in such a way that lake area was properly covered. The samples were stored in portable icebox to minimize the chemical alterations.

To obtain silt and clay fraction from bulk samples, size separation for the samples was carried out in laboratory following the standard sieving and sedimentation method (Ingram, 1970). Samples were air-dried then oven dried at 60 °C for 24 hours. Further, thoroughly homogenized by corning and quartering technique (Ingram, 1970). The samples were sieved on an electrically controlled electromagnetic sieve shaker (Frisch Analysette-3) into 250 mm, 125 mm and <63 mm grain size fractions. This step was followed by separation of clay fraction (<2 mm) from <63 mm grain size particles by Atternburg Cylinder method, which is based on Stoke'^{s} law (Griffiths, 1967).

In order to assess the influence of metals in the Pandoh Lake, the enrichment factor (EF) calculated for each metal in the surface sediments using the formula:

$$EF = (C_x/C_{Al})_s / (C_s/C_{Al})_c$$

Where C_x and C_{Al} refer to the concentration of element X and Al in the surface sediments (s) and earth's crust (c), respectively. Aluminum is used is used here as reference element.

A quantitative measure of the extent of pollution in the Pandoh Lake was calculated from the heavy metal concentration in the surface sediments using the method of Muller (1979), which is known as the Index of Geoaccumulation (I_{geo}).

$$I_{geo} = \log_2 (C_n/1.5\ B_n)$$

Where, C_n is the measured concentration of the heavy metal 'n' in the surface sediments and B_n is the geochemical background value in fossil argillaceous sediments (average shale).

RESULT AND DISCUSSION

Surface sediments of Pandoh Lake were mainly made up of silt and clays with lesser amount of sand. They were characterized by high contents of the finest fractions [generally greater than 60 % of sediment size less than 63 µm] (Table 2). The % organic matter (%OM) was high in the winter (4.78 %) followed by 2.49 % in the summer and 1.79% in the monsoon (Table 2).

The results obtained by acid digestion for total metal content of the Pandoh Lake are given in Table 2. The dominant trace metals are Mn, and Ni followed by Zn, Co, Cu and Cd in surface sediments. Based on concentrations of trace metals the Co is abundant

Table 2: Characteristics of surface water (n=25) and surface sediments (n=9) in Pandoh Lake. Concentrations of elements in [mg/g]; TDS and DO in mg l^{-1}; ORP in [mV]; EC in [µs cm^{-1}].

Pandoh Lake							
Season		Monsoon		Winter		Summer	
	Variable	Range	Avg±SD	Range	Avg±SD	Range	Avg±SD
Water	TDS	10-60	28.08±9.60	30-90	68.88±17.63	30-100	53.20±16.76
	ORP	115-146	135.12±6.70	111-138	128.88±7.85	145-177	169.48±7.79
	EC	40-90	52.68±9.24	100-130	118.12±6.64	60-120	71.60±17.00
	DO	8.42-9	8.75±0.12	4.1-9.1	7.75±1.03	7.21-8.84	8.08±0.46
	pH	6-6.77	6.26±0.18	7.17-8.83	7.79±0.42	5.89-7.78	7.35±0.45
Surface sediment	%OM	1.60-2.17	1.79±0.20	4.35-5.26	4.78±0.30	2.22-2.82	2.49±0.20
	% Silt&Clay	46-67	54.77±6.45	66-82	74.66±4.69	60-71	65.22±3.30
	Cd	1.1-6.2	3.2±1.59	2.8-4.5	3.5±0.56	2.1-5.6	3.8±1.11
	Co	12.2-28.3	22.4±5.34	17.2-26.2	20.0±2.25	11.2-16.0	13.2±1.63
	Cu	8.1-14.2	10.1±1.99	10.2-20.1	13.8±2.89	12-24.1	17.9±4.15
	Fe	4574-6480	5472±676.01	3609-4921	4120±477.69	4121-6320	5599.11±869.31
	Mn	489.2-802.1	592.8±95.9	640.2-910.5	779.5±274.57	170.2-428	257±79.25
	Ni	21.8-46.1	36.8±7.18	23.9-45.1	37.6±8.77	16.2-36.2	26±7.23
	Pb	3.10-8.70	6.40±2.03	7.50-12.10	9.67±2.07	12.10-14.20	13.30±0.74
	Zn	20.1-26.1	23.2±1.80	16.9-47.1	28.3±8.38	18.1-35.1	24.3±4.48
	Al	4.51-9.21	7.64±1.32	10.45-14.24	12.15±1.39	9.49-12.62	10.871.16
	Si	52.42-63.47	57.0±4.03	52.36-70.37	64.83±5.52	50.22-61.4	55.52±3.59

in the monsoon; Mn, Ni and Zn are high in the winter while Cd and Cu is dominant in the summer season. The trend for Fe showed that maximum range was found in the monsoon (4574-6480 µg g-1) followed by the winter (3609-4921 µg g-1) and summer (4121-6340 µg g-1).

The trace element concentrations in sediments of Himalayan Lakes show that the Nainital, Bhimtal, Sattal, and Naukuchiatal are enriched in Co, Cu Ni, Pb and Zn compared with the Pandoh Lake (Table 3). These elements have anthropogenic sources and get concentrated in the sediments either with organic fractions or Fe-Mn hydroxide fraction (Chakrapani, 2002; Jain et al., 2007). The Nainital sediments are rich in organic matter [12 %] compared with Bhimtal [0.15 %], Sattal [0.7 %] and Naukuchiatal [1.9 %] (Chakrapani, 2002). Moreover, the impact assessment of man-related activities on the Himalayan lakes shows that the present status of the Lake Pandoh is better than the Nainital, Bhimtal, and Sattal and Naukuchiatal lakes.

The mean values along with standard deviation of heavy metals in different grain size classes (Table 4) showed that Cd, Co and Zn were high in <63 µm size fractions in all seasons. The distribution pattern of Cu showed that 50 µm, 125-250 µm and 10-20 µm particle sizes yield maximum concentration in the monsoon, winter and summer, respectively. For Fe, high concentration was found in >250 µm grain size in the monsoon

Table 3: Comparative concentration of elements (µg/g) in surface sediments of Himalayan Lakes

Element	Pandoh (M)	Pandoh (W)	Pandoh (S)	Nainital	Bhimtal	Naukuchiatal	Satal
Pb	6.40	9.60	13.30	45.00	10.00	27.30	31.00
Cd	3.20	3.50	3.80	NA	NA	NA	NA
Zn	23.20	28.30	24.30	210.00	41.00	112.00	141.00
Cu	10.10	13.80	17.90	46.00	52.00	49.00	36.00
Mn	592.80	779.50	257.00	619.00	619.00	851.00	1084.00
Ni	36.80	37.60	26.00	60.00	27.00	85.00	76.00
Co	22.40	20.00	13.20	NA	NA	NA	NA
Fe	5472	3708	5595	49140	54460	70256	80220
Al (%)	7.64	12.15	10.87	11.40	11.30	13.60	11.90
Si (%)	57.00	65.83	55.52	42.00	60.30	65.70	64.80

Table 4. Concentration (ìg/g) of elements in different grain size fractions of surface sediments (n=9) in monsoon(M), winter(W) and summer(S) seasons.

Element	Season	Grain Size (μm)								
		<2	5-10	10-20	20-30	30-50	50-<63	63-125	125-250	>250
Cd	M	1.57±0.25	1.21±0.08	5.69±0.20	2.17±0.04	3.35±0.26	3.24±0.21	2.15±0.09	4.83±0.58	2.15±0.17
	W	2.60±0.47	1.00±0.21	4.10±0.36	3.21±0.21	2.47±0.14	4.87±0.18	2.34±0.34	3.12±0.1.20	2.80±0.58
	S	3.17±0.65	3.22±0.14	4.59±0.11	2.30±0.41	4.20±0.13	4.18±0.28	2.31±0.41	2.60±0.24	1.89±.08
Co	M	14.73±1.58	18.44±2.17	16.02±4.16	21.37±3.28	20.24±2.59	32.87±5.24	23.43±6.47	12.68±3.62	15.45±3.27
	W	21.82±0.278	9.44±3.23	23.50±1.55	22.50±4.29	14.49±4.57	29.12±3.67	21.18±1.47	8.14±1.35	14.10±1.78
	S	19.00±0.76	12.57±2.75	8.95±2.74	7.16±0.76	5.53±1.38	13.00±2.47	11.42±1.68	15.90±2.11	13.93±1.46
Cu	M	5.61±0.33	7.49±0.75	5.2±1.24	8.17±1.78	4.49±0.28	11.03±2.17	6.15±1.38	9.25±1.07	6.34±1.50
	W	6.34±1.47	16.82±1.24	9.40±2.07	16.83±2.54	12.19±0.63	10.10±0.98	4.15±1.17	20.47±2.28	8.76±1.03
	S	12.63±3.89	16.30±1.46	18.85±3.56	9.11±1.47	15.38±4.46	15.22±4.23	13.84±2.05	12.25±2.15	5.32±0.42
Fe	M	4446±550	3521±667	3944±257	4213±708	2980±368	4200±563	4312±750	3819±652	5028±805
	W	4139±843	2422±250	5631±658	1927±341	2837±247	2289±239	3540±612	2160±473	2781±227
	S	3920±240	1263±278	3048±578	6029±754	4073±518	5516±874	5721±289	4728±369	5521±639
Mn	M	345.95±154.36	408.00±204.74	413.62±183.26	606.21±224.87	773.84±146.28	280.15±182.00	802.55±252.80	453.72±103.27	629.17±92.47
	W	750.85±114.17	684.20±136.78	573.33±87.69	596.74±108.72	740.45±207.36	583.49±149.44	770.62±119.54	630.54±155.21	810.58±123.50
	S	423.33±89.25	93.15±54.07	270.69±115.36	204.00±124.18	420.26±82.03	199.54±58.29	255.95±73.54	115.76±59.25	199.00±42.17
Ni	M	23.46±5.46	40.29±6.38	22.26±4.85	28.34±1.13	25.16±3.21	32.41±	30.92±14.15	20.33±4.08	27.39±2.92
	W	40.12±7.12	46.20±4.28	41.18±3.26	37.00±5.18	60.92±14.29	14.53±2.07	7.57±1.48	14.24±3.74	20.55±4.11
	S	22.71±6.18	18.89±3.47	21.72±1.75	11.66±2.40	17.17±1.28	17.54±2.39	18.00±4.56	23.85±6.05	11.97±4.75
Pb	M	9.83±1.19	3.76±0.56	5.51±0.47	7.66±1.24	8.02±4.58	7.28±2.44	3.42±0.87	11.19±2.36	7.20±0.87
	W	4.26±1.74	14.21±1.25	10.44±1.98	9.20±2.63	12.74±2.33	10.67±2.53	5.74±1.47	8.10±5.27	12.54±2.63
	S	12.74±2.27	13.92±1.35	6.00±1.47	14.65±2.01	8.43±6.04	13.02±4.78	9.36±4.21	12.00±1.17	13.32±4.08
Zn	M	16.57±1.54	19.22±2.41	25.74±3.57	9.50±1.20	13.86±1.04	24.15±4.40	19.63±3.24	14.55±1.45	16.00±2.07
	W	22.75±2.02	16.19±4.17	15.00±1.47	30.21±2.14	36.35±8.37	40.98±3.97	18.14±3.59	17.40±4.08	32.43±5.29
	S	18.55±1.32	20.41±3.27	20.28±5.52	22.43±6.23	22.40±2.68	23.70±2.57	22.12±0.78	21.00±2.41	22.66±4.89

season while 10-20 and 20-30 μm size particles were the important store house in the winter and summer, respectively. In the monsoon and winter, maximum concentration of Mn was associated with 63-125 μm size particles but in summer <2 μm clay fractions comprised maximum concentration. The distribution pattern of Ni showed that in the monsoon 5-10 μm; in the winter 30-50 μm and 125-250 μm coarse particles led to store high amount in the summer season. The grain size statistical parameters for the Pandoh Lake (Table 5) revealed that the surface sediments were poorly sorted to very poorly sorted, very positively skewed [asymmetry] and very platykurtic to extremely leptokurtic in nature. These behaviors of surface sediments in the monsoon, winter and summer indicates variation in depositional environment.

Seasonal variations observed for total trace metals in surface sediments and different grain size particles of the Pandoh Lake is explicit, which might be the result of seasonal variations occur in depositional environment of surface sediments indicated by seasonal fluctuation in % values of grain size classes. Where not only < 63 μm but also >63 μm particles sizes are important store house of trace elements in the Pandoh Lake. This implies that heavy metals are heterogeneously distributed over the various grain size fractions in different seasons. This could be consequence of geological settings (i.e. parent rock type and topography), climate and water table fluctuation and the consequent chemical weathering of rocks (Jenny, 1941; Loughnan, 1969; Summerfield 1991; Macias

Table 5: Grain size distribution in the Pandoh Lake.

Season	Surface Sediment									
	Feature/Site	1	2	3	4	5	6	7	8	9
Monsoon	Mean	1.93	1.86	1.58	2.27	1.75	1.79	1.80	1.93	1.89
	Std. Dev.	1.66	1.25	2.01	2.45	1.94	2.12	1.83	1.90	1.33
	Skewness	1.71	0.78	2.24	2.07	2.04	2.18	2.02	2.14	0.94
	Kurtosis	2.48	-0.69	5.13	4.50	4.31	4.89	4.34	4.80	0.67
Winter	Mean	1.73	1.64	1.8	1.82	1.58	2.27	1.75	1.93	1.93
	Std. Dev.	2.06	1.31	2.03	1.60	2.01	2.45	1.94	1.90	1.66
	Skewness	2.32	1.82	2.25	2.30	2.24	2.07	2.04	2.14	1.71
	Kurtosis	5.44	3.29	5.19	5.45	5.13	4.50	4.31	4.80	2.48
Summer	Mean	1.84	1.64	1.8	1.80	1.71	1.72	1.71	1.57	1.66
	Std. Dev.	2.12	1.31	2.03	0.96	1.02	0.92	1.33	1.32	1.53
	Skewness	2.31	1.82	2.25	1.65	0.35	0.74	1.50	1.59	1.76
	Kurtosis	5.44	3.29	5.19	2.62	-1.32	-0.88	2.55	2.33	3.29

and Chesworth, 1992; Thomas 1994; Hill et al., 2000; Taylor and Eggleton, 2001) and from man made activities mainly agriculture practices and tourism (Anshumali, 2006). The higher concentration in the fine sediments is generally due to the increase in surface area and the surface properties of the clay minerals. The decrease in the heavy metal concentration in the coarser fraction is due to the increasing population of the detrital minerals, mostly quartz and feldspar.

POLLUTION ASSESSMENT

The enrichment factor (EF) for surface sediments is given in Table 6. The EF for Cd is greater in all seasons while Co is showing high EF only in monsoon and winter. The source of Cd in the Pandoh Lake is mainly runoff from agriculture areas where phosphate fertilizers applied to the farmlands, which most probably contains Cd (Ray and Macknight, 1984). It could also be result of road traffic and tear of tires, which have been described as an important source of Cd emission (Alloway, 1990). The values of EF for Co indicate that the Co pollution has been established in Pandoh Lake. The other potential pollutants that can become problematic in near future are Mn and Pb. Otherwise Cu, Fe, Ni and Zn are still in the phase of evolution to achieve the threshold limit and acts as a pollutant. The EF values for Cu, Fe, Mn, Ni, Pb and Zn are less than unity indicates that they are terrigenous in origin (Szefer et al., 1998). Table 7

The I_{geo} values for the Pandoh Lake sediments are given in Table 7. Seasonal trends indicate that the Cu, Fe, Mn, Ni, Pb and Zn remain in class 0 (background

Table 6 : Enrichment factor for elements in surface sediments of the Pandoh Lake

Site	Cd	Co	Cu	Fe	Mn	Ni	Pb	Zn
Monsoon								
P1	24.36	1.37	0.20	0.13	0.61	0.45	0.29	0.24
P2	14.86	1.46	0.22	0.13	0.73	0.46	0.41	0.21
P3	28.20	1.16	0.23	0.12	0.68	0.52	0.43	0.21
P4	10.63	1.01	0.18	0.12	0.70	0.49	0.35	0.27
P5	14.70	1.25	0.31	0.10	0.57	0.25	0.22	0.24
P6	23.43	1.32	0.22	0.10	0.94	0.44	0.15	0.25
P7	29.03	1.49	0.26	0.11	0.70	0.39	0.42	0.25
P8	28.00	0.64	0.18	0.09	0.74	0.41	0.22	0.25
P9	19.66	0.90	0.19	0.10	0.57	0.35	0.36	0.25
Winter								
P1	13.76	1.08	0.22	0.10	0.94	0.50	0.50	0.21
P2	10.43	0.99	0.27	0.08	0.94	0.51	0.45	0.28
P3	11.63	0.94	0.29	0.07	0.81	0.39	0.50	0.17
P4	15.16	1.01	0.44	0.08	0.88	0.27	0.51	0.28
P5	10.86	1.05	0.36	0.08	0.98	0.50	0.47	0.32
P6	12.53	1.06	0.27	0.08	0.86	0.40	0.50	0.29
P7	9.60	1.32	0.30	0.08	1.01	0.29	0.47	0.49
P8	13.96	1.06	0.31	0.09	0.75	0.49	0.60	0.30
P9	10.63	0.91	0.27	0.10	1.07	0.48	0.37	0.29
Summer								
P1	14.33	0.73	0.40	0.13	0.50	0.37	0.67	0.25
P2	12.03	0.71	0.26	0.12	0.21	0.20	0.62	0.24
P3	14.00	0.67	0.38	0.13	0.33	0.41	0.70	0.24
P4	14.80	0.61	0.27	0.13	0.37	0.33	0.65	0.26
P5	14.36	0.63	0.44	0.09	0.28	0.33	0.70	0.19
P6	14.36	0.67	0.45	0.12	0.24	0.34	0.64	0.25
P7	7.20	0.81	0.53	0.08	0.29	0.18	0.70	0.36
P8	7.20	0.84	0.48	0.13	0.26	0.27	0.69	0.24
P9	18.73	0.90	0.33	0.11	0.20	0.21	0.60	0.25

Table 7: Geoaccumulation index of elements in surface sediments of the Pandoh Lake

I_{geo}	I_{geo}	Element		
		Monsoon	Winter	Summer
>5	6			
4-5	5			
3-4	4	Cd		
2-3	3			
1-2	2		Cd	
0-1	1	Co		Cd
<0	0	Cu, Fe, Mn, Ni, Pb, Zn	Co, Cu, Fe, Mn, Ni, Pb, Zn	Co, Cu, Fe, Mn, Ni, Pb, Zn

concentrations) in the monsoon while Co, Cu, Fe, Mn, Ni, Pb and Zn in the winter and summer seasons suggesting that there is no pollution with respect to these metals in Pandoh lake. Cd and Co shows geoaccumulation rating of 4 and 1 in the monsoon season respectively. It suggests that Cd is 25 fold enriched compared to background values while Co is double the background values. However, Cd is showing geoaccumulation rating 2 (five fold increase) and 1 (background concentrations) in the winter and summer respectively. Maximum enrichment for Cd suggests that the Pandoh Lake is polluted with respected this element.

CONCLUSIONS

The toxic strength of any metal depends on its easy availability and presence of dominant fraction/species rather than the total concentration of metal in the surface sediments. Although Pandoh is a "Mountain Lake" receiving trace metals from natural and anthropogenic sources, it is heavily contaminated with Cd and Co whose concentration (enrichment factor) and geoaccumulation index vary seasonally. The grain size fractionation emphasizes the assorted distribution of metals in surface sediments, which in turn controlled by variation in depositional environmental of Pandoh Lake catchment.

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