

Heavy Metal Fractionation and Mineralogy in Sediments of Nainital Lake, Kumaun Himalayas

A. K. PATRA¹, N. PENDKAR² and G. J. CHAKRAPANI^{1*}

¹Department of Earth Sciences, Indian Institute of Technology, Roorkee - 247 667

²Oil and Natural Gas Commission, Dehra Dun

*Email: gcurfes@itr.ernet.in

Abstract: The major objective of the present study has been to determine the mineralogy and chemical composition of sediments of Nainital lake, a major tourist destination situated in the Kumaun Himalayas. In the present study, we have determined the mineral content in the sediments of the lake and analysed the associations of toxic metals in various chemical fractions such as, metals which are easily released to water from sediments, and metals bound to carbonates, manganese oxides, iron oxides, organic matter and residual matter. Although detrital minerals quartz and feldspar are dominant, calcite, aragonite, illite and gypsum are also present in appreciable quantities. Quartz and illite are the dominant minerals in the coarse fractions of sediments, whereas calcite, aragonite and gypsum are mostly present in finer sediments. Among the various chemical fractions, most of the metal concentrations are associated with the residual fraction, whereas, organic matter fraction is a major sink for Mn, Zn and Cu. Hence, under conditions where organic matter gets oxidized, the metals may be released into the water column, thus resulting in high pollution levels in the lake waters.

Keywords: Heavy metals, Mineralogy, Nainital

Study Area

Nainital lake is situated at 1937 metres above the mean sea level in the district of Nainital in the Kumaun Himalayan region of Uttaranchal State (Fig 1). The hydrological parameters of the lake are presented in Table 1.

The lake is in the Nainital massif, the hills of which encompass a rock succession that includes 1800-2000 million years (My) old granites and sediments which range in age from 1600 to 500-600 My. These older lithologies are in contact with 2-20 My Siwaliks along the Main Boundary Thrust (MBT), which is tectonically very active and is manifested in the large-scale hillside instability in the region (Valdiya, 1980). The lithology around Nainital consists of carbonate rocks, calcareous slates, argillaceous limestones, ferruginous shales, algal dolomites, black shales with marlite, greywacke, siltstones etc. of the Krol Formation (Permo-Triassic) (Das et al. 1994). The Nainital lake is a major tourist destination with a tourist influx of 100,000 per year. The land-use classification in the immediate drainage of the catchment area is forests and shrubs (42%), buildings and hotels (41%), roads (2%), water bodies (10%), playground (1%) and barren lands (4%) (Nachiappan et al. 2000).

Methodology

Bottom sediment samples were collected from Nainital lake from various locations, with an indigenously manufactured sediment sampler from depths of 20-27 meters below surface water. Approximately 1 kilogram of wet bottom sediments collected in polythene bags were

Table 1. Hydrological parameters of Nainital Lake (Sharma et al. 1992)

Parameter	Nainital Lake
Altitude (m)	1937
Longitude	79° 28'E
Latitude	29° 24' N
Length (m)	1432
Breadth (m)	423
Maximum Depth (m)	27.3
Mean Depth (m)	16.2
Surface area (km ²)	0.48
Catchment area (km ²)	3.96
Shore line (m)	3630
Annual rainfall (mm)	2300
Maximum air temperature (°C)	24.6
Minimum air temperature (°C)	3.96
Maximum water temperature (°C)	25
Minimum water temperature (°C)	10
Volume of water (m ³)	5,907,500

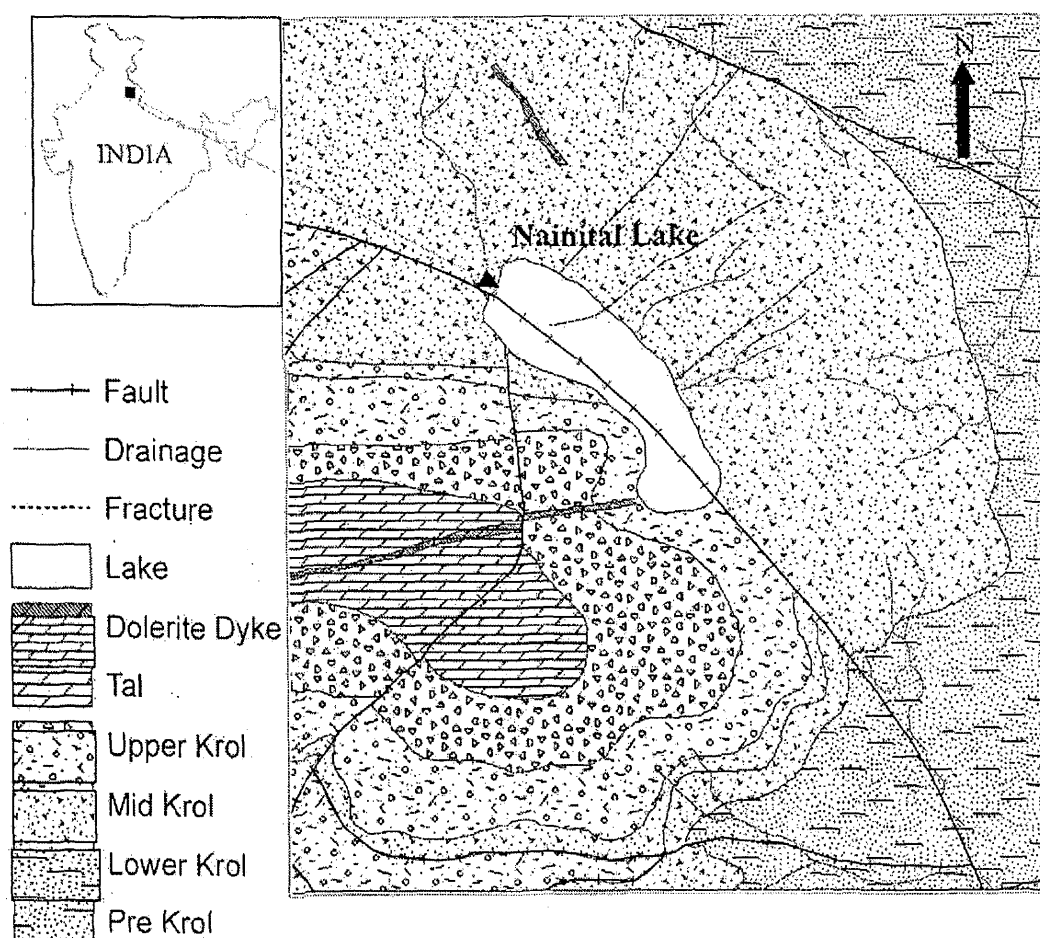


Fig.1. Location of Nainital lake with catchment lithology (after Valdiya, 1980). Tal - Grey Carbonaceous slate, Limestone-marlite. Upper Krol - Limestone-marlite, Dolomite (cherty and phosphatic). Middle Krol - Grey Carbonaceous slate, Dolomitic-limestone, shale. Lower Krol - Calcareous slate, Dolomite, Pockets of gypsum. Pre Krol - Pyritous carbonaceous slate, Limestone

preserved at 4°C before processing for analysis. The sediments were separated into two size fractions (>4 mm and <4 mm) by settling method using lake waters as the fluid media. Mineralogy of the sediments were determined by X-Ray Diffractometer (XRD) after glass slide mounts were prepared and glycolated after removal of organic matter in sediments. The background noise and the corrections as obtained from the silicon standard sample tests were taken into account before interpretation. For interpretation of the powder diffraction data, tables of d-spacings published by the Joint Committee on Powder Diffraction Standards (JCPDS) were used. In general, the average instrumental error was fixed at $2\theta = 0.05^\circ$ and subsequently matched. To determine major oxide compositions in sediments by X-Ray Fluorescence spectroscopy, the dried sediments (bulk) were powdered (<200 mesh) using hand grinder and pulveriser, organic matter was removed and pellets were prepared using pressure disks and boric acid as binder. The

sequential extraction for the trace elements in sediments was carried out following the procedure of Tessier et al. (1979) and Leleyter and Probst (1999). The trace elements in sediments were leached into fractions of, (i) easily dissolvable with water, (ii) associated with carbonates, (iii) manganese oxides, (iv) iron oxides, (v) organic matter and (iv) residual fraction. Trace elements (Fe, Mn, Cr, Ni, Cu and Zn) in these fractions were determined by Atomic Absorption Spectrophotometer (AAS) after standardization and calibration.

Results and Discussion

The chemical composition in terms of major oxides of the bulk sediments is presented in Table 2. SiO_2 , CaO , Al_2O_3 and Fe_2O_3 are the major oxides in the sediments, which make up the bulk of the sediment composition whereas, MgO , Na_2O , MnO and P_2O_5 are present in low amounts. The sediments have relatively high elemental

Table 2. Major oxide compositions (in percent) in the sediments

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	MnO	TiO ₂	P ₂ O ₅	S
N1S	47.40	13.48	5.57	22.95	0.89	0.82	3.31	0.16	0.42	0.75	2.26
N2S	53.50	15.21	6.65	14.03	0.92	0.82	3.87	0.20	0.58	0.66	1.56
N3S	51.86	14.41	6.65	16.52	0.89	0.79	3.65	0.21	0.53	0.62	1.87
N4S	50.09	14.08	6.30	18.98	0.86	0.80	3.67	0.20	0.45	0.59	2.00
N5S	51.48	14.14	6.31	17.68	0.86	0.79	3.64	0.18	0.46	0.53	1.94
N6S	52.15	14.32	6.51	16.15	0.88	0.80	3.73	0.21	0.50	0.57	2.18
N7S	56.07	15.74	7.07	10.36	0.92	0.82	4.17	0.15	0.63	0.63	1.44
N8S	54.08	15.22	7.43	12.89	0.91	0.82	4.19	0.12	0.62	0.68	1.05
N9S	57.48	15.83	7.84	7.24	0.93	0.84	4.07	0.11	0.72	0.83	2.12
N10S	59.57	16.49	7.24	6.46	0.94	0.84	4.24	0.13	0.72	0.76	0.61
N11S	59.07	16.35	7.29	7.12	0.93	0.82	4.04	0.13	0.75	0.68	0.84
N12S	55.19	15.35	6.90	12.23	0.92	0.82	3.97	0.20	0.62	0.67	1.13
N13S	52.87	15.38	6.38	14.84	0.91	0.82	3.91	0.18	0.55	0.62	1.54
N14S	51.60	14.26	6.28	17.47	0.89	0.80	3.62	0.17	0.51	0.60	1.81
N15S	48.74	13.39	5.93	21.3	0.85	0.78	3.38	0.27	0.43	0.70	2.23
N16S	49.16	13.92	6.05	20.52	0.87	0.80	3.48	0.15	0.45	0.59	2.01

sulphur concentrations. The highly anoxic bottom sediments (Eh = -350 V) contain sulphides and are the source of high dissolved sulfate (1024 $\mu\text{mol l}^{-1}$) (Chakrapani, 2002) concentrations. In addition, dissolution of gypsum and pollution source also contributes towards high dissolved sulfate. These bottom sediments are derived from the weathering of rocks from the catchment, from lithologies on the lake bottom and also from contaminated sediments in the form of particles through the numerous drains, which feed the lake. We did not notice any sulfide mineral in the sediments, may be because the sediment-sulfur got oxidized due to treatment with H_2O_2 in the laboratory while in preparation of XRD slides.

Trace elements are reactive chemical species with respect to particles in aquatic systems. Their long-term repository is the sediment, which can either be a source or a sink of chemicals. Hydrous oxides scavenge and transport trace elements to the sediments, where anoxic conditions favor the reductive dissolution of these particles releasing metals to the water column. The heavy metal concentrations in water are pH dependent as acidic pH makes the heavy metals to dissolve better. The determination of total trace elements concentrations in aquatic systems from the sediments does

not indicate the pollution levels, unless association of the metals with various chemical fractions is ascertained to determine its mobility and bioavailability. For example, chromium can not co-precipitate with calcite or dolomite and hence is much less likely to be associated with carbonates and shales, whereas Cu and Ni, are pollutants which get concentrated in water and get precipitated with carbonates.

Almost all of Fe and Cr is associated with the residual fraction in sediments. Cu and Ni have similar preference (80-86%) for residual fraction. A significant amount of Mn (15-30%) is associated with Mn-oxides and organic matter (22-28%). Organic matter content in the Nainital lake sediments is very high (17-23%) (Chakrapani, 2002) which is derived from the degraded and non-degraded litter around the lake and also from the discharged effluents. The presence of Ni, Cu, Fe, Cr, Zn and Mn in the various fractions is presented in Table 3 and their percentage abundances are shown in Fig 2. It is observed that, although most of the metal contents are associated with the residual fraction of the sediments, Mn, Zn, Cu and Ni have significant presence in the organic fraction. The organic acids formed by the decomposition of plant and leaf matter in the lake bottoms, may form organo-complexes with metals. High chelation

Table 3 Trace element concentrations (range in mg/kg, n=5) in different chemical fractions in sediments

Fractions	Fe	Mn	Cu	Cr	Ni	Zn
Water soluble	31.3-166.4	0.6-27.6	0.4-1.3	Nil	Nil	0.2-4.7
Bound to carbonates	Nil	7.1-129.8	Nil	Nil	Nil	0.2-1.6
Bound to manganese oxides	7.2-87.8	137.5-887.0	1.4-2.6	Nil	Nil	4.0-11.2
Bound to iron oxides	57.6-303.0	69.6-437.0	4.9-6.4	Nil	Nil	26.1-59.9
Bound to organic matter	4.5-268.0	200.0-844.7	1.1-11.4	Nil	11.2-27.9	27.0-46.5
Residual fraction	10563-30143	493.0-678.0	69.5-105.3	48.8-133.9	62.7-77.8	380.0-501.0

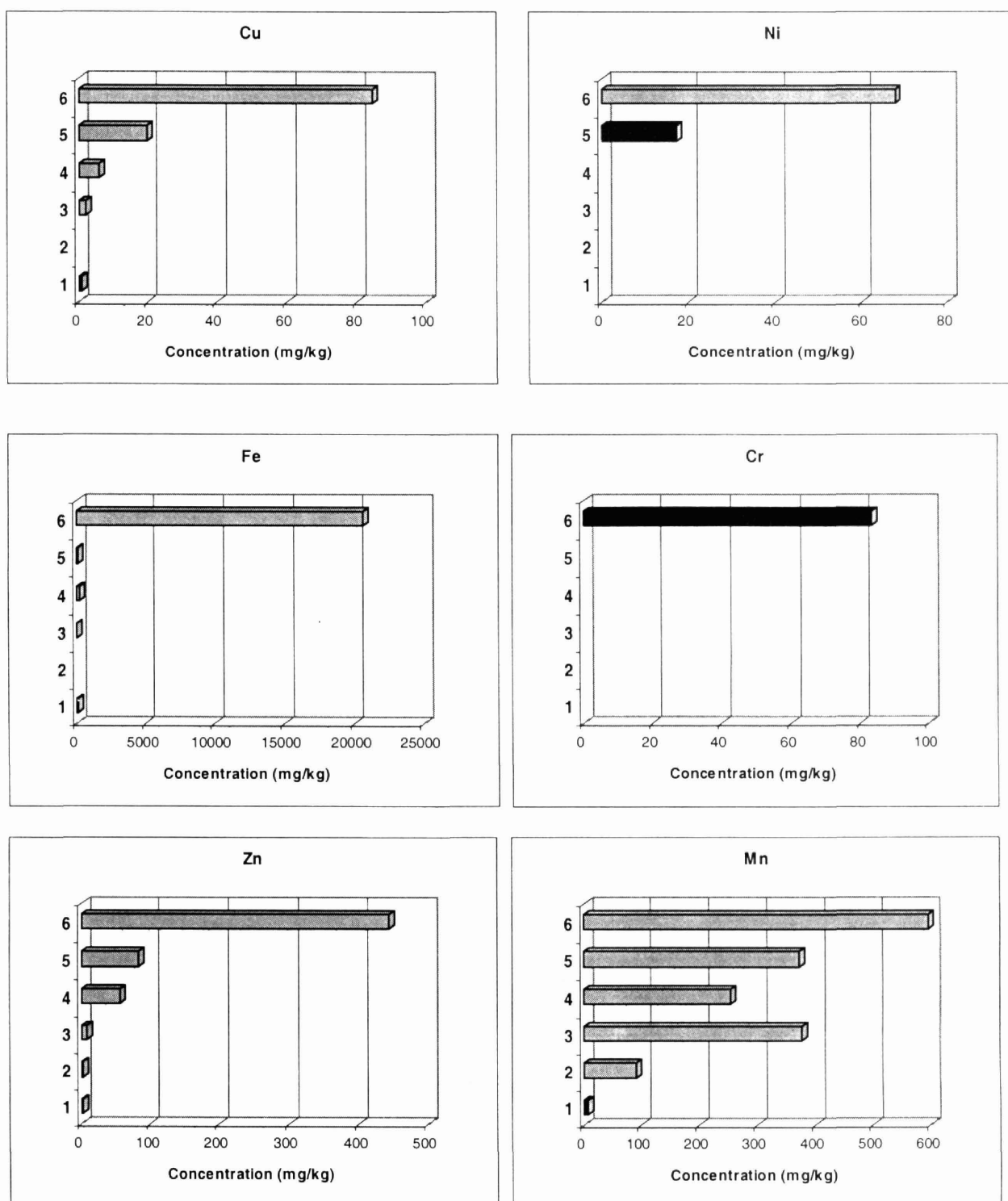


Fig.2. Heavy metal concentrations in different chemical fractions of sediments. **1** - Dissolved with water. **2** - Bound to carbonate. **3** - Bound to manganese oxides. **4** - Bound to crystalline iron oxides. **5** - Bound to organic matter. **6** - After digestion.

Table 4. Mineral abundances in two size fractions of sediments (range in %, semi quantitative, n=5)

Minerals	<4 μm	>4 μm
Quartz	17.5-35.3	42.7-48.6
Feldspar	7.5-8.3	9.1-9.9
Calcite	7.4-35.1	4.2-4.74
Aragonite	5.9-11.6	1.6-5.6
Gypsum	9.8-23.4	3.7-7.0
Illite	4.6-7.8	7.6-12.5
Chlorite	9.4-10.7	15.2-17.6
Vermiculite	1.6-3.8	4.0-7.9

properties of heavy organic acids such as fulvic and humic acids bind the metals. Whenever, oxidizing conditions prevail and the organic matter is oxidized, the metals are released back to the water. Organic matter in sediments are a complex mixture of *in situ* organics, such as lipids, proteins etc. derived from biota and other pollutants such as hydrocarbons, poly aromatic hydrocarbons and poly

chlorinated biphenyls, which are added from human induced environmental changes (Urban et al 1999, Meyers, 2003). The bottom sediments are very dark and muddy in the Nainital lake. The minerals in two different size fractions (<4 μm and >4 μm) from the lake are presented in Table 4. Quartz, feldspar, calcite, aragonite, gypsum, illite, vermiculite and chlorite are the minerals, which are observed in the sediments. There is a clear size demarcation, with the coarse size (>4 μm) showing more abundance of quartz, illite, feldspar, vermiculite and chlorite and the fine fractions (<4 μm) show higher calcite, aragonite and gypsum contents. Sedimentary calcite, aragonite and gypsum are chemical precipitates and require saturated Ca^{2+} , CO_3^{2-} and SO_4^{2-} concentrations in water and later precipitate in fine colloids. The finer sediments are also major sink for heavy metals, because they contain abundant clay minerals, organic matter and Fe-Mn-hydroxides. Thus chemical sediments play a major role in the toxic metal cycling in lakes.

References

- CHAKRAPANI, G. J. (2002) Water and sediment geochemistry of major Kumaun Himalayan lakes, India. *Env. Geol.*, v 43, pp 99-107.
- DAS, B. K., SINGH, M. and BORKAR, M. D. (1994) Sediment accumulation rate in lakes of Kumaun Himalayas, India using ^{210}Pb and ^{226}Ra . *Env. Geol.*, v 23, pp 114-118.
- FORSTNER, U. and WITTMANN, G. T. W. (1984) Metal pollution in the aquatic environment. Springer-Verlag.
- LELEYTER, L. and PROBST, J.-L. (1999) A new sequential extraction procedure for the speciation of particulate trace elements in river sediments. *Inter. Jour. Anal. Chem.*, v 73(2), pp 109-128.
- McLENNAN, M. (1993) Weathering and global denudation. *Jour. Geol.*, v 101, pp 295-303.
- MEYERS, P. A. (2003) Applications of organic geochemistry to paleolimnological reconstructions: a summary of examples from the Laurentian Great Lakes. *Org. Geochem.*, v 34, pp 261-289.
- NACHIAPPAN, P. R., KUMAR, B., SARAVANAKUMAR, U., JACOB, N., SHARMA, S., JOSEPH, T. B. and MANICKVASAGAM, R. M. (2000) Estimation of sub-surface components in the water balance of lake Nainital (Kumaun Himalayas, India) using environmental isotopes. *Proc. Int. Conf. Water Res.*, New Delhi.
- NESBITT, H. W. and YOUNG, G. M. (1982) Early Proterozoic climates and plate motion inferred from major element chemistry of lutites. *Nature*, pp 299.
- SHARMA, A. P., JAISWAL, S., NEGI, V. and PANT, M. C. (1982) Phytoplankton community analysis in lakes of Kumaun Himalaya. *Arch. Hydrobiol.*, v 93, no 2, pp 173-193.
- TESSIER, A., CAMPBELL, P. G. C. and BISSON, M. (1979) Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.*, v 51, no 7, pp 844-851.
- URBAN, N. R., ERNST, K. and BERNASCONI, S. (1999) Addition of sulfur to organic matter during early diagenesis of lake sediments. *Geochem. Cosmochim. Acta*, v 63, pp 837-853.
- VALDIYA, K. S. (1980) Geology of Kumaun Lesser Himalaya, Gyanodaya Prakashan, Nainital, India.

(Received 7 January 2005, Revised form accepted 22 May 2006)