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ORIGINAL ARTICLE

Sediment and hydro biogeochemistry of Lake Nainital, Kumaun Himalaya, India

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Abstract The picturesque Nainital Lake, in the Uttarakhand state of India, is one of the major tourist attractions in the northern part of India. The increasing tourism and population around these lakes are a major concern for the ecology and good sustenance of the lakes. The present study is aimed to understand the behaviour of nutrients and metals in the sediment and their association with chemical forms in the lake. The study was accomplished by studying the water, interstitial water and sediments for major oxides, nutrients and metals in the lake. The different chemical forms of phosphorus and metals in the sediments were done using sequential extraction procedures. The water chemistry (Ca + Mg:Na + K) and the sediment chemistry (CIA and Al_2O_3/K_2O) show that the rocks in the catchment area play an important role in the geochemistry of the lake. The metals in the water also show that the Tallital basin is more polluted than the Mallital basin, may be due to the influence of Bus station. The high concentration of chloride, NH_4, SO_4 and metals in the sediment water interface and the interstitial water shows denitrification, sulfidisation and sulfide oxidation in the anoxic bottom water. The sediment composition shows that the phosphorus in the water is sequestered as carbonate flour apatite, and the metals precipitate as carbonate. The geo- accumulation index shows that the metals zinc, cobalt and nickel show moderate polluted nature than other metals. In general, the lake is less affected by anthropogenic activities. The chemical processes undergoing within the lake, like sulfidisation and sulfide oxidation, oxide dissolution and denitrification and organic matter degradation play an important role in the remobilization of the metals from the lake sediments.

Keywords Nainital · Nutrients · Phosphorus · Trace metals · Fractionation · Geochemical processes

Introduction

Industrialization has led in the last decades to an increased mobilization of contaminants like nutrients and trace metals either as a direct action (e.g. mining and smelting operations) or as an indirect consequence (e.g. acidification of the rain resulting in an increase in the weathering products) (Tessier et al. 1996). Contaminants are transported in both solution and attached to the suspended matter from the continents to the oceans (Davison 1993). In surface waters, the stable phases of the elements are the adsorbed phases; the important carriers are Fe–Mn hydroxides, carbonates, organic matter and clay minerals and settled down along with the sediments (Stumm and Morgan 1996). The permanent accumulation of contaminants poses problems because the sediments act as a source of pollutants long after the pollution of waterways has been abated. The several proxies like organic matter, trace metals, stable isotopes and nutrients are used as indicators of paleoproductivity, paleoredox conditions and influence of catchment for the contaminant source in lakes (Choudhary et al. 2009; Tribovillard et al. 2006; Boyle 2001). These proxies are affected by the redox conditions, biological at the sediment water interface and the anthropogenic activities. However, these proxies can be used to infer the physico-chemical conditions prevailing at the sediments.

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The remobilization and sedimentation of the nutrients and metals are mainly dependent on the oxic condition prevailing at the sediment water interface. The prevalence of the oxic/anoxic condition depends on the circulation of O_2, which at deeper depths depends on the degradation of the organic matter. The degradation of the organic matter consumes the dissolved O_2 and enhances the dissolution of the secondary oxygen sources like nitrate, manganese oxides, iron oxy hydroxides and sulfates are used (Tribovillard et al. 2006 and ref. therein). This biological/chemical process results in the release of the nutrients and trace metals from the sediment (suspended) particles and causes remobilization. The remobilized metals and the phosphorus are precipitated or adsorbed onto the sediment particles. As these elements have both detrital and authigenic origin, precipitated or adsorbed on to the suspended particles, it is imperative to know the chemical form in which these elements are present in the sediments. Hence, to understand the geo chemical reactions, paleoproductivity, paleoredox conditions in the lake ecosystem, it is necessary to know the chemical species of the elements along with the total concentration of the sediments and water (Forstner and Wittmann 1983; Ruttenberg 1992; Tack and Verloo 1995; Warren and Haack 2001; Wang et al. 2003; Callender 2004; Sparks 2005).

The Nainital Lake one of the major tourist attraction in the state of Uttarakhand, India has been intensely affected due to the urban development. The lake receives toxic metals, organic and inorganic pollutants from different sources like soil erosion, illegal construction activities, automobile exhausts and painting of boat in tourist season every year. The steep hills surrounding the lake have immature topography and are prone to landslips and landslides. The illegal construction in the lake catchment have substantially have increased the sediment input to the lake. Because of these anthropogenic activities, the lake is facing serious problem of eutrophication and deterioration of water quality of the lake (Singh and Gopal 2002; Choudhary et al. 2009).

The deterioration of water quality and the urbanisation have attracted many workers for various studies. Pant et al. (1980) observed that, the Lake Nainital is undergoing rapid eutrophication and reported that N, CO_2 and hardness of the water have increased quite alarmingly during the last two decades. Gupta and Pant (1989) have documented the elemental chemistry of sediments in the Nainital Lake. Singh and Gopal (2002) observed the productivity of Nainital Lake to be very high (>8). Ali et al. (1999) in their study on the Nainital Lake observed the lake water to be rich in nutrients and metals and found that the macrophytes in the lake act as a good remover of these metals in the lake. Nachiappan et al. (2000) studied the hydrodynamics of the Nainital Lake using numerical modelling and stable isotopes. Das et al. (1995), Chakrapani (2002) and Das (2005) studied the major ion chemistry of the Kumaun Lakes. Das et al. (1995) estimated the rate of sedimentation on core sediments using Pb^{210} isotope method and observed that, amongst all the lakes in the region, the Nainital Lake has higher sedimentation rate as compared to the other lakes. Jain et al (2008) studied the speciation of the metals in the lake sediments. Choudhary et al. (2009) carried out the paleoenvironmental and paleoproductivity of the lake using the hydrocarbon and stable isotope studies. Even though, the Nainital Lake is extensively studied, the geochemical processes undergoing in the lake is hardly attended. In the present study, we used various geochemical parameters in water, pore-water and sediments to understand the physico-chemical characteristics undergoing in the lake ecosystem.

Study area

Nainital lake (29°24′N and 79°28′E) forms a valley-like feature trending NW–SE at an altitude of 1,938 m from mean sea level and is situated in the Lesser Himalayan zone of Kumaun, comprising a number of beautiful lakes of which Nainital is the most famous (Fig. 1). It is a crescent shaped lake (1.5 km long and 0.36 km wide), which is traversed by a major longitudinal fault known as the Nainital Lake Fault (Valdiya 1980; Das et al. 1995). The maximum and mean depths of the lake are 26 and 18 m, respectively, and its catchment area comprises a large population of about 40,000 inhabitants. The lake has 22 inlet nullahs, 9 of which are permanent and act as the major conduits of polluted sludge and silt which drains off into the lake. The springs Pardadhara and Chunadhara springs feeds the lake. The lake is divided into Mallital (northeast) basin and Tallital (southwest) basin due to the presence of a submerged transverse ridge running east–west about 8 m below the lake surface. The annual rainfall in the catchment of Lake Naini ranges from 2,000 to 2,500 mm. The ambient temperature varies from −5 to 30°C and the monthly mean air temperature ranges from 8 (January) and 21.5°C (May), and the average relative humidity is about 64% (Pant et al. 1980; Saravana kumar et al. 2001).

The lake receives toxic metals, organic and inorganic pollutants horn different sources viz., high soil erosion, illegal construction activities and tourism development, heavy litter inputs, automobile exhaust, domestic discharge and recreational uses of lake water, etc. However, the indiscriminate construction activities and concerning indifference of the people towards proper disposal of wastes and municipal sewage have aggravated deterioration of the lake water quality. Since the lake water is solely being used for drinking purposes, toxic metals present in

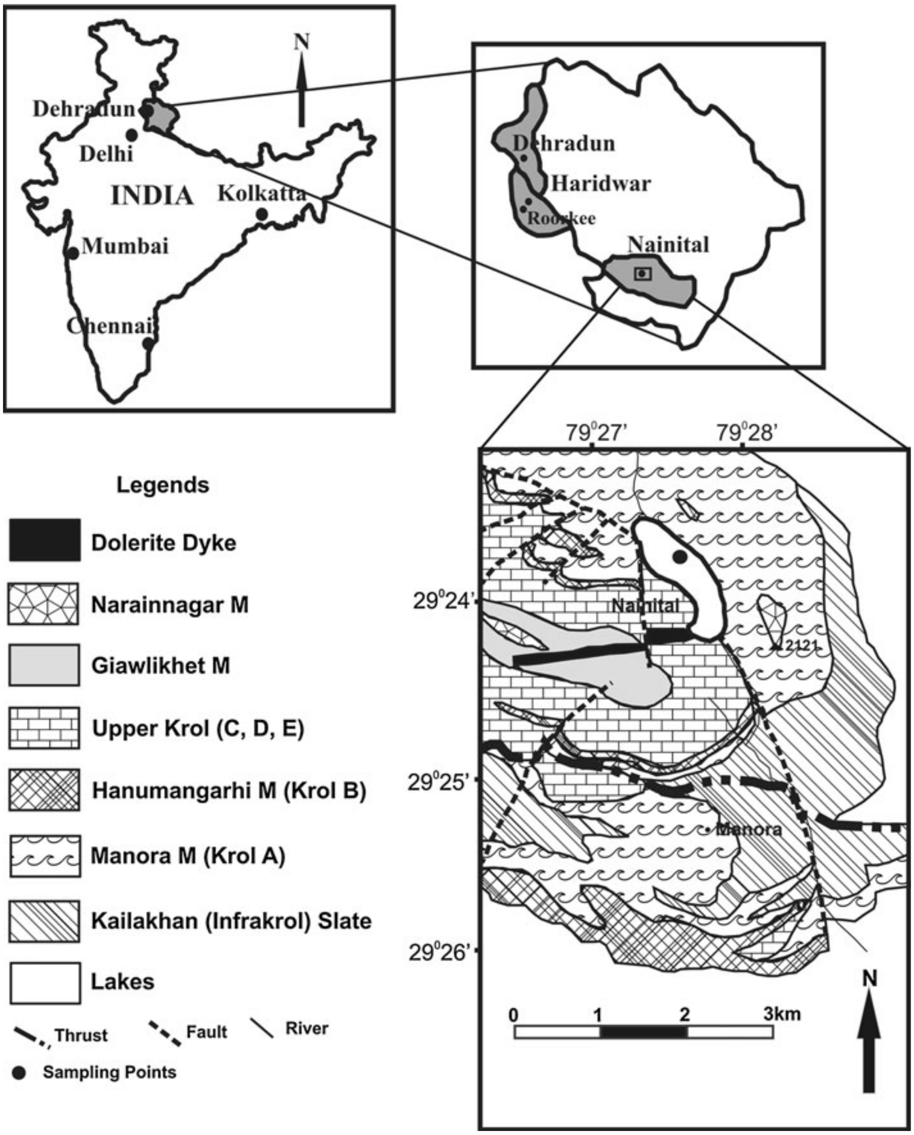


Fig. 1 Geology and location map of the study area

the water may enter into the food chain and cause serious health hazards to local population (Ali et al. 1999; Singh and Gopal 2002; Saravana kumar et al. 2001; Chakrapani 2002).

Geology and geomorphology of the study area

The Naintal Hill forms a synclinorium, which is cut diagonally into two parts by a fault called the Naini Fault (Fig. 1). The catchment area is surrounded by the lithology of the Krol Formation (Precambrian) consisting mainly of carbonate rocks, such as limestone, dolomite, gypsum, calcareous slates, ferruginous shales, greywackes, etc. (Das et al. 1995; Chakrapani 2002; Das 2005; Choudhary et al 2009). The northwestern part is made exclusively of argillaceous limestone and marlites, whereas the southwestern part comprises dolomite with limestone and black carbonaceous slates (Valdiya 1988). It is believed that the subrecent rotational movements were responsible for the blockade of the Balia River, in its upper reaches, resulting in the formation of Lake Naini. The drainage pattern of the lake catchment is controlled by both geology and structure with the very few streams in the western part and the several parallel to sub parallel streams in the east following the faults and joints (Valdiya 1988).

Methodology

Sample collection

Water samples were collected from the surface of the lake in 2006 and both surface and deep-water samples at three depth intervals during 2008. The interstitial water samples were collected by centrifuging the sediments at 7,500 rpm for 1hr. The water samples were filtered through 0.45 µm cellulose nitrate membrane filter papers using a powered vacuum filtration unit. The water samples for the metal analysis were filtered immediately in the field by a hand powered vacuum of 250 ml volume filter unit and were acidified to <2.0 pH by adding a few drops of supra pure nitric acid. The sediment samples were collected from the deepest part of the lake using a gravity corer (Fig. 1). The collected cores were segmented into sub-samples of 2 and 5 cm (for extracting interstitial water) thickness each in the field immediately. The samples were stored in refrigerated condition in clean and airtight polythene bags.

Sample analysis

Water analysis

The initial measurements of pH, Eh and temperature were carried out in the water and sediment samples immediately after sample collection in the field. Briefly, alkalinity in the water samples were analysed by acid titration (gran plot). The major cations and anions in the water samples were measured using Metrohm Basic Ion Chromatograph after calibrating the instrument with the standards prepared in the laboratory. Dissolved phosphorous and silica were analysed using UV-Vis Spectrophotometer (Clesceri et al. 1998). Dissolved trace elements (Fe, Al, Mn, Co, Cr, Cu, Ni, Pb and Zn) in the water were analyzed using DRC 3000 Elan, Perkin Elmer ICP-MS. The laboratory standards procured from Perkin–Elmer were used to calibrate the instrument.

Sediment analysis

The core sediment samples were air dried and powdered. The organic matter and carbonate content of the sediment samples were measured by igniting the samples at 550 and 950°C, respectively, in a muffle furnace (Rippey et al. 1982; Kaiserli et al. 2002). The mineralogy of the sediment samples was determined using Powder XRD (Rigaku—Generic name) and major oxides by XRF (Siemens SRS 3000 sequential X-ray Spectrometer). The rock standard SDO-1 was used for XRF study with errors not exceeding 5%. The mineralisable nitrogen was determined using Kjeldahl instrument (Jaguar—Generic name). The biogenic silica was determined after digesting the sediment samples with 1 M NaOH at 150°C (Hartikainen et al. 1996) and analysed using UV-Vis spectrophotometer. Organic matter in the sediments was removed by treatment with H_2O_2 and digested using tri-acid ($HCl + HNO_3 + HF$) method. The digested samples were analyzed for trace metals and sulfur using DRC 3000 Elan, Perkin Elmer ICP-MS. The USGS standard SCO-1 was used to calibrate the instrument for the total trace metal (Fe, Mn, Co, Cr, Cu, Ni, Pb and Zn) and sulfur analysis.

Phosphorus fractionation

The phosphorous fractionation in the sediment samples were carried out following the SEDEX method (Table 1; Ruttenberg 1992). The major fractions determined were: Exchangeable; Iron bound; Authigenic apatite, Calcium carbonate and Biogenic apatite bound; Detrital apatite bound and Organic matter bound. The dried sediment samples were homogenously grinded, from which 0.5 g of the sample was used for phosphorous fractionation. A rotary shaker was used for shaking the samples. All the experiments were carried out at room temperature. The samples were washed with specific reagents and millipore water after every step and were added to the previously extracted fraction.

Metal fractionation

The fractionation of metals (Fe, Mn, Co, Cr, Cu, Ni, Pb and Zn) associated with different chemical fractions was carried out using the seven step procedure (Table 2) developed by Leleyter and Probst (1999). The seven-step procedure extracts the water soluble, exchangeable, carbonate bound, manganese oxide bound, amorphous iron

Table 1 Brief outline of SEDEX extraction procedure (Ruttenberg 1992)

Fraction	Reagent	Reaction time (h)
Exchangeable and loosely bound P	1 M $MgCl_2$ (pH = 8.0)	2
Fe bound P	Sodium (0.3 M) Citrate, (1 M) Bicarbonate and 1.25 g Dithionite (pH = 7.6)	8
Authigenic apatite, $CaCO_3$ bound P, and biogenic apatite	1 M Sodium Acetate Buffer (pH = 4.0 with acetic acid)	6
Detrital P	1 M HCl	16
Organic P	Ash (@ 550°C) + 1 M HCl	16

Table 2 A brief description of the metal fractionation procedure (Leleyter and Probst 1999)

Fraction	Reagent	Reaction time	Temp (°C)
Dissolved with water	Water	30 min + shaking	20
Really exchangeable	1 M magnesium nitrate	2 h + shaking	20
Bound to carbonates	Sodium acetate at pH 4.5 (HoAc)	5 h + shaking	20
Bound to Mn oxides	0.1 M hydroxyl ammonium chloride	30 min + shaking	20
Bound to amorphous Fe oxides	0.2 M ammonium oxalate–0.2 M oxalic acid	4 h (in dark) + shaking	20
Bound to crystalline Fe oxides	0.2 M ammonium oxalate–0.2 M oxalic acid–0.1 M ascorbic acid	30 min + shaking	80
Bound to organic matter	0.02 M HNO_3, 35% H_2O_2	30 min + shaking	85
	3.2 M ammonium acetate (pH 2 with HNO_3)		
Residual	Aqua regia + HF (digestion)		89

oxy hydroxide bound, crystalline oxide bound and organic matter bound. The residue was digested using tri-acid method to determine the residual phase.

Results

Water composition

The pH of the water in the Nainital (Table 3) is alkaline (~8) in the water column and at the sediment-water interface and interstitial waters show near neutral (~7) pH. The redox potential of the lake (Table 3) shows that the water column is oxic in nature in (Eh = +230 mV) and at the sediment–water interface it show anoxic condition (−60 mV). The interstitial water show very high anoxic condition with the Eh going up to −274 mV.

Major ions and nutrients in water

The major cations chemistry varies widely with magnesium (>55%) dominating the water column of the Nainital lake and calcium is the next abundant element (Table 3) sodium and potassium are present in low concentrations in the lake. The interstitial water and the sediment–water interface show high concentrations compared to the water

Table 3 Water chemistry of the lake—major ion chemistry (μM)

Sample ID	pH	Eh (mV)	Na	K	Ca	Mg	NH_4	F	Cl	NO_2	NO_3	PO_4	SO_4	SiO_2	HCO_3
Depth-0^T	8.22	0	361	77.6	1109.7	1750.8	BDL	2.8	252.3	BDL	104.7	3.4	1108	24.9	3855.4
7 m	8.37	0	352.7	69.3	1115.7	1778.7	BDL	2.8	217.2	BDL	99.4	3.2	1131.3	24.9	3880.2
14 m	8.26	0	432	85	1132.5	1792.7	BDL	2.9	221.4	BDL	104.8	3.6	1158	27	3787.3
21 m	8.17	0	373.4	86.6	1180.9	1822.3	BDL	0.5	411.4	BDL	91.4	3.5	1085.5	26.4	3884.2
Depth-0 ^{M}			452.9	32.6	1170.2	1881	BDL	0.4	233.6	BDL	95.5	3.7	1109.7	25.7	3888.2
7 m			349.4	81.4	1154.5	1781.3	BDL	2.5	188	BDL	86.8	3.7	967.5	173.8	3786.3
14 m			374.3	67.5	1124	1744.7	BDL	0.6	210.5	BDL	102.4	3.8	1105.7	24.4	3885
21 m			381.6	70.1	1170.3	1802.6	BDL	2.3	209.5	BDL	97.7	3.3	1066.6	23.6	4001.2
Depth-0 ^{M}	8.09	0	354.8	72.1	1171.2	1827.4	BDL	2.4	199.6	BDL	93.2	3.3	1069.5	24.9	3889.8
7 m	8.31	231	397.7	82.2	1223.2	1717.2	BDL	0.3	225.3	BDL	91.8	1.2	1055	22.6	3749.7
14 m	8.27	233.8	391	79.4	1196.4	1890.8	BDL	2.4	279.9	BDL	99.8	1.9	1180.8	23.6	2935.9
21 m	8.38	231.6	373.9	77.3	1256.9	1786.8	BDL	0.5	262.9	BDL	91.5	0.8	1074.3	26.2	3701.8
SWI	7.62	−60	318.9	69.4	1239.8	1795.7	0	2.1	1950.3	0	520.6	1.1	1140.4	24.9	3651.2
0–5 cm	7.15	−223	260.5	76.7	6058.1	4532.2	116.8	2.6	243.4	10.4	83.9	0.2	14823.1	158.3	17841.7
5–10 cm	7.21	−190	253.9	206.4	6357.9	4270.5	371.4	1.2	510.4	3.8	10.7	0.5	15167.5	109.3	18724.6
10–15 cm	7.29	−274	520.1	132.8	5452.8	3815	BDL	7.1	283.9	7.5	702.3	0.8	11810.5	153.2	16058.9
15–20 cm	7.31	−239	650.3	174.4	5302.6	4721.3	BDL	5.6	254.7	195.3	175.5	0.5	13603.4	167.8	15616.7
20–25 cm	7.36	−220	276.2	105.4	4697	3840.8	650.2	22.9	221.6	3.1	10.5	0.4	11690.8	153.8	13833.2
25–30 cm	7.38	−190	312.8	128.3	6104.7	5120.9	888.8	7.2	213.2	2.9	6.7	0.3	16347.7	125.2	17978.8
30–35 cm	7.53	−150	287.7	111.8	5592.1	4109	800.1	35.2	201	1.2	3.3	0.3	14049.2	118.8	N.A

SWI sediment water interface, *BDL* below detection limit

Table 4 Water chemistry of the lake-dissolved trace metals

Sample ID	Fe (μM)	Mn (μM)	Al (μM)	Co (nM)	Cr (nM)	Ni (nM)	Cu (nM)	Pb (nM)	Zn (nM)
Surface	7.0	0.5	3.4	4.2	113.8	57.7	18.2	18.8	198.1
14 m	6.5	0.4	3.0	3.7	113.2	59.8	15.1	4.5	119.3
Surface (Tallital)	6.2	0.4	3.3	3.2	49.8	53.2	15.8	7.6	94.4
14	6.1	0.4	2.8	3.0	127.5	53.5	19.4	5.3	79.3
SWI	10.1	2.0	25.4	7.0	102.3	63.5	30.7	17.6	312.2
PW 0–5 cm	28.7	0.1	0.2	13.5	186.2	276.8	33.2	0.1	54.6
PW 5–10 cm	29.7	0.5	0.5	13.9	189.7	285.8	32.8	0.0	58.8
PW 15–20 cm	23.0	0.1	0.8	10.9	167.6	229.3	41.8	0.1	124.6
PW 25–30 cm	27.6	0.1	0.7	15.9	148.3	281.7	45.1	0.1	52.7

SWI sediment water interface

column. Calcium and magnesium dominate in Nainital. Among the anions bicarbonate dominates the water column in the lake, which constitute >75% of total anions in the lake. Sulfate (~20%) is the next dominant anion in Nainital. Phosphorus concentration in the Nainital Lake is much higher (3.78 μmol/l). The anions concentration in the sediment–water interface and the top 10 cm of the sediment column increases dramatically. Bicarbonate and sulfate show very high concentration in the interstitial water (Table 3) and chloride shows high concentration in the sediment–water interface. Phosphorus concentration is less in the interstitial water column of the Nainital Lake.

Dissolved metals

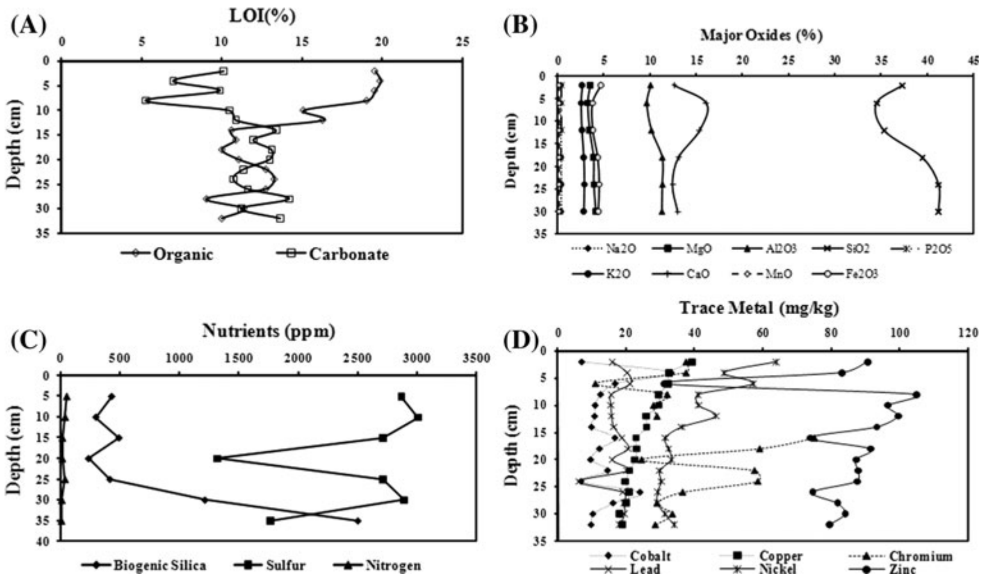
The trace metal concentration in the Nainital is different within the lake, with the Tallital (extreme north) having high concentration than that of the Mallital (extreme south). The metal concentration increases up core in the water column (Table 4) The metal concentration in the lake at the sediment–water interface and the top 10 cm of the interstitial water increases many folds (Table 4), the concentration of the metal decreases with depth thereafter in the interstitial water column.

Sediment composition

Organic matter and carbonates

The loss on ignition (LOI) indicates the approximate organic contents of the sediments (Fig. 2a). The present study indicates that the lake is rich in organic matter (>10%). The organic content of lake increases up core with the top 10 cm containing high amounts of organic matter. The organic carbon contents in lake also behave similar to that of the total organic matter. The carbonate content, which represents minerals, such as dolomite and calcite, is

Fig. 2 Various sediment geochemical parameters in the lake



very high in the Nainital lake sediments (6–14%) increases up core.

Major oxides

The major oxide composition of the sediments is presented in Fig. 2b. Silica (SiO_2) is the dominant oxide in the lake (37–41%), followed by Al_2O_3 and CaO in the Nainital lake. The other oxides, K_2O and Na_2O are almost constant throughout the core (1–3%) in the lake.

Nutrients

The phosphorus concentration (Fig. 2b) is high in the Nainital (>0.3%) and shows increasing trend up core. The total sulfur (Fig. 2c) content in the sediments of Nainital Lake is higher (1,760–3,000 mg/kg) lake and increases up core. The mineralisable nitrogen (Fig. 2c) also shows similar characteristics to that of phosphorus and sulfur Nainital showing higher concentration (56–11 mg/kg). The biogenic silica (Fig. 2c) shows an opposite trend; the Nainital lake shows lesser concentration (300–1,200 mg/kg).

Phosphorus fractionation

The biogenic apatite + calcium carbonate bound fraction (Fig. 3) contains most of the phosphorus (>90%) and shows a decreasing trend up core. The exchangeable fraction is the next dominant fraction in the sediments followed by the organic fraction.

Total metal concentration

The metal concentrations (mg/kg) at different depths in the lake sediments are presented in the Fig. 2d. The metal zinc dominates the trace metals in sediments with concentration varying from 74 to 105 mg/kg. The metals nickel and chromium are the next dominant metals with concentrations ranging from 25 to 75 mg/kg and from 29 to 64 mg/kg, respectively. The concentration of the metals, copper, cobalt and lead are less than 20 mg/kg throughout the core. In generals, the metals cobalt, chromium and nickel show increasing up core trend with the metal zinc showing the reverse trend. The metals copper and lead does not show any marked difference in their concentration throughout the core.

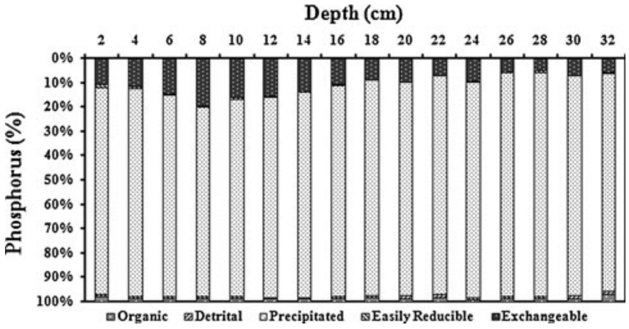


Fig. 3 Phosphorus in different fractions in the sediments of Lake Nainital

Heavy metal fractionation

The metals fractionation in the sediments shows that most of the sediments present as carbonate followed by the oxide fraction (Fig. 4a–h). The association of metals in different fraction is given below.

Iron

Residual > Amorphous iron oxide > Carbonate > Crystalline iron oxide > Organic > Manganese oxide bound > Easily exchangeable > Water dissolvable.

Manganese

Carbonate > Manganese oxide > Residual > Amorphous iron oxide > Crystalline iron bound > Organic > Easily exchangeable > Water dissolvable.

Cobalt

Carbonate > Manganese oxide > Amorphous iron oxide > Crystalline iron oxide > Organic > Residual > Easily exchangeable > Water dissolvable.

Chromium

Crystalline iron oxide > Residual > Amorphous iron oxide > Organic > Water dissolvable > Easily exchangeable.

Nickel

Carbonate > Residual > Organic > Crystalline iron oxide > Amorphous iron oxide > Easily exchangeable > Water dissolvable > Manganese oxide.

Copper

Carbonate > Amorphous iron oxide > Manganese oxide > Crystalline iron oxide > Organic > Residual > Easily exchangeable > Water dissolvable.

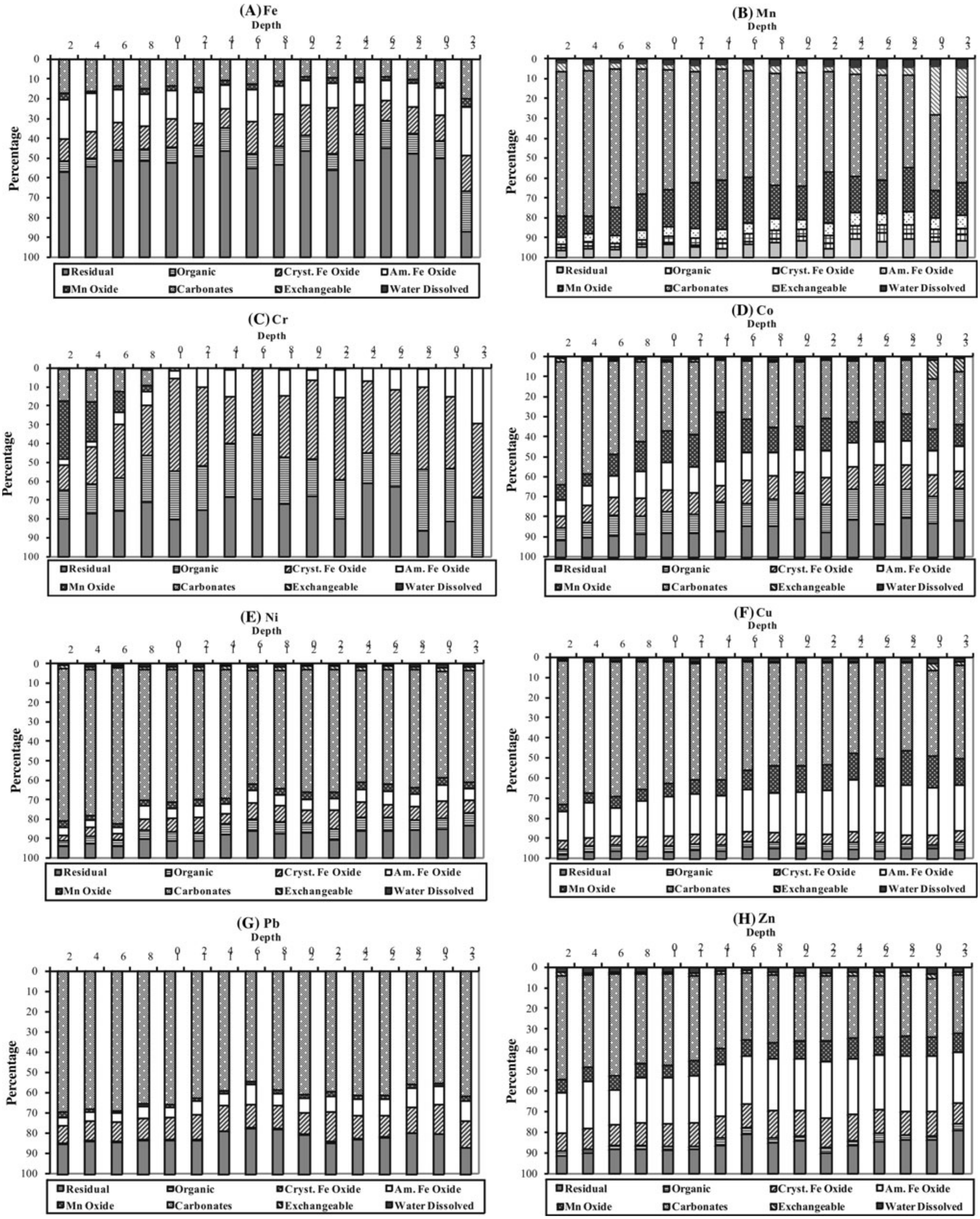


Fig. 4 Trace metals in different fractions of the sediments in the lake

Lead

Carbonate > Residual > Crystalline > Amorphous > Manganese oxide > Organic > Water dissolvable > Easily exchangeable.

Zinc

Carbonate > Amorphous iron oxide > Residual > Crystalline iron oxide > Manganese oxide > Organic > Easily exchangeable > Water dissolvable.

Discussion

Major ion chemistry

Among the major cations, magnesium dominates in the Nainital lake. This might be due to the dominance of minerals, such as dolomite and calcite in the catchment rocks (composed of Limestone of Krol–Tal Formation) of the Nainital Lake. The water chemistry of Nainital falls in magnesium bicarbonate facies (Bartarya 1993). The sodium and potassium concentration in the water column of the lake is very low as compared to calcium and magnesium. Sodium is almost constant throughout the water column in the lake. The concentration of potassium is low in the lake, which might be due to the low mobility of potassium. The dominance of the elements calcium followed by magnesium in the interstitial water might be due to the dissolution if the minerals like calcite and dolomite (limestone) from the sediments. The Ca + Mg:Na + K ratio (Fig. 5) of the water column and the water above the sediment column is ~7 and the interstitial water is >30 shows that the Nainital Lake is dominated by the dissolution of carbonate minerals in the sediment column. The dissolution of the carbonate minerals in sediments can also be inferred from the reduction of pH from alkaline to near neutral.

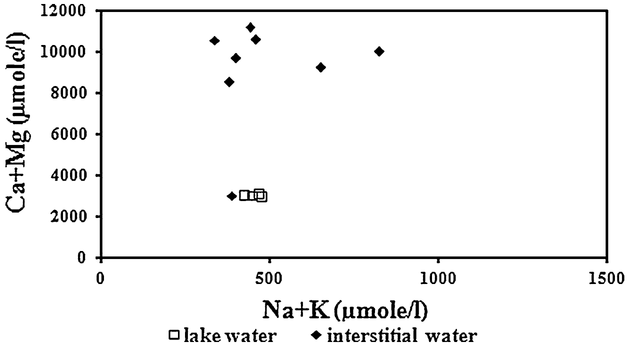


Fig. 5 The Ca + Mg:Na + K graph showing the dominant dissolution pattern in the water and interstitial water column

Bicarbonate (Table 3) dominates among the anion concentration in the lake water chemistry, whereas sulfate shows a considerable increase in the interstitial water chemistry; this may be due to the dissolution of gypsum or oxidation of pyrite (in Nainital) derived from the catchment. The concentration of nitrate reduces in the interstitial water and the concentration of ammonium increases with depth. This indicates denitrification in the anoxic zone, where nitrate reduces to form ammonia/free nitrogen (Schwientek et al. 2008). The high concentration of dissolved sulfate in the interstitial water can also be attributed to the reduction of iron and nitrate in the anoxic zone resulting in the oxidation of sulfide minerals (Pauwels et al. 2000; Schwientek et al. 2008; Choudhary et al. 2009). The high concentration of phosphate in the water column of the Nainital can be attributed to the weathering of the country rocks (apatite in the Krol formation) or the domestic sewage draining into the lake. The phosphorus bearing mineral apatite is not abundant in the catchment, hence anthropogenic source, such as domestic waste disposal into the lake, may play a significant role in the increased phosphorus concentration in the lake water. The low concentration of phosphorous (Nainital lake) in the interstitial water might be due to the sequestration of phosphorus by carbonate flour apatite.

The metal concentration in the water column of the Nainital Lake (Table 4) varies within the sub-basins, Tallital shows high concentration compared to the Mallital, may be due to the presence of a bus station causing high vehicular pollution (Singh and Gopal 2002). The high concentration of zinc in the water column may be due to the sewage draining into the water and the vehicular and the scrapheap wastages being drained into the water (Sparks 2005). The metals are present in very high concentration in the sediment–water interface and at the top 10 cm of the interstitial water in the lake. This may be due to the release of metals from metal oxides, because of changes in the oxic condition (Guo et al. 1997; Boyle 2001). The manganese concentration is low in the interstitial water of Nainital Lake (Table 4), a plausible reason could be due to the sequestration of manganese, released due to the reduction of manganese oxide, by the dominant carbonate phase. The metals cobalt, chromium and nickel (Table 4) show increased concentration indicating the dissolution of oxide minerals. The metals aluminium, copper, lead and zinc (Table 4) show decrease in concentration, may be precipitating with carbonate minerals or may be sequestered by the organic matters, since the presence of organic matter enhances the adsorption of these metals into the surface sites (Calvert and Pederson 1993; Morel and Price 2003).

Sediment geochemistry

Organic matter and carbonates

The organic content and the organic carbon (derived by dividing the organic content by 2.1; Paasche et al. 2004) in the lake sediments increase up core. Although, peripheral parts of Nainital Lake are highly populated, the catchment of the lake is well forested. The increase in organic matter (Fig. 2a) is very high in the top 10–12 cm of the sediment core indicating high productivity in the top layer of the sediment core (Rippey et al. 1982). The carbonate content which indicates the presence of minerals, such as calcite and dolomite, is high in the Nainital Lake and show the presence of these minerals in the sediments (Fig. 2a). The increasing concentration of carbonate with depth indicates the diagnosis of these minerals with depth.

Major oxides

The major oxide chemistry of the lake shows similar trend to the catchment lithology. The high concentration of CaO and MgO in the Nainital Lake (Fig. 2b) may be due to the presence of the calcareous rocks, such as limestone, dolomite and calcareous shales in the catchment area. Depletion in potassium content in the sediments can be used as an index of the chemical maturity of sediments and consequently a proxy for the intensity of chemical weathering (Schneider et al. 1997; Zabel et al. 2001). The Al_2O_3/K_2O ratio is used to know the influence of the soil erosion in the catchment area. The Al_2O_3/K_2O ratio (4–9) of the lake shows dominance of soil erosion (Das 2007). The chemical index of alteration (CIA) is widely used to determine the amount of weathering that the catchment rocks suffered (Nesbitt and Young 1982). This determines the weathering of feldspars relative to unaltered rocks and is defined as,

$$\mathrm{CIA} = [Al_2O_3/(CaO^* + Na_2O + K_2O + Al_2O_3)]\times 100$$

where CaO* denotes the Ca in silicate fraction. Generally, the concentration of CaO is considered to have been derived from the silicate rocks when $CaO \leq NA_2O$, and if $CaO > Na_2O$, the concentration of Na_2O is considered as silicate CaO (Roddaz et al. 2006). The CIA of unaltered feldspar is 50%. The higher CIA% denotes higher degree of weathering in the catchment area. The CIA values of the study area show that the lake catchment area undergoes high degree of weathering. The Nainital Lake with CIA of around 75% shows weathering of the greywacke and argillites in the catchment area.

Nutrients

Sulfur concentration in the lake shows that the Nainital Lake is enriched in sulfur this may be due to the presence of the minerals pyrite and gypsum (Infra Krol, Krol-Tal formations) in the catchment area. The domestic effluent discharge in to the Nainital Lake may also add significant amounts of sulfur.

Mineralisable nitrogen (Fig. 2c) is the amount of nitrogen available for the organisms. The high concentration of the mineralisable nitrogen in the up core may be due to the reduction of nitrate (denitrification) and the formation of free nitrogen and ammonia at the sediment–water interface (Pauwels et al. 2000; Schwientek et al. 2008). High concentration of the nitrogen from might also be due to increasing input of nitrate due to deforestation (Choudhary et al. 2009).

It has been shown that bacteria, algae and high plants use silica for their growth. The silica is deposited as thin (~100 nm) amorphous and often granular crusts which coat the wall (Coradin and Lopez 2003). The silica present in the cells of the organisms is termed as biogenic silica. The diatoms frustules are the dominant organisms possessing silica, and hence are considered to be the source of major part of the biogenic silica, and thus the concentration of the biogenic silica is directly proportional to the amount of diatoms in the sediments. The diatoms frustules settle faster from the water column and their slow rate of dissolution causes high concentration of the biogenic silica in the sediments. The low concentration of biogenic silica in the Nainital Lake (Fig. 2c) may be due to the absence of abundant diatoms in the lake (Pant et al. 1980).

Phosphorus in the sediments in the lake is obtained from the lithology and through the domestic wastes and agricultural runoff (Ruttenberg 2004). Total phosphorus concentration in the Nainital is similar to that of the total phosphorus of the major moderately eutrophic to hypereutrophic lakes around the world. The lake Erken (Rydin 2000), Xuanwu and Yue (Wang et al. 2005), Hyper eutrophic lakes, have similar concentrations to that of the Nainital The high concentrations of phosphorus in this lake is due to the draining of domestic sewage sludge and agricultural wastes into the lake (Rydin 2000; Wang et al. 2005). The high concentration of phosphorus in the Nainital may be due to the presence of pockets of apatite in the catchment area (Krol formation). The high Al_2O_3/K_2O ratio in the lake sediments also indicates the dominance of soil erosion in the catchment and input of phosphorus in the form of runoff, mostly as anthropogenic inputs.

Phosphorus fractionation

The lake shows dominance of phosphorus concentration (>90%) in the biogenic apatite (CFAP) fraction (Fig. 3). Phosphorous in this fraction is considered to be refractory and immobile, which acts as a natural controller of eutrophication (Penn and Auer 1997; Rydin 2000; Pardo et al. 2003). The dominance of this fraction is because of the nature of phosphorous to bind with calcium. The dissolution of calcium carbonate rocks (limestone) in the catchment aid in nucleating the calcium bound phosphorous precipitation (Kleiner and Stabel 1989; Olila and Reddy 1997). Nainital shows high concentration of phosphorus in the exchangeable fraction and show a decreasing trend up core. The dissolution of iron/metal bound complexes at high anoxic condition releases phosphorus (Rydin 2000; Pardo et al. 2003) which in turn is adsorbed on to the sediment particles leading to increasing concentration in the exchangeable fraction, making phosphorous available for the algae and plants (Zhou et al. 2001).

Metals

The metals enter the lake through the weathering of the catchment rocks. The manganese concentration (Fig. 2d) is almost similar to that of the average carbonate rock. The trace metal (Fig. 2d) concentration of the lake is much higher than the average carbonate rocks, which indicates some other additional source for the metals. The presence of a bus station near the lake and the draining of the domestic wastes into the lake are the major identified anthropogenic sources. The decreasing concentration of the metals cobalt, chromium and nickel is due to reduction of iron and manganese oxides and simultaneous release of these metals into the interstitial water (Gambrell et al. 1991; Davison 1993; Koretsky et al. 2006). Almost uniform concentration of the metals, copper, lead and zinc show that they are unaffected by the redox condition and retained in the sediments by the carbonate or sulfide minerals (Davison 1993; Boyle 2001).

The sedimentation rate of the lake helps to identify the anthropogenic activities, which took place in the catchment area in the recent past. The average annual sedimentation rate in Nanital lake is 50 mm (Choudhary et al. 2009). The increasing concentration of the metals from depth to the surface shows that, there is increasing pollution in and around the lake. The metals copper, zinc, nickel and lead in the Nainital Lake (Fig. 2d) show maximum concentration up core. The geo-accumulation index (Muller 1979) of metals in the sediments has been used to find the influence of anthropogenic effect in the lakes. It is determined by the following equation,

$$I_{\text{geo}} = \ln[C_n/(1.5 \times B_n)]$$

where, C_n is the concentration of the metal in the sediment, B_n is the back ground value of the metal; generally the value of average shale proposed by Turekian and Wadepohl (1961) is used. The pollution state of the lake sediments are determined by the I_{geo} value, which varies from 0 to 6, where, 0 denotes uncontaminated sediments, 3 denotes, moderately polluted, and 6 denotes highly/strongly polluted sediments. The I_{geo} value for the Nainital Lake shows that the metals having uncontaminated, moderately polluted nature in general. The metal lead shows an uncontaminated to moderately contaminated nature throughout the core indicating vehicular pollution. The metal chromium and nickel with moderately contaminated character in the up core shows increasing pollution in recent past. The metals, copper and zinc with moderately polluted to moderately strongly polluted character shows the influence of pesticides and sewage sludge (Sparks 2005). The metal, cobalt shows very highly polluted nature of the sediments.

Metal fractionation

Iron and manganese are the two metals whose biogeochemical cycle in the aquatic environment determines the fate of almost all metals. Iron is one of the most abundant metals in the Earth's crust and dominates in the lacustrine sediments (Davison 1993). The high concentration of iron in the oxide fractions (Fig. 4a) in the Nainital Lake may be due to settling down as the amorphous iron oxy-hydroxides. The amorphous iron oxide with aging, transforms to the stable crystalline iron oxides (Tessier et al. 1996). The reduction of the precipitated iron oxy-hydroxides is dominant at the sediment–water interface where organic decomposition dominates, although all the iron oxy-hydroxides are not released (Davison 1993). The dissolution of iron oxides is predominantly dominated by microbial activity at high anoxic condition (Eh $>$ -130 mv) (Guo et al. 1997). In case of the Nainital lake the dissolved iron oxides are precipitated down as iron carbonate or sulfide due to the presence of these molecules in abundant quantity. In the presence of sulfides, the dissolution of these oxides enhances the formation of iron sulfides, mostly of mackinawite (Huerta-Diaz and Morse 1992; Cooper and Morse 1998).

The dominance of the carbonate fraction (Fig. 4b) may be due to the precipitation of manganese as carbonate at anoxic conditions (Koretsky et al. 2006). The very low concentration of manganese in the oxide fractions is due to the characteristic of manganese to dissolve faster than iron in the anoxic condition. The dissolution of manganese is enhanced in the presence of organic matter (Davison 1993), causing its release into the water column. The released manganese is adsorbed onto the settling clay particles and mineral surfaces and also adsorbed onto the carbonates. The manganese oxides, which have escaped dissolution, might have transformed to the most stable forms with aging at depth.

Chromium, cobalt and nickel show similar characteristics in chemical forms. They prefer manganese and iron oxy-hydroxide forms, over the other forms (Scholz and Newmann 2007). All the three metals show high concentration in carbonate fraction showing increasing trend up core; chromium and cobalt show drastic increase compared to nickel. The high amount of cobalt in the carbonate fraction in the Nainital Lake may be due to the presence of high concentration of carbonates and due to the prevalence of high anoxic condition in the lake. In general, cobalt shows high concentration in crystalline iron oxide (Fig. 4c), followed by the organic fractions (Koretsky et al. 2006). At lower Eh, cobalt prefers to associate with the oxides and organic matters. Chromium may enter an aquatic system anthropogenically through the landfills, scrapheap in the form of oxides and organic and inorganic ligands. Chromium, generally, is absorbed by iron oxide minerals than any other phases and settles down on the sediments. The decreasing trend up core of the crystalline iron oxide phase (Fig. 4d) compared to the amorphous iron oxide phase, may be due to the transformation/aging of the amorphous iron oxide to crystalline iron oxides. The reduction of these oxides may cause the release of chromium from the sediments (Gambrell et al. 1991; Davison 1993; Koretsky et al. 2006). In the presence of organic matter, chromium binds with humic substances (Guo et al. 1997; Koretsky et al. 2006). Nickel found to be present in the organic and residual fraction (Fig. 4e) (Panda et al. 1995; Staelens et al. 2000; Zhai et al. 2003). This is due to the adsorption of nickel by the formation of ligands in the presence of high organic content (Jacobs et al. 1985). It has been found that nickel at high anoxic condition binds with the oxides to undergo reduction and is released to the water column. The high concentration of chromium in the exchangeable and water dissolvable fraction is also due to the release of chromium by the dissolution of iron and manganese oxides. The released nickel is also adsorbed or co-precipitated by the carbonates (Yu et al. 2001) in the presence of high carbonate content as in the case of Nainital.

The metals copper, zinc and lead are chalcophilic in nature; copper (Fig. 4f) and zinc (Fig. 4h) are micronutrients and gets settled along with the readily oxidisable organic matter. These metals at high anoxic conditions generally are associated with the carbonate, and sulfides and organic matter and are not affected by the redox conditions (Davison 1993; Yu et al. 2001). This is a major reason for the dominance of the carbonate fraction in the highly anoxic Nainital lake sediments. The high concentration of lead in residual fraction (Fig. 4g) shows its natural origin. The dominance of carbonates and the oxides in the sediments shows precipitation of lead from the overlying water column.

In essence, all the metals shows high concentration in the carbonate fraction might be due to the adsorption or precipitation of the metals by carbonate that are dissolved from the oxides and organic. At high anoxic conditions, the metals released from the metal oxides prefer to bond with the carbonate phase (Yu et al. 2001).

Saturation of minerals in the water column and interstitial water and mineral composition

The wateq4f speciation model was used to find the saturation indices of various minerals in the lake water and XRD was used to identify the mineral composition in the lake sediments. The minerals quartz, feldspar, muscovite, biotite and carbonate minerals like calcite, dolomite are the dominant minerals in the lake sediment. The minerals like calcite, dolomite, and amorphous silica peaks in the XRD is also supported by the over saturation of these minerals in the water column and sediment water interface. The minerals hydroxyl apatite and carbonate flour apatite (FCO_3 Apatite) show oversaturation in the water and interstitial waters, with dissolution of manganese phosphate in sediment water interface, shows that they acts as main sink for phosphorus in sediments. The metals present mainly as free metal ions in the water column. The precipitation of oxide minerals like ferrihydrite, and manganese hydroxides is supported by their presence in the top sediment layer. The prevalence of anoxic condition results in their dissolution at deeper part of the core. The sulfide mineral pyrite is also present throughout the core.

Summary: possible geochemistry in the lake

The chemistry of the lake do not vary widely in case of the major ions, whereas, the concentration of dissolved phosphate and metals vary with depth. The concentration of the metals, iron, manganese and aluminium and their saturation levels support possible formation of iron-manganese/aluminium oxy-hydroxides in the oxic layer of the lake. The decreasing concentration of the metals with depth may be due to the co-precipitation or incorporation of these metals on to the iron–manganese oxy-hydroxides. The change in concentration of the metals in the sediment–water interface and the interstitial water is controlled by the redox potential. The drastic increase in the concentration of chloride, sulfate, and the metals shows the dominance of the reduction and oxidation mechanism in the anoxic layer.

An increase in the concentration of the metals in this layer indicates reduction of oxy-hydroxide layer, resulting in the release of the metals into the water column. The presence of ammonia in the anoxic layer indicates reduction of nitrate. The increase in chloride concentration may be due to the formation of sulfides, $M(H_2O)_5(Cl)^+ + HS^- \rightarrow M(H_2O)_5(HS)^- + Cl^-$ (Bi-sulfide complexation)—where, M denotes the metal ion.

The formation of iron ferrihydrite acts as a possible scavenger of the metals in the sediments. Not all the oxides formed are reduced even at high anoxic condition, resulting in the dominance of the oxide phase in the sediments. Manganese released due to the decomposition of organic matter and by the reduction of sulfides in the anoxic layer may be scavenged by the carbonates in the sediments. However, sulfidisation of zinc and cobalt are faster than that of iron, thus preventing the pyritization of iron (Davison 1993). Phosphorous is dominantly associated with the carbonate flour apatite, indicating carbonate as the chief sequester of this element. The dissolution of iron oxides in the anoxic layer may be a potential source for phosphorous in the interstitial water.

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