NUTRIENTS AND HEAVY METALS IN KUMAUN HIMALAYAN LAKES

A THESIS

Submitted in partial fulfilment of the
requirements for the award of the degree
of
DOCTOR OF PHILOSOPHY
in
EARTH SCIENCES

by

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in this thesis entitled **NUTRIENTS AND HEAVY METALS IN KUMAUN HIMALAYAN LAKES** in partial fulfilment of the requirements for the award of the Degree of Doctor of Philosophy and submitted in the Department of Earth Sciences, Indian Institute of Technology Roorkee, Roorkee is an authentic record of my own work carried out during a period from July 2005 to November 2008 under the supervision of Dr. G. J. Chakrapani and Dr. Sri Niwas, Professors, Department of Earth Sciences, Indian Institute of Technology Roorkee, Roorkee, India.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other University/Institute.

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This is to certify that the above statement made by the candidate is correct to the best of our knowledge.

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ABSTRACT

The Kumaun Himalayan lakes, Nainital Bhimtal, Sattal and Naukuchiatal, situated in the administrative state of Uttarakhand, are 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 behavior of nutrients and metals in the lake sediments and their association with different chemical forms in the sediments deposited during the past few decades. The study was accomplished by collection of water samples at different depths and core sediment samples from the deepest part of the lakes. Major ions and dissolved metals concentrations were analyzed in the surface water, deep water and interstitial (pore) waters. The core samples were sliced at different depth intervals and analyzed for major oxides composition at each depth sample; nutrient fractionation (easily exchangeable, reducible, $CaCO_3$ bound+ biogenic apatite, detrital apatite, organic) and heavy metals fractionation (water dissolvable, exchangeable, carbonates, manganese oxides, amorphous iron oxide, crystalline iron oxide, oxidisable and residual) in each sample were also carried out following standard sequential extraction procedure. The total concentration of nutrients (P, N and S) and metals (Fe, Mn, Co, Cr, Ni, Cu, Pb and Zn) in the water column, interstitial water and the sediments varied differently. The major water chemistry (major ion composition) and sediment chemistry (major oxides composition) along with the Ca+Mg: Na+K ratio, chemical index of alteration, and Al_2O_3/K_2O ratios in the water and sediments respectively, indicate the major influence of catchment lithology, especially carbonate weathering and soil erosion in the catchment area. The high concentration of chloride, sulfate and ammonium in the interstitial waters show processes such as denitrification, sulfidization and sulfide oxidation dominating the anoxic bottom of the lakes. The metal chemistry shows that, the Nainital Lake is more polluted in Tallital basin compared to the Mallital basin. The high concentrations of the metals, copper, zinc, chromium and nickel indicate contributions from domestic and agricultural wastes and vehicular pollution inputs in to these lakes. The saturation indices in water show the formation of iron oxide minerals, goethite, ferrihydrite and others, in the oxic layer of the lakes. These minerals are dissolved in the anoxic bottom layers of the highly anoxic Nainital Lake; the metals form carbonate phase rather than the oxide phase. The other three lakes show that all the oxide minerals are not reduced in the anoxic condition, thus leaving behind some metals in the sediments. The relationship between phosphorus and other major elements in the sediments shows the preference of phosphorus for calcium, rather than for iron and aluminum in these lakes. The presence of carbonate flour apatite, inferred from the high concentration of phosphorus in this fraction, acts as a main sink for phosphorus in sediments. The trace metal geochemistry in the sediments also shows the major influence of source rocks. The geo-accumulation index shows, the Nainital Lake to be moderately polluted with respect to chromium and nickel, and strongly polluted with zinc, copper and cobalt, where as the other lakes show high levels of lead and cobalt contamination in the sediments. The metal fractionation studies show the influence of catchment lithology and redox potential in the speciation of metals. The high anoxic condition of the Nainital Lake shows that the metals are associated with the dominant carbonate phase compared to the oxide phase, where as in the other lakes, chromium and nickel prefer iron oxide phase, cobalt prefers manganese oxide phase, and zinc is associated with organic matter. The study shows the catchment lithology, organic matter and redox potential, significantly

affecting the speciation and bioavailability of phosphorus and metals in the lake sediments.

The overall geochemical processes taking place in the lakes are inferred from the present study. The precipitation of the oxy-hydroxides acts a major sink for the metals and phosphorus in the water column. The oxy-hydroxides are reduced in the anoxic layer, resulting in the release of the metals and phosphorus; sulfidisation of the metals takes place at the anoxic layer. The dominance of carbonate in the Nainital Lake acts as major sink for the metals and phosphorus into the sediments. In other lakes, the organic complexes act as a significant sink for the metals and the carbonates for phosphorus. The diffusive metal flux estimated for the Nainital lake shows that the metal flux is high for redox sensitive metals (Fe, Mn, Ni) compared to the less sensitive metals (Cu, Pb, Zn). The positive flux values indicate release of the metals from the sediments. Taking the observed lake processes, suitable remediation methods may be suggested in future studies. The study shows that the metals and phosphorus are mainly sequestered onto the sediments by carbonates in the Nainital Lake., The change in pH may result in the dissociation of carbonates, and thus the metals and phosphorus. Providing sand capping to the bottom sediments and any suitable amendment material, may reduce the metal and phosphorus flux from sediments to water. The Nainital Lake is more urbanized and polluted compared to the other three lakes, Bhimtal, Sattal and Naukuchiatal, may be due to abundant vegetation and less urbanization around these lakes.

The thesis on **"Nutrients and Heavy Metals in Kumaun Himalayan Lakes"** has been organized in to six chapters. A brief introduction, outline and objective of the study have been described in Chapter 1. Details of the study area are presented in Chapter 2. Chapter 3 deals with nutrient fractionation in the lake sediments, and

Chapter 4 deals with fractionation of heavy metals in sediments. Chapter 3 and Chapter 4 have been covered with literature on global lake studies, objective, methodology, and results and discussion of the data obtained from the selected Kumaun Himalayan lakes. A gist of the lake processes in operation in the present study, flux and suggested remedial measures are enumerated in Chapter 5. The major conclusions from the study are presented in Chapter 6, followed by all the references cited in the thesis.

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(P.PURUSHOTHAMAN)

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Chapter 1

INTRODUCTION

1.1 Preamble

Most of the lakes are characterized by finite boundaries and comparatively limited mobility of materials and, hence, provide a more tractable venue as natural laboratories for mechanistic studies. Several concepts and processes of current interest in aquatic ecosystems were first defined and examined in lakes (Heckey and Kilhan, 1988; Wetzel, 2001). Lakes serve as a source of water for life in the lakes and also serve humans outside in several ways, such as source of drinking water, irrigation, fisheries, industrial and domestic needs, socio-economy and, are highly aesthetic. The major source of water for the lakes is from precipitation and small streams/springs draining the lake basin. The lake water composition depends mainly on the lithology of the catchment area. However, recent human activities around lakes have also imprinted their signatures on water flux and lake water quality. In addition to water, the sediments are also an important component of lakes and act as both source and sink for the contaminants (Forstner and Wittman, 1983; Holtan et al. 1988). The contaminants are transported both in solution and attached to the suspended matter from the catchment area (Salomons et al. 1987). The permanent accumulation of contaminants possess problems, because sediments act as a source of pollution long after the pollution of overlying water has been abated (Harder et al. 2007). Natural processes and man-induced changes in external parameters may cause rapid mobilization of the accumulated pollutants. Major factors influencing the solubility, mobility and bioavailability of various elements in terrestrial and aquatic environments are (Kabata- Pendias, 2001), (i) lowering of pH, (ii) changing redox conditions, (iii) increased occurrence of natural and synthetic complexing agents, and (iv) increased salt concentrations. All these phenomena play significant roles in the deterioration in lacustrine environment.

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 (Stumm and Morgan, 1996). Adsorption is the process of binding of ions onto the surface of the particles. The reactions at the solid surfaces mainly arise because of, (i) existence of unfulfilled charge requirements of molecules or functional groups (e.g., hydroxyl, carboxyl, phosphoryl) at the solid surface; (ii) unique properties of the water itself causing it to be a polar molecule; (iii) presence of dissolved constituents with non- neutral charges; and (iv) the inherently dynamic nature of the aquatic system (Warren and Hacck, 2001).

The major nutrients, phosphorus, nitrogen, silica and the metals cause eutrophication of lake ecosystems. The nutrients are introduced into a lake system through the streams and springs, in both particulate and dissolved forms. In the solution phase, metals and nutrients are present as free ions or as inorganic and organic complexes. In the solid phase, the main adsorbing phases are clay minerals, Fe, Mn and Al- oxy-hydroxides, organic matter etc. The elements are also present in mineral lattices. Co-precipitation and precipitation of these elements in authigenic mineral phases occur under changing environmental conditions. In the anoxic environment, formation of sulfides and complexes with organic matter dominate over other phases. These sediment bound elements are remobilized or released in to the water column often at the sediment-water interface. Hence, lake pollution studies must involve sediment bound elements. At the same time, it is also imperative to study metals and nutrients associated with various chemical fractions of sediments, because the total metal concentration is not a proper indicator of bioavailability. The mobility, toxicity and bioavailability of an element is possible only when speciation (chemical forms) of the element is completely understood (Koretsky, 2000). Thus, the strong inter-relationship between the various components plays an important role in lake chemistry and its pollution status.

1.2 Studies on Kumaun Himalayan Lakes

Although the importance of speciation and fractionation studies have been realized, limited studies have been carried out on the sediments of Lakes of India. 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. Handa et al. (1982) reported phosphate (PO_4-P) concentration to be above critical levels in the Nainital Lake. Pandey et al. (1983) observed that rainfall contributed significant amounts of phosphorous and nitrogen and also found that the forest land lost nutrients very quickly compared to the non-forested land. Khanna and Jalal (1985) studied the physico-limnological aspects in Naukuchiatal Lake. Pant and Joshi (1987) studied the phytoplankton population in the Sattal Lake. Gupta and Pant (1989) have documented the elemental chemistry of sediments in the Nainital Lake. Singh and Gopal (1999) observed the productivity of Nainital Lake to be very high (>8) in Bhimtal Lake. 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. Nachaiappan et al. (2000) studied the hydrodynamics of the Nainital Lake using numerical modeling and stable isotopes. Bartarya (1993) studied the water chemistry of the Kumaun Himalayan lakes. Das et al. (1995), Chakrapani (2002); 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. Shukla and Bora (2005) have proposed a sedimentation model using lithostratigraphic signatures and observed that the lakes were formed due to the blocking of the valley by debris flow. Kotlia et al. (2000) studied the paleoclimate in the Bhimtal and Naukuchiatal region. Metal fractionation studies in Nainital Lake sediments have been carried out by Jain (2008). However, detailed investigations of nutrients and heavy metals in core sediments, going back from the last few decades up to the recent times in the Kumaun Himalayan Lakes, are still lacking, and hence the present study is aimed at filling the gap.

1.3 Objective

The major objective of the present study is to understand the association of nutrients and heavy metals in the various chemical fractions of the lake sediments, from four Kumaun Himalayan lakes, namely, Nainital, Bhimtal, Sattal and Naukuchiatal.

The study has been accomplished by, (i) collection of core samples from the lakes, which were deposited during the past few decades, (ii) separating them into various depth segments, (iii) isolating the sediments in to various chemical fractions, (iv) analyzing various nutrients and heavy metals by standard analytical procedures, and finally, (iv) collating the entire data generated for various interpretations related to the lake processes.

Chapter 2

STUDY AREA

The study area includes the four lakes, Nainital, Bhimtal, Sattal and Naukuchiatal in the Kumaun Himalayan region in the Uttarakhand State of India (Fig. 2.1)

2.1 Nainital Lake

The crescent shaped Nainital Lake is situated at 29°24' N and 79°28' E at an altitude of 1938 m above mean sea level. The kidney shaped lake was formed due to tectonic activity. The rotational strike-slip as well as dip-slip motion caused the blocking of a matured perennial stream, and forming the lake. The vertical displacement between the Naini and Deopatta peaks is of the order of 80m, while in the Balia ravine just SE of the bus station, it is 20m (Valdiya, 1988). The lake has two sub-basins Mallital and Tallital divided in the middle by a ridge. The Mallital receives water through the Bara Nala, which drains from the spring 'Paradara' and Tallital receives water through the spring 'Siphadara'. Many small streamlets flowing through the fractures of the catchment area also find their way in to the lake. Some of the hydrological parameters of the lakes are presented in Table 2.1.

Plate. 2.1 Google Earth® Image of the study area showing the topography and the Lakes

Plate. 2.2 Photographs of the Lakes

Nainital

Bhimtal

Plate. 2.3 Photographs of the Lakes

Sattal

Naukuchiatal

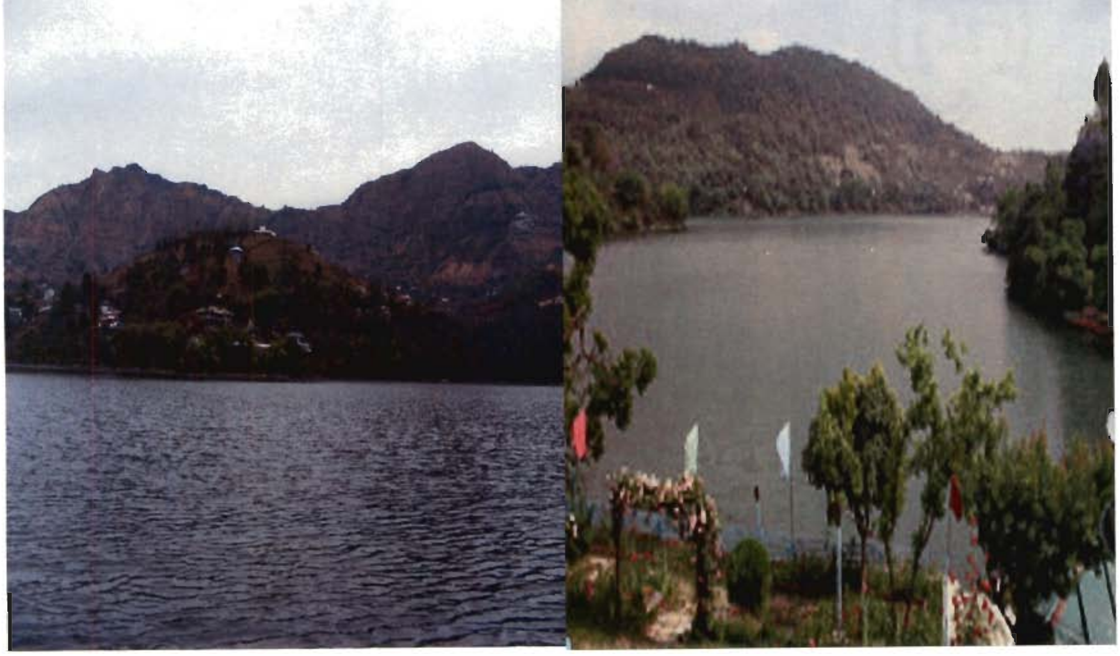


Table 2.1 Hydrological parameters of the Kumaun Himalayan Lakes

Parameter	Nainital (Sharma et al. 1982)	Bhimtal (Gupta and Pant, 1989)	Sattal (Pant and Joshi, 1987)	Naukuchiatal (Khanna and Jalal, 1985)
Altitude (m)	1,937	1,331	1,300	1,320
Longitude	79° 28’ E	79° 36’ E	79° 32’ E	79° 35’ E
Latitude	29° 24’ N	29° 24’ N	29° 24’ N	29° 19’ N
Length (m)	1,432	1,974	1,300	1,050
Breadth (m)	423	457	190	675
Max. Depth (m)	27.3	25.8	20	42.25
Mean Depth (m)	16.2	11.5	8	21.89
Surface Area (km^2)	0.48	0.85	0.4	0.375
Catchment Area (km^2)	3.96	11.4	4284	3.25
Shoreline (m)	3,630	4,023	3,750	3,600
Average Rainfall (mm)	2,300	1,711	1,741.2	n.a
Max. Air Temp (°C)	24.6	33	26.1	n.a
Min. Air Temp (°C)	0.5	1.5	n.a	n.a
Ma.x Water Temp (°C)	25	28	n.a	n.a
Min. Water Temp (°C)	10	14	n.a	n.a
Volume of Water (m^3)	5,907,500	4,245,700	2,598,500	7,055,000

n.a. = data not available

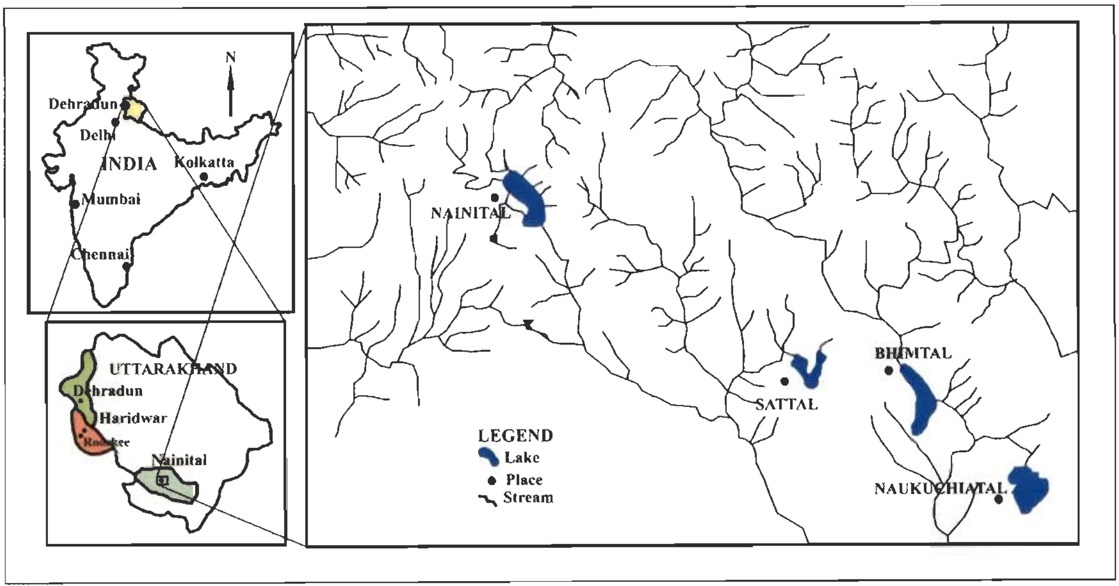


Figure 2.1 Location and drainage map of the study area (not to scale) (modified after Bartarya, 1993)

2.2 Bhimtal and Naukuchiatal

The sparsely populated town of Bhimtal (at an altitude of 1,331 m) and Naukuchiatal (at an altitude of 1,320 m) comprising the lakes Bhimtal and Naukuchiatal lakes are located at 29°20’N; 79°36’E and 29°19’N; 79°35’E respectively

(Table 2.1). The formation of the Bhimtal–Naukuchiatal lake system was related to a WNW-ESE trending strike-slip fault (Raina and Dungrakoti, 1975; Valdiya 1980; Bartarya, 1988) traversing the area. It is believed that the Bhimtal Lake had been part of a bigger lake, which was about 7–10 km long and 1 km wide and later dried in Holocene times (Sinha and Pal, 1978; Khanka and Jalal, 1985; Shukla and Bora, 2005).

Bhimtal is also one of the important towns and tourist places in the Nainital district, however it is less urbanised compared to Nainital. The newly formed industrial area in the outskirts of Bhimtal has a possible influence and major impact on the water quality of the lake. The lake receives major amounts of water through a stream draining into it and the outflow also occurs through a stream. The Naukuchiatal on the other hand receives its major water through the springs and streamlets draining in its catchment area (Valdiya, 1988).

2.3 Sattal

The Sattal Lake is located at 29°21'N; 79°32'E (Table 2.1) at an altitude of 1,370 m, surrounded by a small village with sparse settlement. The lake derives its name from the seven depressions or lakes within itself. The seven lakes or depressions were formed as a result of the blockade of the ravines due to debris flows (Valdiya, 1988), which resulted due to the movement caused by the Sattal- Punatal fault.

2.4 Drainage Pattern

The drainage pattern of the Naini Hills is (Fig. 2.1) of trellis type and is altogether different from the Siwalik range in front of it (Valdiya, 1988). The streams draining on this hill are structurally controlled and generally follow the faults and fractures, which meet on their way downstream.

2.5 Landuse

The watershed of the Nainital hills is substantially covered with forests, which is dominated with Oak and Cyprus trees. The increasing land-use around the lakes due to tourism cause serious problems in the catchment of the lakes (AHEC, 2002). Figure 2.2 shows the progress in increasing population in and around the lakes due to tourism and urban development since 1901 (Singh and Gopal, 2002). Table 2.2 presents the various anthropogenic activities during the year 2001 in the Nainital watershed. The lakes receive a lot of sediments due to unplanned construction, deforestation and other developmental activities. The activities of converting the forest area into barren areas have resulted in increased soil loss in the catchment of the lakes.

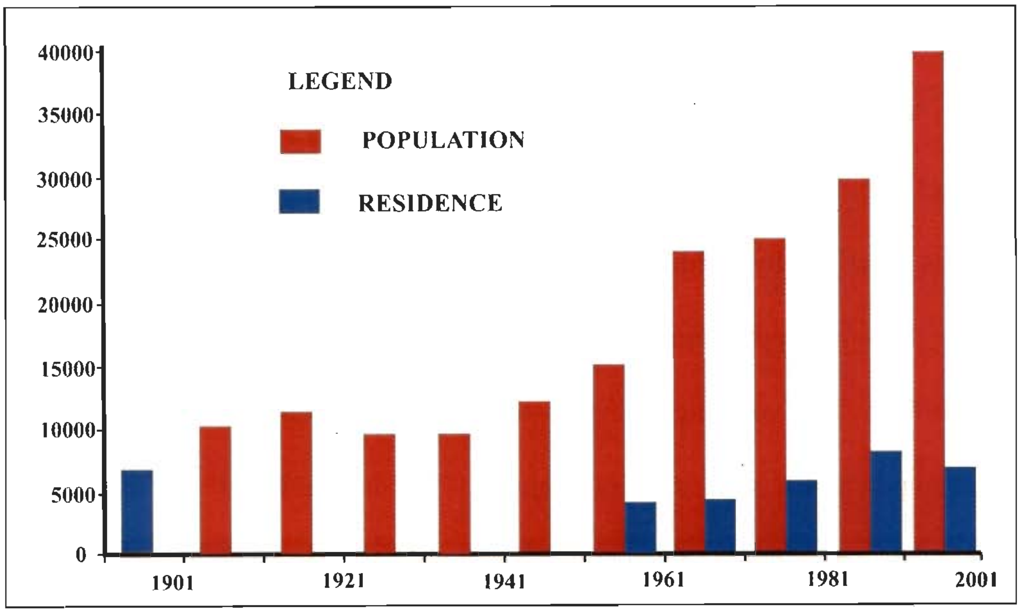


Figure 2.2 Increase in population in and around the Lakes (After: Singh and Gopal, 2002)

Table 2.2 Anthropogenic activity around Naintal Lake (After: Singh and Gopal, 2002)

Anthropogenic Activity	
Permanent population	39,840
Tourist population	~ 3,10,000 yr^{-1}
Hotels	120
Shops	900
Residences	8000

2.6 Geology

The lithology of the Naini Hills ranges from the rocks of Paleoproterozoic to Terminal Proterozoic. The rocks of the Bhimtal, Sattal and Naukuchiatal consisting of Bhimtal Formation and Bhawali Quartzite are of Paleoproterozoic, and the rocks of the Nainital area consists of the Krol and the Tal Formation of Terminal Proterozoic age.

Valdiya (1988) studied the detailed geology of the Naini hills and classified the rocks into different formations. The geology (Table 2.3, Fig. 2.3) of the Naini Hills as described by Valdiya (1988) is briefly discussed below.

The Amritpur granite is thrust over by the quartzites associated with volcanics and tuffites. The volcanics consists of Bhimtal Volcanics, amygdaloidal- vesicular basalts and chlorite schists (Varadarajan, 1974; Shah and Merh, 1978; Valdiya, 1988) with dykes traversing the volcanics at some places (Raina and Dungrakoti, 1975). The Bhimtal volcanics are succeeded by quartz- arenite interbedded with the slates, basalts and tuffites and are termed as Bhowali Quartzites. These two rock formations dominate the Bhimtal and Naukuchiatal region. The Sattal region consists of the rocks of Jantwaliagaon Formation, which consists of carbonaceous phyllite/ slate and thinly bedded marmorized limestone with intercalations of quartzite and chloritic phyllite (Raini and Dungrakoti, 1975), apart from the Bhimtal Volcanics and Bhowali

Quartzites. The limestone of this area contains pockets of dolomite, siderite and magnesite.

Table 2.3 Geology of the study area (after, Valdiya, 1988)

Mossourie Group	Tal Formation	Narain Member (=Middle Tal)
		Giwalikhet Member (= Lower Tal)
	Krol Formation	Sherwood Member (= Krol E)
		Bist College Member (a local facies)
		Pashandevi Member (= Krol D)
		Barapatthar Member (= Krol C)
		Hanumangarhi Member (= Krol B)
		Monora Member (=Krol A)
	Blaini Formation	Kailakhan Slates (=infra Krol)
		Pangot Member (=Blaini)
Jaunsar	Jaunsar Upper	Lariakantha Quartziter (=Nagthal Fm)
		Bhumiadhar Fm (= chandpur Fm)
		Betalghat Fm (=Mandhali of Jaunsar hills)
MBT Salari Thrust	Jaunsar Lower	Jantwalgaon limestone (lenticular)
		Bhawali Quartzite
		Bhimtal Volcanics
	Amritpur Granite	
	Lower Siwalik	

The Nainital area is mainly composed of carbonate rocks and have been unequivocally identified as Krol by Middlemiss (1890), Auden (1942), Heim and Gansser (1939), Awasthi (1970), Hukku et al. (1974), Pal and Merh (1974), Pande (1974) (described it as Nainital Formation), Valdiya (1981) and Sharma (1981). The

Krol Formation of this area consists of calcareous slates, which alternate with marllites and argillaceous limestones (Krol A); ferruginous shales interbedded with algal dolomites and pockets of gypsum (Krol B) (Nautiyal, 1955); Dolomitic limestone and calc- arenite and calc- lutite with pockets of oolite (Krol C); Black shales with argillaceous or carbonaceous limestone and greywacke and siltstone with subordinate slates (Krol D); Massive dolomite which are cherty and phosphatic at some places and are associated with the conglomerates and oolitic calcarenite and carbonaceous shale (Krol E).

The succession of carbonaceous shale with subordinate dolomitic limestone characterized by nodules, laminae, and stringers of phosphatic material, are followed upward by purple green shales intercalated with muddy fine- grained sandstone and siltstone is recognized as the Tal (Valdiya, 1980).

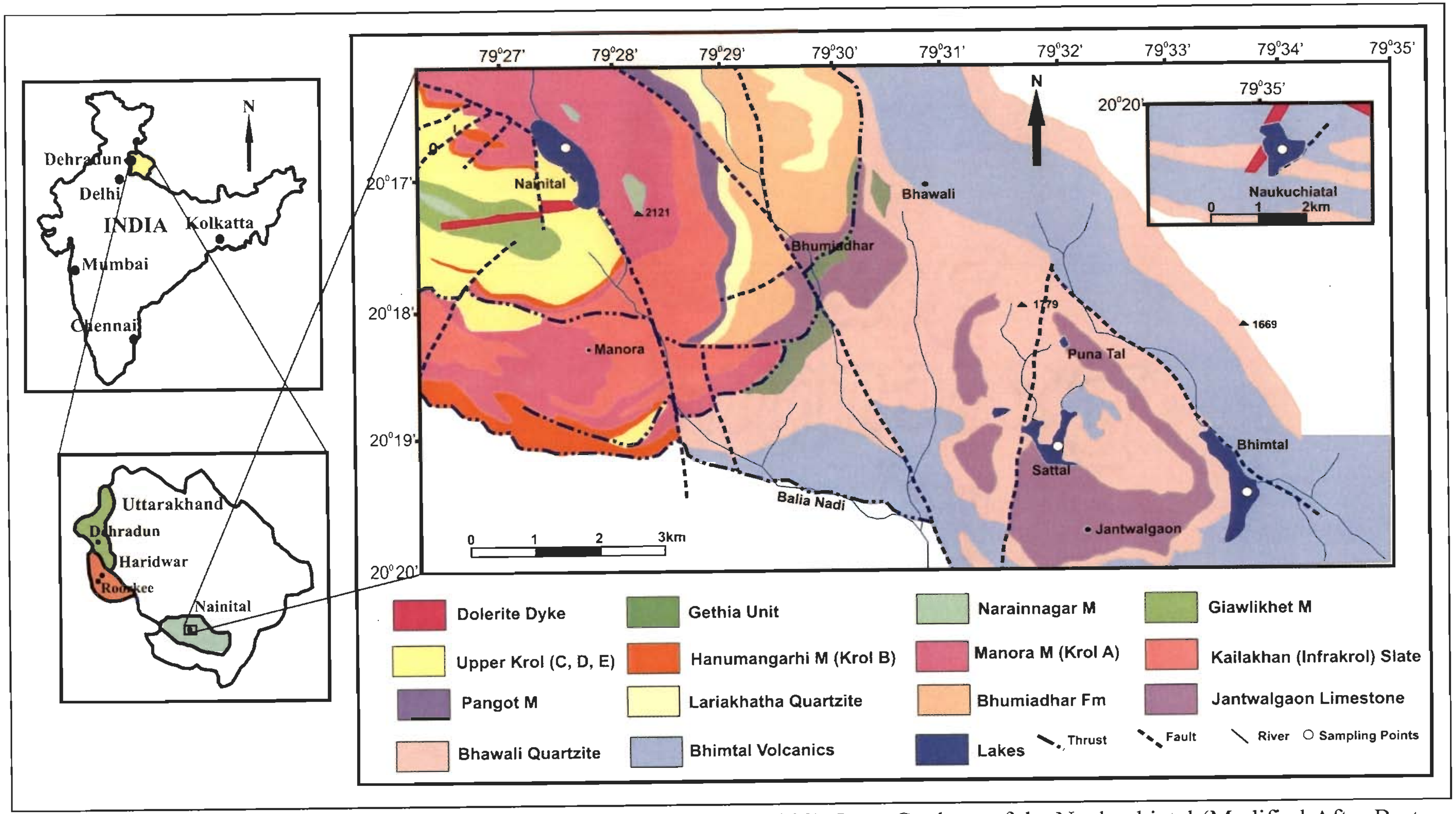


Figure 2.3 Geological Map of the Study area (Modified After, Valdiya, 1988); Inset Geology of the Naukuchiatal (Modified After Bartarya, 1993)

Plate. 2.4 Field Photographs


Water Sampling


Gravity Corer


Retrieval of sediment core

Plate. 2.5 Field Photographs

Slicing of sediment core in the field

Field analysis of pH, Eh, and bicarbonate

Chapter 3

NUTRIENTS

3.1 Objective: Assessment of Nutrient Fractionation in the Lakes

3.1.1 Nutrients in Aquatic Environment

The nutrients are those elements which help in the growth of organisms thriving in the lakes or elsewhere. The elements, C, S, H, O, N, P and Si are the major nutrients in aquatic systems. The elements C, S H, O and N have a source in the atmosphere in elemental forms and Si has a rock source and, hence, is available to the organisms through interactions with the water surface. However, phosphorus does not have any significant presence in the atmosphere, thus, making phosphorus play an important role in the growth of algal blooms in lake ecosystems. Nitrogen and phosphorus are the two major nutrients, which determine the organic productivity in a lake and thus are termed as limiting nutrients. The nutrients P, S and N interact with each other and play a major role in the release of the other, from sediments to the water column and vice versa. Correll et al. (2000) observed that the reduction of total nitrogen in summer takes place due to the retention of nitrate in the winter and spring and that of phosphorous, due to retention in both inorganic and organic forms. The nitrogen present as nitrate in the water column inhibits the release of phosphorus from the sediments and, thus, prevents reduction of Fe and SO_4 (Uhlmann and Paul, 1994; Smolders et al. 1997; Aravena and Robertson, 1998; Pauwels et al. 1998; Tesoriero et al. 2000). Because nitrate gets reduced in anoxic condition by nitrate reducing bacteria, the associated Fe^{II} ions result in the formation of Fe^{III} (Nielsen and Nielsen, 1988; Straub et al. 1996; Weber et al. 2001), thereby increasing the binding of phosphorus with the settling iron hydroxides (Golterman, 1995). The nitrate ion also oxidizes FeS_x resulting in the release of $SO^{=}_4$ ions again, and in the immobilization of phosphorus (Lucassen et al. 2004; 2005). The suggested equations for denitirification are (Pauwels, 2000; Schwientek et al, 2008),

$$5FeS_2 + 14NO_3^- + 4H^+ \rightarrow 7N_2 + 10SO_4^{2-} + 5Fe^{2+} + 2H_2O \quad (3.1)$$

$$NO_3^- + 5Fe^{2+} + 6H^+ \rightarrow 0.5N_2 + 5Fe^{3+} + 3H_2O \quad (3.2)$$

Summarising (3.1) and (3.2)

$$5\ FeS_2 + 15NO^{3-} + 10H^+ \rightarrow 7.5N_2 + 10SO_4^{2-} + 5Fe^{3+} + 5H_2O \quad (3.3)$$

Silicon is present in the water column as dissolved silicic acid and silicate ions. The dissolved silica is used for growth by micro-organisms such as diatoms, and plays a crucial role in the organic activity in lakes (Conley et al. 1993). The increased anthropogenic activity, such as, agricultural activities, sewage sludge etc. cause increased input of the two limiting nutrients N (Kao et al. 2004b) and P in to the lakes. The increased input of landslide debris and the occasional dumping of road cutting materials into the lake in mountainous areas, significantly increase silica input to the lake by addition of finer materials (with increased surface area), resulting in higher silica dissolution. Although anthropogenic source of silica is negligible, the increased input of N and P causes the ratios N: Si and P: Si to be significantly higher and eventually cause disorder in the lake system (Conley et al. 1993). The metals also act as micro-nutrients; however, their concentrations above the desired quantity cause lethal problems in the aquatic ecosystem. The concentrations of both phosphorus and metals in the lake system depend on the pollution activities in the catchment area, and through weathering of catchment rocks. The dissolved phosphorus and metals are significantly controlled by redox conditions and by the composition of the lake sediments. Life in the lake can be controlled and safe guarded by controlling the input of phosphorus and metals into the lake system.

3.1.2 Phosphorus in Aquatic Environment

The study of phosphorus in lakes has been of great interest, since it acts as a critical nutrient controlling eutrophication. Phosphorus is usually the limiting nutrient in freshwater ecosystems, whereas, nitrogen limits primary production in marine systems (Kaiserli et al. 2002; Ruttenberg 2004; Jordan et al. 2008). Phosphorous may enter an aquatic system in particulate or dissolved form (Ramanathan et al. 1995), and may be adsorbed by the particles before settling down (Penn and Auer, 1997). The phosphorous bearing mineral apatite is the sole natural source of phosphorus for an aquatic system; hence lithology in the catchment area plays an important role in the concentration levels of phosphorus in the lakes. The concentration of phosphorus in the water column depends on the physico-chemical conditions prevailing in the lake system (Furumai and Ohagaki, 1989; Paikaray et al. 2008). The deposition of phosphorus in the lake occurs by, (i) sedimentation of phosphorus minerals imported from the drainage basin, (ii) adsorption or precipitation of phosphorus with inorganic compounds, such as co-precipitation with Fe and Mn, adsorption with clays, amorphous oxy-hydroxides or similar materials, (iii) phosphorus associated with carbonates, (iv) sedimentation of phosphorus with autochthonous organic matter, and (v) uptake of phosphorus from the water column by algal and other microbial communities and to a lesser extent by submerged macrophytes with eventual transport back to the sediments by translocation and deposition with detritus (William and Meyers, 1972; Bostrom et al. 1988; Wetzel, 1990; 2001).

Phosphorus in sediments is not directly available for the aquatic organisms (Ramm and Scheps, 1997; Zhou et al. 2001) however, minor variations in physicochemical conditions release phosphorus from sediments to the overlying water. To understand the burial and diagenesis of phosphorous in the sediments, it is necessary to identify, separate and quantify the various solid-phase reservoirs of sedimentary phosphorous. The most promising methods for separation and quantification of various phosphorous reservoirs are the sequential extraction techniques (Ruttenberg, 1992), which take advantage of the fact that different solid phases show dissimilar reactivity towards different solutions. The sediments are extracted with a series of extractants, each chosen to selectively dissolve a single phase or group of phases of similar chemical characteristics (Ruttenberg, 1992). Beginning with the pioneering studies of Chang and Jackson (1957), significant research has been carried out related to phosphorus fractionation into its main chemical forms (associated with Ca, Fe and Al), on both soils (Petersen and Corey, 1966; Williams et al. 1976; Hedley et al. 1982) and sediments (Hieltjes and Lijklema, 1980; Barbanti and Sighinolfi, 1988; de Groot and Golterman, 1990; Ruttenberg, 1992; Ruban et al. 2001). Phosphorous release from sediments to water column has been studied extensively by many workers, in both freshwater and marine environments. A variety of chemical and physical controls have been proposed on phosphorus mobilization from sediments. The influence of oxic condition on phosphorous mobility show that phosphorous gets released from the Fe-Mn oxy-hydroxides at lower Eh (anoxic condition) (Mortimer, 1941; Buffle et al. 1989; Gunnars and Blomqvist, 1997; Olila and Reddy, 1997). Ringwood and Keppler (2002) suggested that a small variation in pH (0.2 to 0.5), significantly affects the release of phosphorus and in its mobility. Curtis (1989) and Caraco et al. (1989; 1993) studied the possible influence of sulfate on phosphorus mobilization. The dissolved sulfate competes with phosphorous in occupying the Fe- Mn oxide sorption sites causing mobilization of phosphorous (Clavero et al. 1997). The importance of pH as a factor influencing the dissolution of phosphorous has been intensively investigated

(Jacoby et al. 1982). The role of pH in silicate concentration studied by many workers (Hingston et al. 1967; Obihara and Russell, 1972; Jacoby et al. 1982; Tuominen et al. 1998; Koski Vahala et al. 2001) has led to the conclusion that, silicate ions directly compete with phosphate ions for the sorption sites. They observed that the silicate ions prefer Fe-Mn oxide sorption sites, and hence compete with phosphorous. This in turn increases the release of phosphorous. Koski–Vahala et al. (2001) observed that increase in pH and silica caused increase in the phosphorous mobilization. Jordan et al. (2008) observed that phosphorus mobility increased with increased salinity.

3.1.3 Selected Global Studies - Nutrients

Tipping (1981) studied the possible kinetics involved in the adsorption of humic substances onto goethite in three different lake sediments. Stabel (1986), and Kleiner and Stabel (1989) observed that phosphorus co-precipitates along with calcium carbonate. Hobbs et al. (2005) observed that phosphorus mobilization in Lake Lough Carra of Ireland, a calcareous lake, was mainly due to the adsorption of phosphorus onto the ferrous oxy-hydroxide instead of calcium. Ruttenberg and Berner (1993) from speciation model results on the interstitial water and the extracted phase of the phosphorous in the sediments of the continental margin suggested that phosphorous forms authigenic apatite compared to other forms. Cooke et al. (1993) studied the role of iron, aluminum and calcium in the internal loading of phosphorus in deep lakes and observed that phosphorus inactivation was useful in controlling the trophic state of polymictic soft water lakes. Golterman (1988) studied the phase equilibrium between iron and calcium phosphate and studied (Golterman, 1995) the role of iron oxide, sulfide and phosphate in the phosphate exchange between sediment and water. Slomp et al. (1996) observed that iron bound phosphorous acts as an intermediate between the organic bound phosphorous and authigenic apatite in continental platform. Wu et al. (2001) observed iron cycle influencing phosphorus regeneration in lake sediments of China. Murphy et al. (2001) also obtained similar results in the release of phosphorus due to the reduction of iron oxy-hydroxides in Lake Biwa. Azzoni et al. (2005) studied the role of iron and sulfur cycle in the phosphorus mobilization in lake sediments.

Olila and Reddy (1997) studied the effect of redox potential in the mobilization of phosphorus in Lake Apopka and Okeechobee. Murray and Gottgens (1997) studied yearly variations in phosphorus using Lead-210 and Cesium-137 dating in lake sediments. Kopacek et al. (2005) studied the control of aluminum on phosphorous sorption in lake sediments. Followed by the study of Meyer and Gloss (1980), Hartikainen and other workers (Hartikainen et al. 1996; Tuominen et al. 1998; Koski Vahala et al. 2001; de Vicente et al. 2008; Tallberg et al. 2008) observed that silicate ions directly compete for the sorption sites of metals and aluminum oxides and prevent phosphorus sorption in lake sediments.

3.2 Methodology

3.2.1 Sample Collection

Water samples were collected from the surface of the lake in 2006 and deep water samples at three depth intervals during 2008. The interstitial water samples were collected by centrifuging the sediments at 7500 rpm for 1hr. The water samples were filtered through 0.45µm cellulose nitrate membrane filter papers using a powered vacuum filtration unit. The sediment samples were collected from the deepest part of the lake using a gravity corer. The collected cores were segmented into sub-samples of 2 cm thickness each in the field immediately. The samples were stored in refrigerated condition in clean and air-tight polythene bags.

3.2.2 Sample Analysis

A simplified flow chart describing the sample collection and the different analysis is shown in Fig. 3.1. 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 U-Vis Spectrophotometer (Clesceri et al. 1998).

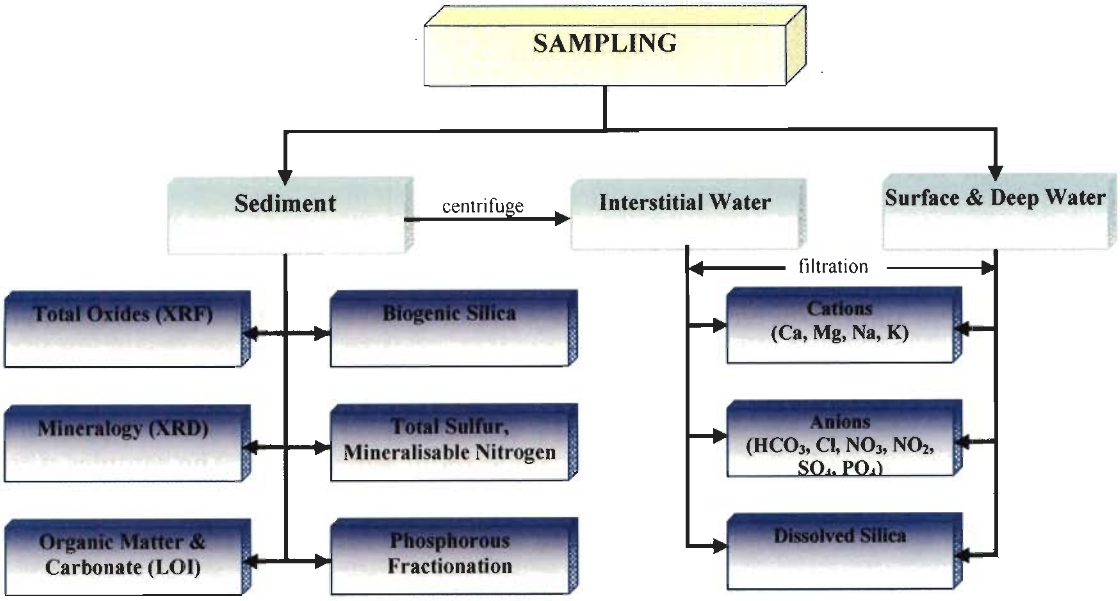


Figure 3.1 Flow-chart showing sampling and analysis of various parameters in water and sediments

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 (Dean, 1974; 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 1M NaOH at 150° C (Hartikainen et al. 1996) and analysed using U-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 analysed for total sulfur using DRC 3000 Elan, Perkin Elmer ICP-MS. The USGS standard SCO-1 was used to calibrate the instrument for total sulfur analysis.

3.2.2.1 Phosphorus Fractionation

The phosphorous fractionation in the sediment samples were carried out following the SEDEX method (Table 3.1, 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 0.5g 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.

Table 3.1 Brief outline of SEDEX extraction procedure (Ruttenberg, 1992)

Fraction	Reagent	Reaction time
Exchangeable and Loosely Bound P	1M $MgCl_2$ (pH= 8.0)	2 hours
Fe Bound P	Sodium- (0.3M) Citrate, (1M) Bicarbonate and 1.25g Dithionite (pH= 7.6)	8 Hours
Authigenic Apatite, $CaCO_3$ bound P, and Biogenic Apatite	1M Sodium Acetate Buffer (pH= 4.0 with Acetic Acid)	6 Hours
Detrital P	1M HCl	16 Hours
Organic P	Ash (@ 550 °C) + 1M HCl	16 Hours

3.3 Results

3.3.1 Water Composition

The pH of the water in the different lakes differs widely. The Nainital (Table 3.2) is alkaline (~8) and the other lakes show lesser pH (7.8-7.3) (Table 3.2) in the water column. The water at the sediment-water interface and interstitial waters show near neutral (~7) pH in the Nainital lake and slightly acidic nature in the other lakes (6-6.5). The redox potential of the lakes shows that the water column is oxic in nature in (Eh= +230mV, +280mV, 275mV and +199mV in Nainital, Bhimtal, Sattal, Naukuchiatal respectively) (Table 3.2) the lakes except Naukuchiatal lake, which shows anoxic condition in the water column and the water at the sediment-water interface (-60mV, -140mV, 88mV and -120mV in Nainital, Bhimtal, Sattal, Naukuchiatal respectively) and the interstitial water shows anoxic condition. The Nainital Lake shows high anoxic condition with the Eh reduced to -274mV in the interstitial water and the other lakes show sub-oxic condition or low anoxic condition with the Eh values less than -130mV.

Table 3.2 Water chemistry of the lakes- Physical parameters

Sample ID	Temp.(° C)	pH	Eh(mV)	EC(mS/cm)	TDS(mg/l)
		Bhimtal			
Surface	8	7.65	253.5	0.116	76.8
5M	8	7.49	286	0.1216	73.9
10M	8	7.5	282	0.1226	85.2
15M	8	7.64	282	0.1197	78.9
Above Sediment	8	7.46	-140	0.192	127.0
PW 0-5 cm	0	7.01	-125	0.558	446.4
PW 5-10 cm	0	6.88	-129	0.462	369.6
PW 10-15 cm	0	7.11	-140	0.33	264.0
PW 15-20 cm	0	6.6	-120	0.265	212.0
PW 20-25 cm	0	6.82	-125	0.182	145.6
		Nainital			
Tallital Surface	5	8.22	0	0.386	255.0
7M	5	8.37	0	0.373	246.0
14M	5	8.26	0	0.393	259.0
21M	5	8.17	0	0.394	260.0
Mallital Surface	5	8.09	0	0.367	243.0
7M	5	8.31	231	0.385	255.0
14	5	8.27	233.8	0.394	254.0
21M	5	8.38	231.6	0.373	245.0
Above Sediment	5	7.62	-60	0.667	441.0
PW 0-5 cm	0	7.15	-223	0.937	749.6
PW 5-10 cm	0	7.21	-190	0.965	772.0
PW 10-15 cm	0	7.29	-274	0.496	396.8
PW 15-20 cm	0	7.31	-239	0.45	360.0
PW 20-25 cm	0	7.36	-220	0.537	429.6
PW 25-30 cm	0	7.38	-190	0.708	566.4
PW 30-35 cm	0	7.53	-150	0.775	620.0
		Naukuchiatal			
Surface	10	7.47	198.5	0.0945	62.2
10m	10	7.66	232	0.0998	65.0
20m	10	7.58	75	0.198	130.0
30m	10	7.33	-120	0.0882	88.2
Above Sediment	10	6.99	-110	0.229	152.0
PW 0-5 cm	0	6.99	-127	0.196	156.8
PW 5-10 cm	0	6.98	-100	0.142	113.6
PW 10-15 cm	0	6.89	-80	0.077	61.6
PW 15-20 cm	0	6.79	-70	0.068	54.4
PW 20-25 cm	0	6.82	-68	0.038	30.4
PW 25-30 cm	0	6.76	-57	0.062	49.6
		Sattal			
Surface	9	7.47	230.1	0.0779	51.3
3M	9	7.53	237	0.0774	51.9
6M	9	7.8	250	0.0627	41.5
9M	9	7.65	275	0.0644	42.4
Above Sediment	9	7.54	88	0.141	93.0
PW 0-5 cm	0	5.66	-103	0.255	204.0
PW 5-10 cm	0	6.1	-62	0.078	62.4
PW 10-15 cm	0	6.24	-60	0.106	84.8
PW 15-20 cm	0	6.56	-54	0.066	52.8
PW 20-25 cm	0	6.18	-70	0.072	57.6

Table 3.3 Water composition (μM) of the lakes- Major ion chemistry

SampleID	Na	K	Ca	Mg	NH$_4$	F	Cl	NO$_2$	NO$_3$	PO$_4$	SO$_4$	SiO$_2$	HCO$_3$
						Nainital							
Depth-0^{T}	361	77.6	1109.7	1750.8	N.A	2.8	252.3	N.A	104.7	3.4	1108	24.9	3855.4
7m	352.7	69.3	1115.7	1778.7	N.A	2.8	217.2	N.A	99.4	3.2	1131.3	24.9	3880.2
14m	432	85	1132.5	1792.7	N.A	2.9	221. 4	N.A	104.8	3.6	1158	27	3787.3
21m	373.4	86.6	1180.9	1822.3	N.A	0.5	411.4	N.A	91.4	3.5	1085.5	26.4	3884.2
Depth-0^{M}	452.9	32.6	1170.2	1881	N.A	0.4	233.6	N.A	95.5	3.7	1109. 7	25.7	3888.2
7m	349.4	81.4	1154.5	1781.3	N.A	2.5	188	N.A	86.8	3.7	967.5	173.8	3786.3
14m	374.3	67.5	1124	1744.7	N.A	0.6	210.5	N.A	102.4	3.8	1105.7	24.4	3885
21m	381.6	70.1	1170.3	1802.6	N.A	2.3	209.5	N.A	97.7	3.3	1066.6	23.6	4001.2
Depth-0^{M}	354.8	72.1	1171.2	1827.4	N.A	2.4	199.6	N.A	93.2	3.3	1069.5	24.9	3889.8
7m	397.7	82.2	1223.2	1717.2	N.A	0.3	225.3	N.A	91.8	1.2	1055	22.6	3749.7
14m	391	79.4	1196.4	1890.8	N.A	2.4	279.9	N.A	99.8	1.9	1180.8	23.6	2935.9
21m	373.9	77.3	1256.9	1786.8	N.A	0.5	262.9	N.A	91.5	0.8	1074.3	26.2	3701.8
Above Sediment	318.9	69.4	1239.8	1795.7	0	2.1	1950.3	0	520.6	1.1	1140.4	24.9	3651.2
PW 0-5 cm	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
PW 5-10 cm	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
PW 10-15 cm	520.1	132.8	5452.8	3815	N.A	7.1	283.9	7.5	702.3	0.8	11810.5	153.2	16058.9
PW 15-20 cm	650.3	174.4	5302.6	4721.3	N.A	5.6	254.7	195.3	175.5	0.5	13603.4	167.8	15616.7
PW 20-25 cm	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
PW 25-30 cm	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
PW 30-35 cm	287.7	111.8	5592.1	4109	800.1	35.2	201	1.2	3.3	0.3	14049.2	118.8	N. A

Bhimtal													
Depth-0	140.1	36.5	597.4	278.6	3.8	3.3	57.5	0	23.4	0.1	28.6	25.7	1381.4
5m	105	47.7	644.3	267.5	N.A	3.4	77.3	0.4	43.7	0.3	39.6	29	1504.2
10m	140.2	48.6	655.1	271.5	N.A	3.1	93.6	0	44.2	0.1	38.8	31.8	2141
15m	118.2	40.9	649.8	258.7	N.A	3.5	75.8	0.4	43.4	0.2	39.3	26.2	1742.2
Above Sediment	133	45.4	661.4	317.6	N.A	3.7	104.1	0.7	52.5	0.1	47.5	28.3	1529.4
PW 0-5 cm	817.2	10.6	1868.3	522.8	450.2	6.7	319.2	0	1.9	0.3	893.3	142.4	N.A
PW 5-10 cm	1292.4	70.3	2875.5	727.9	127.9	5.6	170.9	1.2	3.8	0.1	6070.8	122.7	6649
PW 10-15 cm	N.A	N.A	N.A	N.A	N.A	39.5	128.2	0.4	4.2	0.11	3755.1	166.5	N.A
PW 15-20 cm	1105	48.4	1156	385	71.4	1.2	123.3	0.6	3.5	0.1	3036.2	163.7	2673
PW 20-25 cm	48.4	59.2	473.4	183.7	628.2	1.2	131	1.9	2.2	0.3	1126	153.2	1094.6
Sattal													
Depth-0	102.4	52.5	313.3	194.7	0	4.4	22.3	0	1.6	0.1	15.4	28.2	1074.8
3m	76.6	36.4	467.6	254.4	0	3.3	22.9	0	1.9	0.3	17.8	25.7	1047
6m	81.2	43.9	306.8	202.5	0	4.4	22	3.1	2.1	0.1	16.6	26.4	1047
9m	81	47.8	305.1	88.3	0	1	20.7	0	1.5	0.1	15.7	29.2	924.3
Above Sediment	72	27.2	318.9	236	5.8	4.1	427.3	0.8	10.5	0.3	35.4	30.8	966.2
PW 0-5 cm	895.7	202.7	1260.3	624.6	67.4	1.1	43.7	0	86.8	0.1	3454.6	98.5	3818.2
PW 5-10 cm	1132.2	89.3	1054.2	549	68.9	27.6	115.1	3	21.2	0.1	2894.5	94	N. A
PW 10-15 cm	N.A	N.A	N.A	N.A	N.A	15.8	48.5	0.8	6	0.1	2836.4	123.3	N.A
PW 15-20 cm	1395.7	110.2	876.3	394.6	33.8	8.3	33.4	0.6	3.6	0.1	3087.7	125.8	2654.9

PW 20-25 cm	1321.6	103.6	891.2	406.4	32.2	7.6	39.4	0.7	4	0.1	3058.2	110.6	2700.1
						Naukuchiatal							
Depth-0	115	25.9	510.9	238.5	0	2.3	170.8	0	2.8	0.1	16.7	25.4	1399
10m	108.1	41.9	502.2	234.6	7.4	20.6	94.4	0	3.8	0.1	20.8	18.8	1631.3
20m	71.2	28.6	657.6	203.7	71	3.5	41.3	0	0.3	0.6	9.7	71.2	2010.5
30m	314.7	19	655.6	231.1	35.4	0.8	36.6	0	4	0.9	6.9	108.8	2237.6
Above Sediment	411.2	17.6	722.3	208.4	0	3.5	41.5	0	1.9	0.2	8.4	140.3	2465.4
PW 0-5 cm	864.8	0	1997.5	649.3	206.9	5.2	312.9	7	44.1	0.1	4202.3	134.8	N. A
PW 5-10 cm	810.2	0	982.4	352.1	59.5	8.4	67.3	0	7	0.1	2157.6	116.9	3353.3
PW 10-15 cm	880.9	64.9	1072.8	386	0	8.1	63.9	0	2.4	0.2	2492.1	149.3	3661.7
PW 15-20 cm	902.6	0	577.9	208.7	43.2	29	49.4	1.7	2.8	0.5	1374.1	120	1972.6
PW 20-25 cm	471.7	47.3	435.2	151.3	N.A	9.3	56	1	3	0.2	1026.8	111.8	1485.4
PW 25-30 cm	774.5	0	443.3	129.2	40.1	8.8	55.8	1	2	0.3	1063.1	125.8	1513.1

N.A- Data Not Available/ below detection limit; PW- interstitial (Pore) water, T= Tallital; M= Mallital

3.3.1.1 Major Ions and Nutrients in Water

The major cations chemistry vary widely between the lakes with magnesium (>55%) dominating the water column of the Nainital lake (Table 3.3; Fig. 3.2 A) and calcium (>50%) dominating the other lakes (Table 3.3; Fig. 3.2 C, E, G). Calcium is the next abundant element to dominate the Nainital Lake (Table 3.3; Fig. 3.2 B) and magnesium dominates the other lakes (20-40%) (Table 3.3; Fig. 3.2 D, F, H), sodium and potassium are present in low concentrations in all the lakes. The interstitial water and the sediment-water interface show high concentrations compared to the water column. Calcium and magnesium dominate in Nainital, where as calcium and sodium dominate interstitial water chemistry of the other three lakes.

Among the anions bicarbonate dominates the water column in all the lakes, which constitute >75% of total anions in Nainital lake (Table 3.3; Fig. 3.3 A) and >95% in the other lakes (Table 3.3; Fig. 3.3 C, E, G). Sulfate (~20%) is the next dominant anion in Nainital and chloride (~10-15%) in the other lakes. Phosphorus concentrations in the lakes are very less (0.05-0.3μmol/l), although the concentration in the Nainital Lake is much higher (3.78μmol/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 3.3; Fig. 3.3 B, D, F, H) and chloride shows high concentration in the sediment-water interface. Phosphorus concentration is less in the interstitial water column of the Nainital Lake and the other lakes show increased concentration in the interstitial water column.

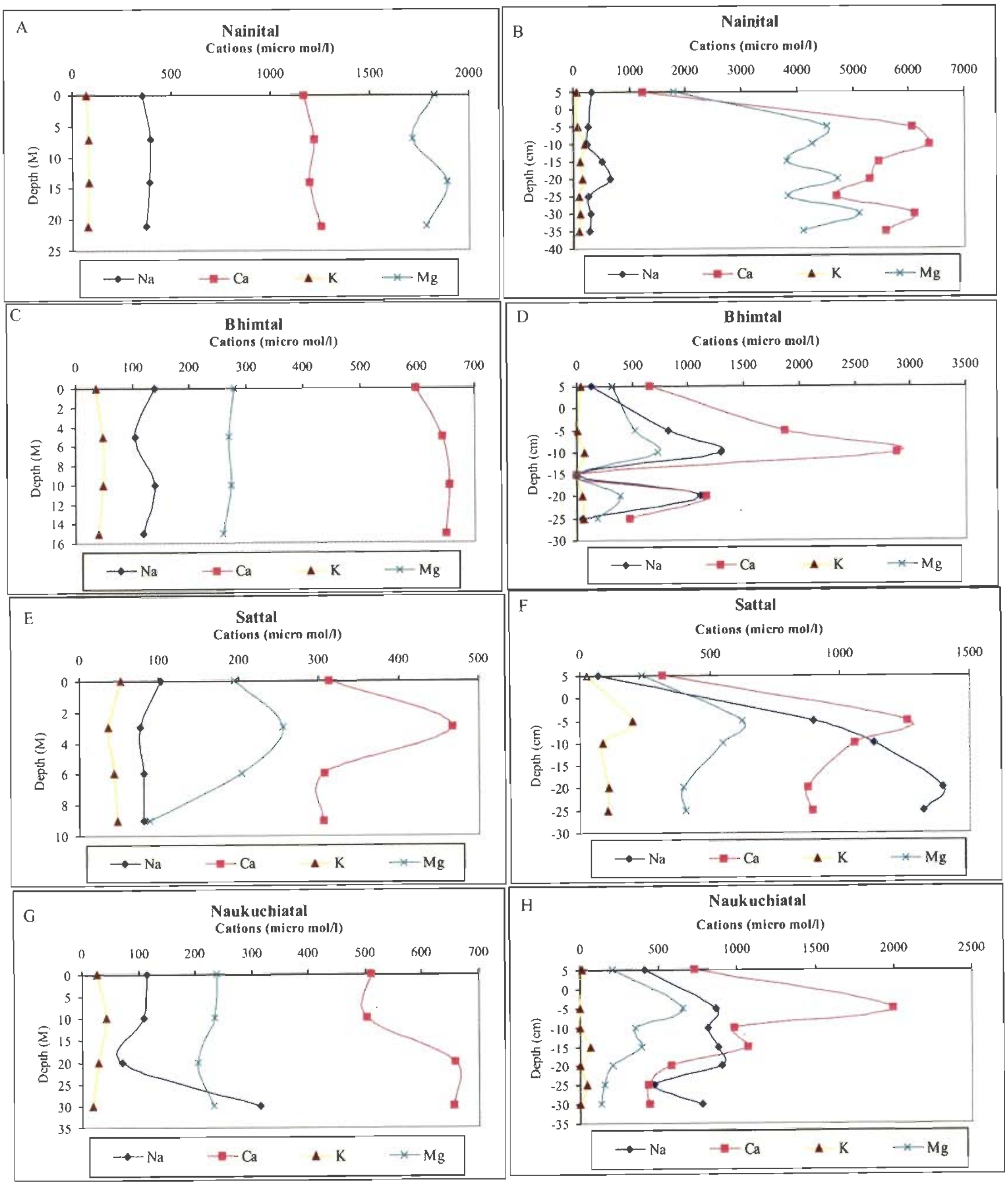


Figure 3.2 Cations variation in the water and interstitial waters in the lakes (A, C, E, G- Water Column; B, D, F, H- Interstitial water)

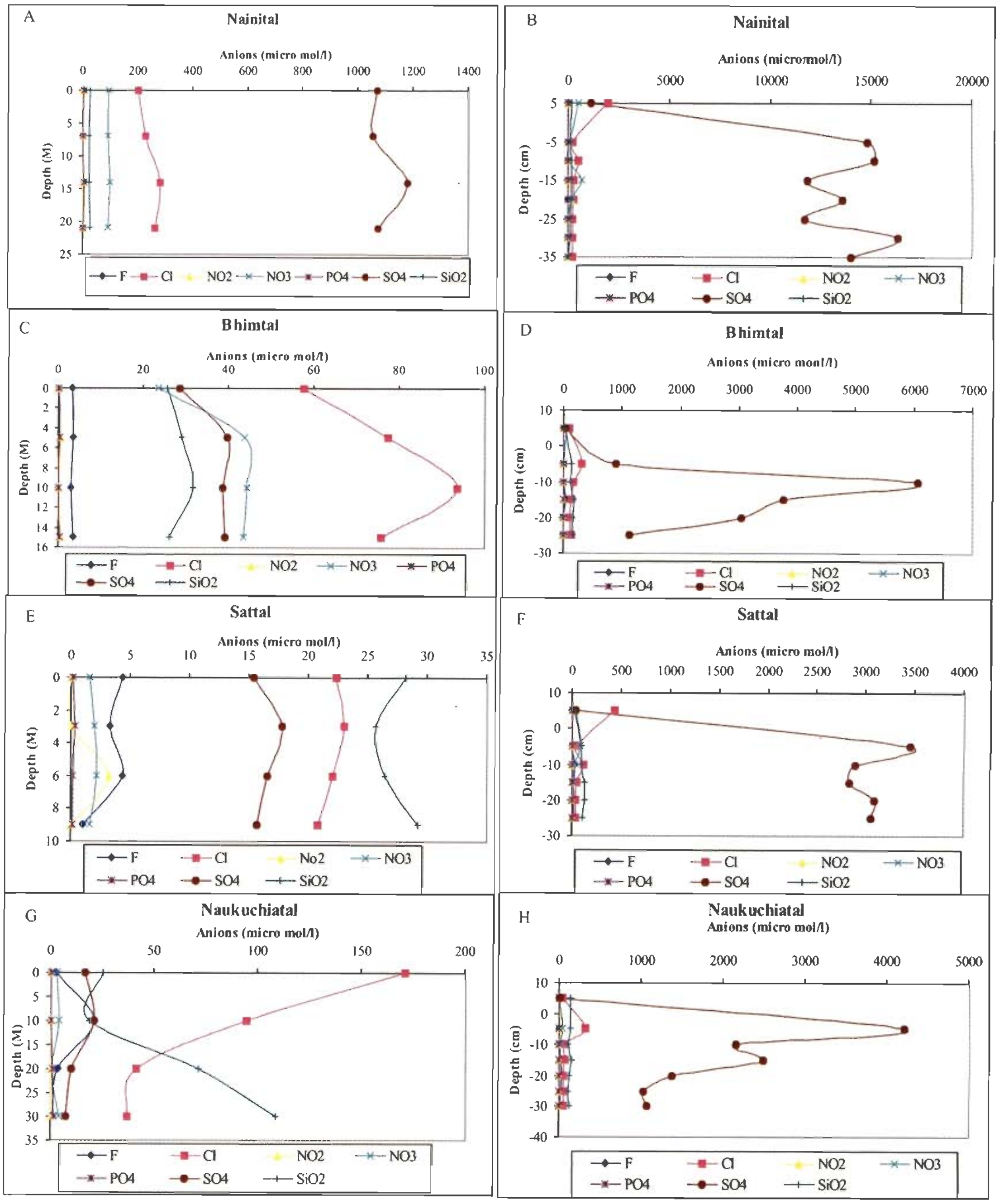


Figure 3.3 Anions variation in the water and interstitial water in the lakes (A, C, E, G- Water Column; B, D, F, H- Interstitial water)

3.3.2 Sediment Composition

3.3.2.1 Organic Matter and Carbonates

The loss on ignition (LOI) indicates the approximate organic contents of the sediments (Table 3.4). The present study indicates that all the lakes are rich in organic matter (>10%). The organic content of the lakes increases up core with the top 10cm containing high amounts of organic matter. The organic carbon contents in the lakes also behave similar to that of the total organic matter. The carbonate content, which represents minerals such as, dolomite and calcite, is very high in the Nainital lake sediments (6-14%) compared to the other lakes (<3%). The carbonate content in the Nainital Lake increases up core (Fig. 3.4) where as the other lakes show negligible variation through out the core.

Table 3.4 Organic matter and carbonate contents in the lakes

Depth (cm)	NAINITAL		BHIMTAL		SATTAL		NAUKUCHIATAL	
	Organic Matter (%)	Carbonate (%)	Organic Matter (%)	Carbonate (%)	Organic Matter (%)	Carbonate (%)	Organic Matter (%)	Carbonate (%)
0-2	19.6	10.1	14.1	2.1	26.1	2.2	14.3	1.7
2-4	19.9	7.0	13.9	1.7				
4-6	19.5	10.0	11.1	2.0	20.2	1.5	24.8	2.5
6-8	19.0	5.2	10.6	1.9	19.0	2.0	26.0	2.2
8-10	15.1	10.5	11.8	1.5	17.7	1.2	23.0	3.0
10-12	16.3	10.9	9.6	3.9	17.0	5.6	23.0	2.5
12-14	10.6	13.3	9.0	2.9	14.9	2.6	21.9	2.8
14-6	10.9	12.0	12.1	1. 3	14.4	1.5	12.4	1.8
16-18	10.0	13.1	11.0	2.4	12.8	0.5	16.2	2.8
18-20	11.0	13.0	12.0	1.6	14.0	1.6	16.8	2.3
20-22	12.7	11.3	11.4	1.5	18.2	1.44	15.6	2.3
22-24	13.3	10.7	9.8	1.2	17.0	1.4	17.0	2.4
24-26	12.7	11.6	10.0	1.6	12.6	0.8	17.8	1.9
26-28	9.0	14.2	7.3	1.7	9.2	1.1	17.0	2.1
28-30	11.4	11.2	7.4	2.4	11.7	1.3	16.8	2.2
30-32	10.0	13.6	8.9	2.1	9.2	1.5	14.5	2.3

3.3.2.2 Major Oxides

The major oxide composition of the sediments is presented in Table 3.5. Silica (SiO_2) is the dominant oxide in the lakes (37- 62%), followed by Al_2O_3 and CaO in the Nainital lake, whereas the other lakes show high Fe_2O_3 $_{(T)}$ (Fig. 3.5). The other oxides, K_2O and Na_2O are almost constant through out the core (1-3%) in the lakes.

Table 3.5 Major oxides composition of sediments at different layers (in %) in the lakes

Depth (cm)	SiO_2	CaO	MgO	Na_2O	K_2O	Al_2O_3	P_2O_5	Fe_2O_3 (T)	MnO	TiO_2	LOI%
Nainital											
0-2	37.3	12.6	3.5	0.3	2.6	10.1	0.4	4.7	0.1	0.5	27.7
4-6	34.5	6.1	3.2	0.3	2.5	9.7	0.4	3.7	0.1	0.4	27.5
10-12	35.3	5.4	3.5	0.3	2.6	10.2	0.4	3.8	0.1	0.4	25.4
16-18	39.4	3.1	3.9	0.4	2.8	11.3	0.3	4.3	0.1	0.5	21.8
22-24	41.2	2.5	3.9	0.4	2.9	11.4	0.3	4.5	0.1	0.5	22.6
28-30	41.2	3.0	4.2	0.4	2.8	11.3	0.3	4.4	0.1	0.5	21.3
Bhimtal											
0-2	45.1	1.4	7.5	0.5	1.5	11.6	0.2	13.3	0.1	1.0	15.9
4-6	46.1	1.2	8.1	0.5	1.5	11.8	0.2	13.9	0.1	1.0	12.6
10-12	46.9	1.0	7.8	0.6	1.5	12.0	0.2	13.7	0.1	1.0	13.1
16-18	46.4	1.0	7.7	0.6	1.5	11.7	0.2	13.4	0.1	1.0	13.1
22-24	47.2	1.0	8.8	0.7	1.5	12.2	0.2	14.8	0.1	1.1	10.9
28-30	50.9	1.1	8.6	0.9	1.5	12.4	0.2	12.3	0.1	1.2	9.6
34-36	46.2	1.0	9.6	0.7	1.5	12.9	0.2	15.5	0.1	1.1	9.7
Sattal											
0-4	55.9	0.6	2.4	0.3	2.5	10.4	0.4	7.6	0.1	0.7	27.8
4-6	57.1	0.5	2.3	0.3	2.5	11.4	0.4	7.4	0.1	0.7	21.4
10-12	56.6	0.5	2.4	0.3	2.7	12.2	0.3	7.3	0.1	0.8	21.6
16-18	55.4	0.6	2.5	0.3	3.3	12.9	0.2	7.6	0.1	0.8	13.2
22-24	54.3	0.7	2.3	0.3	2.9	12.0	0.5	7.7	0.1	0.8	18.2
26-28	54.9	0.5	2.5	0.3	3.8	15.3	0.3	8.6	0.1	0.9	10.1
Naukuchiatal											
0-4	61.9	1.2	2.9	0.5	1.5	9.0	0.2	7.2	0.1	0.7	15.8
4-6	62.2	1.2	3.1	0.6	1.7	10.0	0.1	7.3	0.1	0.7	26.6
10-12	60.8	1.2	0.0	0.6	1.7	9.6	0.1	7.2	0.1	0.7	24.6
16-18	61.5	1.2	2.8	0.6	1.6	8.2	0.1	6.7	0.1	0.7	18.6
22-24	60.0	1.2	2.9	0.6	1.7	8.6	0.1	7.1	0.1	0.7	18.7

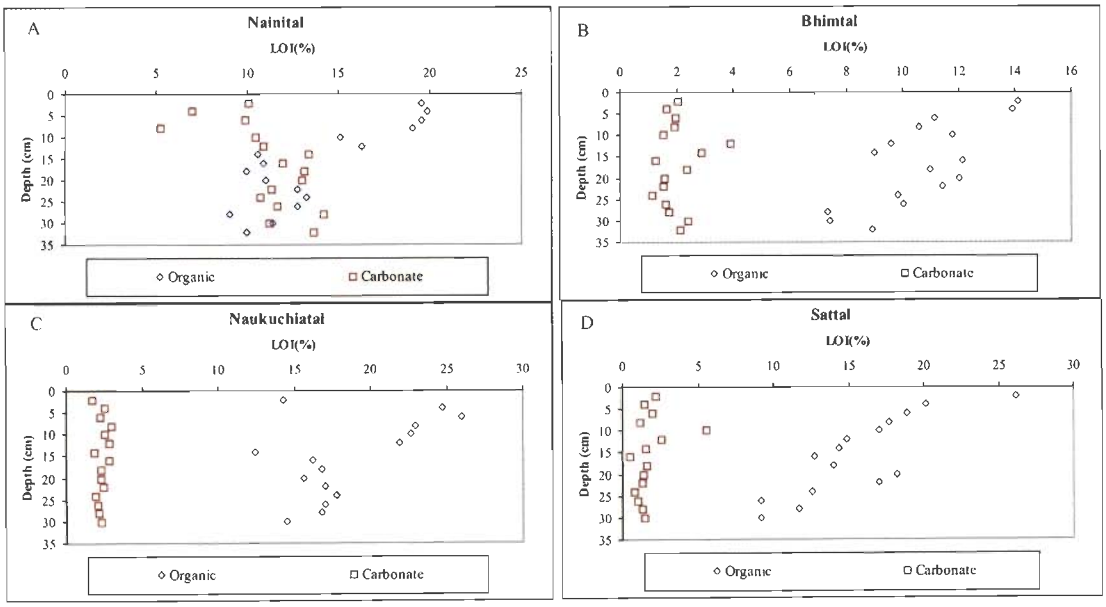


Figure 3.4 Organic and carbonate content in the lake sediments

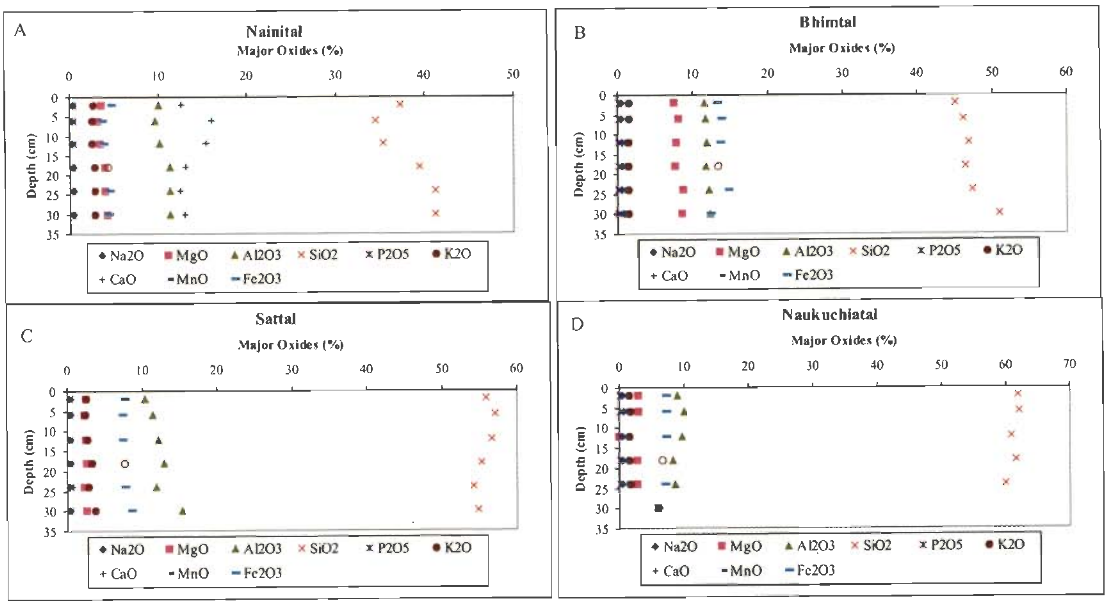


Figure 3.5 Variations in major oxides in sediments at different depths

3.3.3 Nutrients

The phosphorus concentration (Table 3.5; Fig. 3.5) is high in the Nainital and Sattal lake sediments (> 0.3%) compared to the other two lakes (<0.15%), and shows increasing trend up core. The total sulfur (Table 3.6; Fig. 3.6) content in the sediments of Nainital Lake is higher (1760- 3000mg/kg) compared to the other three lakes and increases up core. The other three lakes have comparatively low sulfur content with the concentration varying between 599- 1762 mg/kg (Bhimtal), 1700- 2100 mg/kg (Sattal) and 899- 1466 mg/kg (Naukuchiatal) respectively. The mineralisable nitrogen (Table 3.6; Fig. 3.6) also shows similar characteristics to that of phosphorus and sulfur with the Nainital showing higher concentration (56- 11 mg/kg) compared to the other lakes (15-30 mg/kg). The biogenic silica (Table 3.6; Fig. 3.6) shows an opposite trend; the Nainital lake shows lesser concentration (300- 1200 mg/kg) compared to the other three lakes (>300 mg/kg).

Table 3.6 Total sulfur, nitrogen and biogenic silica in sediments of different depths in the lakes

Depth (cm)	Total Sulfur (mg/kg)	Nitrogen (mg/kg)	Biogenic Silica (mg/kg)
	NAINITAL		
0-5	2872.3	56.0	429.7
5-10	3014.2	42.0	297.2
10-15	2716.0	19.6	491.3
15-20	1323.8	18.2	235.6
20-25	2717.1	45.0	415.8
25-30	2891.9	14.0	1217.0
30-35	1770.1	11.2	2507.0
	BHIMTAL		
0-5	1762.4	15.2	4366.0
5-10	1243.6	21.0	4130.0
10-15	1318.1	19.6	4204.0
15-20	1028.0	18.2	3845.0
20-25	599.7	15.4	3533.0
	SATTAL		
0-5	1700.1	37.8	3282.0
5-10	1547.6	29.4	3157.0
10-15	1771.0	28.0	3256.0
15-20	2154.3	23.8	3214.0
20-25	1007.8		
	NAUKUCHIATAL		
5-10	1054.6	16.8	3966.0
10-15	899.5	21.0	3750.0
15-20	904.1	21.0	3403.0
20-25	1466.9	19.6	3576.0
25-30	899.9	18.2	3650.0

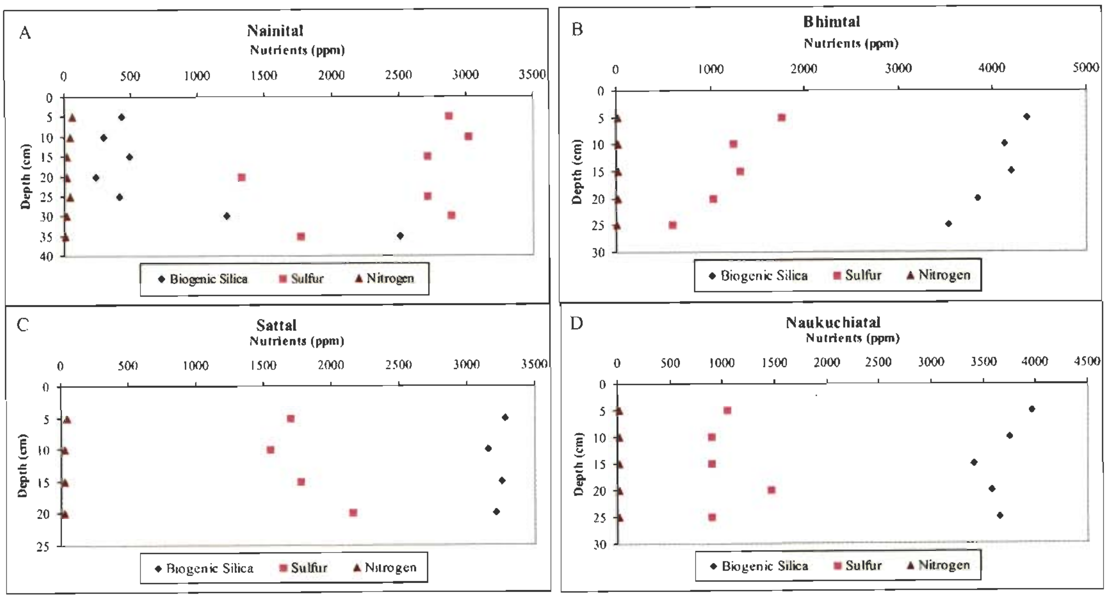


Figure 3.6 Variations of nutrients in the sediments at different depths

3.3.4 Phosphorus Fractionation

The biogenic apatite + calcium carbonate bound fraction (Fig. 3.7 A) contains most of the phosphorus (>90%) and shows a decreasing trend up core. The exchangeable fraction is the next dominant fraction in the Nainital and Bhimtal, followed by the organic fraction. In Sattal lake, phosphorus is predominantly associated with reducible fraction followed by organic fraction, where as in the Naukuchiatal Lake, phosphorus is associated with biogenic apatite + calcium carbonate bound fraction.

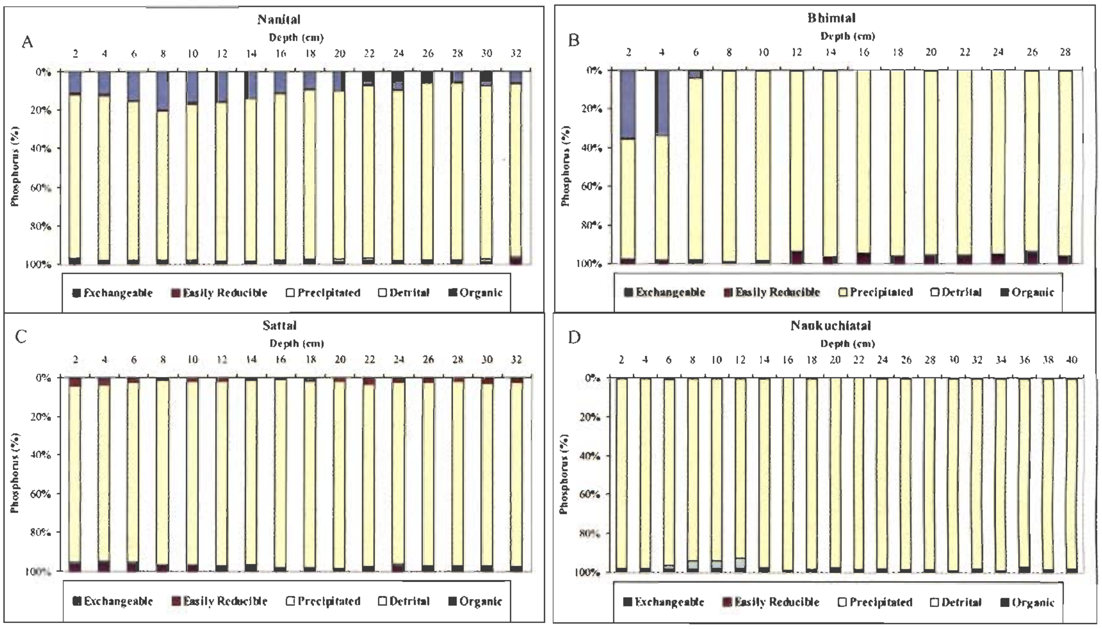


Figure 3.7 Phosphorus fractionation in sediments at different depths

3.4 Discussion

3.4.1 Major Ion Chemistry

Among the major cations, magnesium dominates in the Nainital lake (Table 3.3; Fig. 3.2), while calcium dominates the other three lakes (Bhimtal, Sattal, Naukuchital) (Table 3.3; Fig. 3.2). 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 and the presence of Bhimtal volcanics and the metamorphic rocks in the catchment of the other lakes. The water chemistry of Nainital falls in magnesium bicarbonate facies and other lakes in the calcium bicarbonate facies (Bartarya, 1993). The sodium and potassium concentration in the water column of the lakes is very low as compared to calcium and magnesium. Sodium is almost constant throughout the water column in the lakes except Naukuchiatal which shows high concentration in the anoxic water column. This might be due to the dissociation of sodium from the organic matter by a sudden change in Eh (Boyle, 2001). The concentration of potassium is low in all the lakes, which might be due to the low mobility of potassium. The interstitial water shows high concentration of calcium in all the lakes, but the dominance of calcium and magnesium in the Nainital may be due to the dissolution of minerals, calcite and dolomite (limestone) from the sediments. The dominance of sodium in interstitial water of other lakes, especially in the Sattal and Naukuchiatal, may be due to the release of sodium from the dissolution of feldspars and other silicate minerals and dissociation from the organic matter in the sediments. The Ca+Mg: Na+K ratio (Fig. 3.8) of the water column and the water above the sediment column, ~ 7 in Nainital and between 4 - 6 in Bhimtal, Sattal, and Naukuchiatal, indicates the predominance of carbonate weathering. The Ca+Mg: Na+K ratio in the interstitial water of Nainital is >30 and Bhimtal is 2.8-1.3 and in the other two lakes, it is almost 1. This shows that the Nainital Lake is dominated by the dissolution of carbonate minerals in the sediment column and the other lakes show higher silicate dissolution in the sediments.

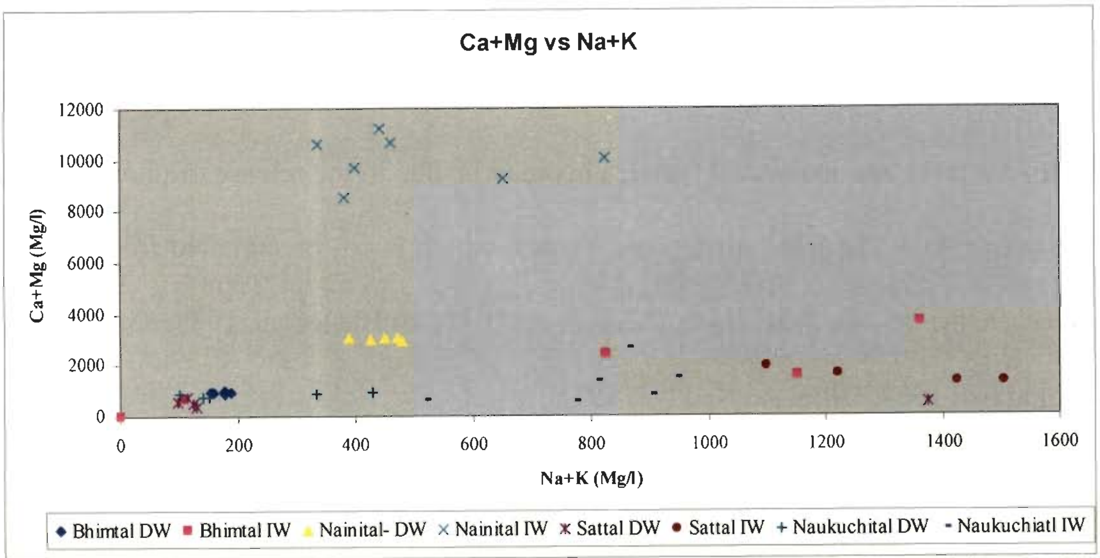


Figure 3.8 The Ca+Mg: Na+K ratio in the water column (DW: Water Column; IW: Interstitial Water)

Bicarbonate (Table 3.3; Fig. 3.3) 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 (Table 3.3; Fig. 3.3) 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, 2000; Lucassen et al. 2004; 2005; Schwientek et al. 2008). 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) (Table 3.3; Fig. 3.3) in the interstitial water may also sequester phosphorus by carbonate flour apatite. The other three lakes show high concentration of phosphorus in the water column above sediment layer and interstitial water. This may be due to the release of phosphorus by the reduction of the iron- manganese oxides, which is co- precipitated from the oxic layer, in the anoxic lake layer (Mortimer, 1941; Buffle et al. 1989; Gunnars and Blomqvist, 1997; Olila and Reddy, 1997).

3.4.1.1 Saturation of minerals in the water column and interstitial water

The wateq4f speciation model was used to find the saturation indices of various minerals in the lakes. The minerals calcite, siderite, aragonite and dolomite are oversaturated in the Nainital Lake (Table 3.7), whereas these minerals are absent in the other three lakes (Table 3.7). This indicates the precipitation of these minerals from the water column in Nainital Lake. The phosphorus in the water column mainly remains as orthophosphate and manganese phosphate. The mineral hydroxyl-apatite is undersaturated in the lakes other than Nainital (SI= 1). The over-saturation of the carbonate flour apatite (FCO_3 Apatite) (Table 3.7) shows that, this mineral acts as a main sink for phosphorus in these lakes. Silica generally occurs as silicate ion in the water and interstitial column. The minerals quartz, chalcedony and amorphous quartz mostly show under-saturation in the water column, and shows over-saturation in the interstitial water column in Nainital Lake (Table 3.8), thus indicating precipitation in the sediment column. The other lakes show under saturation of these phases in the entire lake.

Table 3.7 Saturation indices of different minerals in the water column

Minerals	Nainital	Bhimtal, Sattal and Naukuchiatal
$Al(OH)_3$ (a)	-1	-0.8- -0.7
Aragonite	0.3- 0.2	-0.8- -0.7
Calcite	0.4- 0.45	-0.6
Chalcedony	-0.8- -0.7	-0.8- -0.7
Cristobalite	-0.7- -0.6	-0.7- -0.6
Cupric Ferrite	9	14- 13
Cuprite	1.9	-7- -5
Cuprous Ferrite	14	12
Dolomite (d)	0.3- 0.2	-2
Dolomite (c)	0.9	-1.8
FCO_3 Apatite	16	4- 3
$Fe_3(OH)_8$	2	5- 4.5
$Fe(OH)_{2.7}Cl_{0.3}$	5	7.5
Ferrihydrite	0.8	3
Fluorapatite	2	-4.5
Goethite	5.9	8
Hematite	13.7	18.5
Hydroxyapatite	1	-6
Illite	1.2	1- 0.5
Kaolinite	3.8	4
Kmica	7.9	8- 7.5
Magnetite	15.8	19- 18
$MnHPO_4$	0.25	-0.7
Montmoril BF	1.8	2.5- 2.1
Montmoril AB	1.7	1.7- 2
Montmoril Ca	1.3	1.9- 1.4
Quartz	-0.3	-0.3
Siderite (d)	0.12	-1.4
Siderite (c)	0.43	-1
Vivianite	-0.95	-7- -6

(a)- Amorphous, (c)- Crystalline, (d)- Dis-ordered solids

Table 3.8 Saturation indices of different minerals in interstitial water column

Minerals	Nainital	Bhimtal, Sattal and Naukuchiatal
$Al(OH)_3$ (a)	-1.2- -0.5	-0.27- -0.08
Aragonite	0.4- 0.2	-1.2- -0.6
Calcite	0.6- 0.3	-1.5- -0.5
Chalcedony	-0.08- -0.08	-0.8- -0.2
Cristobalite	0.18- 0.05	0.1- 0.07
Cupric Ferrite	-	-7
Cuprite	1.8- 1.1	1.8- 0.6
Cuprous Ferrite	8- 6	6- 9
Dolomite (d)	0.143	-4.5- -2.5
Dolomite (c)	0.8- 0.4	-3.5- -1.5
FCO_3 Apatite	11- 7	6- 1.5
$Fe_3(OH)_8$	-	-
$Fe(OH)_{2.7}Cl_{0.3}$	-	0.7- -0.3
Ferrihydrite	-6- -5	-6.5- -3.5
Fluorapatite	-4- -1	-10- -4
Goethite	-1.5- -0.2	-1.5- -0.5
Hematite	-1- -0.5	5- -1.5
Hydroxyapatite	-6- -4	-12- -7
Illite	4.5- 2.5	5- 3
Kaolinite	5- 6	8- 6.5
Kmica	9- 11	11
Magnetite	1.8- -1.09	6- -2
$MnHPO_4$	-2	0.01- -0.14
Montmoril BF	3- 1.88	4- 2.5
Montmoril AB	1.7- 0.3	2.1- 0.89
Montmoril Ca	5.5- 4.5	6.8- 4.2
Quartz	0.6- 0.4	0.6- 0.45
Siderite (d)	0.12	-1.8- -0.8
Siderite (c)	0.4- 0.2	-0.4- -0.6
Vivianite	-4.5	-9- -4.5

(a)- Amorphous, (c)- Crystalline, (d)- Dis-ordered solids

3.4.2 Sediment Geochemistry

3.4.2.1 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 (Table 3.4; Fig. 3.4) is very high in the top 10-12cm of the sediment core indicating high productivity in the top layer of the sediment core (Rippey et al 1982). Singh and Gopal (1999) observed that the primary productivity in the Nainital Lake is more than 8 times higher than that of the mesoeutrophic Bhimtal Lake. Sattal and Naukuchiatal show very high organic content (Table 3.4; Fig. 3.4) in the up core; this may be due to the thick forest cover around these lakes which act as main source of organic matter. 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 (Table 3.4; Fig. 3.4). The increasing concentration of carbonate with depth indicates the diagenesis of these minerals with depth.

3.4.2.2 Major Oxides

The major oxide chemistry of the lakes shows similar trend to the catchment lithology. The high concentration of CaO and MgO in the Nainital Lake (Table 3.5; Fig. 3.5) may be due to the presence of the calcareous rocks such as limestone, dolomite and calcareous shales in the catchment area. The major oxide chemistry of the other three lakes are similar to that of the Bhimtal formation and Bhowali Quartzites (Raina and Dungrakoti, 1975; Bhat and Ahmad, 1987) and to that of the metabasites of Bhimtal and Bhowali area (Varadarajan, 1974) indicating the major influence of catchment lithology in sediment compositions. The high silica concentration in the lakes may be due to the partial dissolution of silica in the amygdules of the basalts and quartzites.

A 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 studied lakes 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,

$$CIA= [Al_2O_3/ (CaO^*+ Na_2O+ K_2O+ Al_2O_3)] \times 100 \qquad (3.4)$$

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 <= 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. The other three lakes have higher CIA (>77%) with Bhimtal having CIA> 80%, which indicates weathering of the phyllites and quartzites in the catchment area.

3.4.3 Mineral Composition

The mineralogy of the sediments shows the influence of the lithology of the catchment area (Table 3.9). The Nainital Lake (Table 3.9) is dominated by the carbonate minerals, calcite and dolomite. The sediments are also dominated by quartz, feldspars (albite) apatite, muscovite, biotite, kaolinite and illite etc. The iron oxide minerals, ferrihydrite and goethite are more abundant towards the top layer of the cores, as compared to the bottom sediments, probably due to the dissolution of these minerals in anoxic conditions. The presence of iron sulfide mineral, pyrite has been noticed at the top of the sediment core. The presence of greigite in down core is because of the transformation/aging of mackinawite in to greigite (Hunger and Benning, 2007). The mineralogy of the other three lakes (Table 3.9) is almost similar. The minerals present in these lake sediments are quartz, feldspar, augite, magnetite, pumpellyite, epidote, sphene and chlorite, which are similarto the source rocks (Varadarajan, 1974; Shah and Mehr, 1978). The presence of clay minerals kaolinite, illite is due to the dissolution of the feldspars and the silicates in the catchment area. The minerals ferrihydrite and goethite in the top layer of the core indicates their precipitation which decreases with depth.

Table 3.9 Mineral composition of the lake sediments

Depth (cm)	Nanital	Bhimtal	Sattal	Naukuchiatal
0-2	Qz, Cal, Dol, Py, Felds, Goe, Bio, Kao, I, M, Ap, Ferri, Mac, Mus, FeOx, Gy, Haus	Qz, Ch, Bio, Ep, Mus, Kao, Pr, Sp, Felds, Au, He, Mt, Hbl, Goe, Mac, Pum		
2-4	Mus, Qz, Felds, Kao, I, M, Ap, Cal, Dol, Py, Goe, Haus, Ferri, Mac, FeOx	Qz, Ch, Bio, Ep, Mus, Kao, Pr, Sp, Felds, Au, He, Mt, Hbl, Goe, Mac, Pum, Dol/ Ap_{hyd}		
4-30	Mus, I, M, Kao, Felds, Qz, Cal, Dol, Ap, Ferri, Goe, Mac, Greig	Qz, Ch, Bio, Ep, Mus, Kao, Pr, Sp, Felds, Au, He, Mt, Hbl, Goe, Mac, Pum , Dol/ Ap_{hyd}, Mac		

Minerals:

Apatite (**Ap**), Augite (**Au**), Biotite (**Bio**), Calcite (**Cal**), Chlorite (**Ch**), Dolomite (**Dol**), Epidote (**Ep**), Feldspar (**Felds**), Feoxyhydroxide (**FeOx**), Ferrihydrite (**Ferri**), Goethite (**Goe**), Greigite (**greig**), Gypsum (**Gy**), Hausmaunnite (**Haus**), Hematite (**He**), Hornblende (**Hbl**), Hydroxy Apaptite (**Ap_{hyd}**), Illite (**I**), Kaolinite (**Kao**), Mackinawite (**Mac**), Magnetite (**Mt**), Montmorillonite (**M**), Muscovite (**Mus**), Prehnite (**Pr**), Pumpellyite (**Pum**), Pyrite (**Py**), Quartz (**Qz**), Sphene (**Sp**).

3.4.4 Nutrients

3.4.4.1 Phosphorus

Phosphorus in the sediments in the lakes is obtained from the lithology and through the domestic wastes and agricultural run off (Ruttenberg, 2004). Total phosphorus concentration in the Nainital and Sattal lakes is similar to that of the total phosphorus of the major moderately eutrophic to hyper eutrophic lakes around the world (Table 3.10). The total phosphorus concentrations in the lakes differ widely irrespective of their trophic status. The concentration of the total phosphorus in the lakes Vesijarivi, Onondaga, Apopka and Okeechobe is much higher (Table 3.10) compared to the Kumaun Himalayan lakes, may be due to the increased urbanization and pollution in the lakes. The lake Erken, Xuanwu and Yue, Hyper eutrophic lakes, have similar concentrations (Table 3.10) to that of the Nainital and Sattal. The lakes

Taihu and Hingze are similar to that of the Bhimtal and Naukuchiatal. The high concentrations of phosphorus in these lakes are due to the draining of domestic sewage sludge and agricultural wastes into the lakes (Rydin, 2000; Wang et al. 2005). The high concentration of phosphorus in the Nainital and Sattal (Table 3.5; Fig 3.5) may be due to the presence of pockets of apatite in the catchment area (Krol formation and Jantwalaiagaon limestone of Nainital and Sattal respectively).The phosphorus content in the less forested catchment of the Nainital basin is low compared to that of the forested lands of the Sattal, which result in high flux of phosphorus from the forested land (Singh and Gopal, 1999). 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.

Table 3.10 Total phosphorus contents in various global lakes

Lake	Country	Total P mg kg^{-1}	References
Lake Vesijarvi	Finland	2647	Hartikainen et al. (1996)
Lake Onondaga	USA	2.56-3.09	Penn and Auer (1997)
Lake Apopka	Florida, USA	42 (mmol kg^{-1})	Olila and Reddy (1997)
Lake Okeechobee	Florida, USA	39 (mmol kg^{-1})	Olila and Reddy (1997)
Lake Erken	Sweden	1814	Rydin (2000)
Lake Chao	China	217-221	Wang et al. (2005)
Lake Poyang	China	366	Wang et al. (2005)
Lake Taihu	China	420- 809	Wang et al. (2005)
Lake Hongze	China	631	Wang et al. (2005)
Lake Xuanwu	China	1062	Wang et al. (2005)
Lake Yue	China	1640	Wang et al. (2005)
Lake Verlorenvlei	South Africa	740	Das (2007)
Lake Zeekoevlei	South Africa	998- 1663	Das (2007)
Nainital	India	1800- 1100	Present Study
Bhimtal	India	680- 970	Present Study
Sattal	India	990- 2150	Present Study
Naukuchiatal	India	550- 740	Present Study

3.4.4.2 Sulfur

Sulfur concentration in the lakes shows that the Nainital Lake (Table 3.6; Fig. 3.6) is enriched in sulfur compared to the other lakes. This may be due to the presence of the minerals pyrite and gypsum in the catchment area. The domestic effluent discharge in to the Nainital Lake may also add significant amounts of sulfur. The low concentration/absence of sulfur bearing minerals may be the reason for low concentration of sulfur in other three lakes.

3.4.4.3 Nitrogen

Mineralisable nitrogen (Table 3.6; Fig. 3.6) 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 (Eq. 3.1- 3. 3).

3.4.4.4 Silica

Silica in the lakes dominates the major sediment chemistry, with the Sattal and Naukuchiatal (Table 3.5; Fig. 3.5) constituting more than 50%. The dominance of the silica in these lakes may be due to the catchment lithology (quartzites) and the presence of silica bearing micro organisms.

3.4.4.4.1 Biogenic Silica

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 (Table 3.6; Fig. 3.6) may be due to the absence of abundant diatoms in the lake (Pant et al. 1980). The increasing concentration of biogenic silica with depth may be due to the presence of diatoms and consequently lesser dissolution rate of the diatoms (Teodoru et al. 2006).

3.4.5 Relation of Phosphorus, Calcium, Iron and Aluminum

The bioavailability of phosphorus mainly depends upon its association with other elements in the lake; calcium, iron and aluminum being abundant elements play a major role in sequestering phosphorus in the sediments. Phosphorus is known to chemisorb calcium than any other metal (Meyer and Gloss, 1980). The positive correlation coefficient of calcium (R^2= 0.59; 0.74; 0.63 in Nainital, Bhimtal, and Naukuchiatal respectively) (Fig. 3.9) in the lakes shows that the calcium is preferred by phosphorus compared to the other metals. Golterman (1988) observed that even a very low amount of iron in the sediments transforms calcium bound phosphorus to iron bound phosphorus. The very low positive correlation of iron in all the lakes (R^2= 0.39; 0.24; 0.03 and 0.43 in Nainital, Bhimtal, Sattal and Naukuchiatal respectively) (Fig. 3.9) shows a negligible amount of sorption of phosphorus on to iron takes place. Although aluminum is also considered to be a good sorption site (as aluminum hydroxide) for phosphorus, the high anoxic condition and organic matter content of the lakes makes it least preferable for phosphorus, because they are very sensitive to the changes in redox conditions.

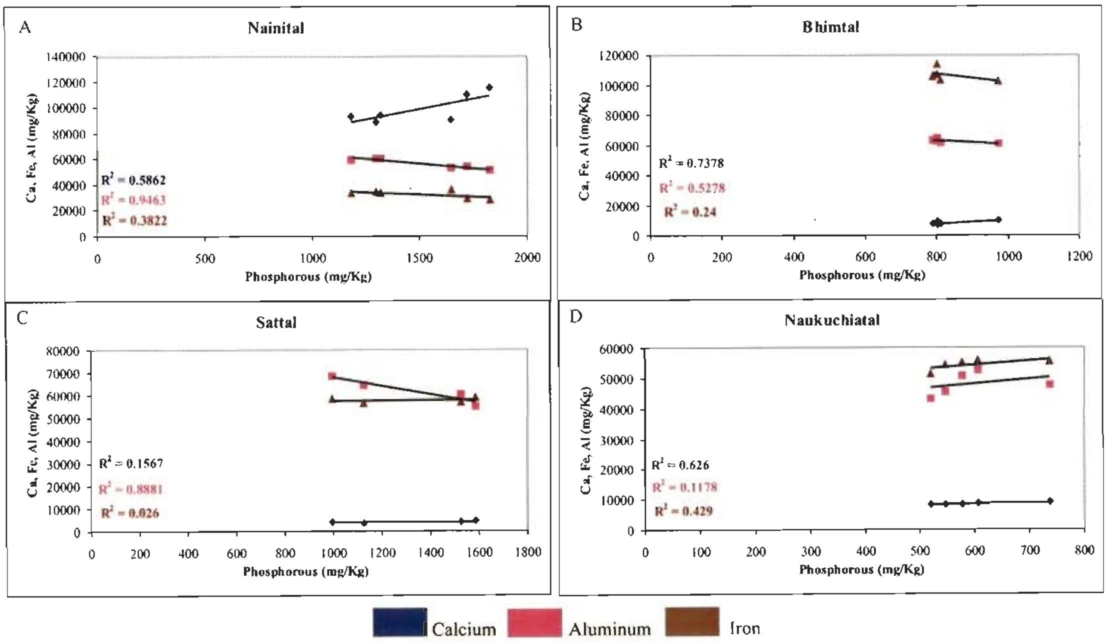


Figure 3.9 Relationship between P with Ca, Fe, Al in the lake sediments

3.4.6 Phosphorus Fractionation

All the lakes show dominance of phosphorus concentration (>90%) in the biogenic apatite (CFAP) fraction (Fig. 3.7). 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; Medeiros et al. 2005). 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 and Bhimtal lakes (Fig. 3.7) show 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; Fytianos and Kotzakioti, 2005).

Phosphorus does not or rarely binds with organic matter as the sorption site where it is blocked by the organic acids as well as complexation of exchangeable Al and Fe. However, presence of organic matter may increase the sorption of dissolved organic phosphorus (von Wandruszka, 2006). In Sattal and Naukuchiatal lakes (Fig. 3.7) the high organic matter content can act as a good competitor for dissolved organic phosphorus than the calcium and carbonates, which are present in less concentration. The increasing trend up core in this fraction is due to the release of phosphorous from the organic matter due to diagenesis of sediments (Penn and Auer, 1997). A less concentration of the detrital fraction (Fig. 3.7) indicates occurrence of limited apatite or phosphorus bearing minerals in the catchment area. The phosphorous in the labile forms namely iron oxides, exchangeable and organic matter gets transformed to the stable carbonate flour apatite with aging (Penn and Auer, 1997). In case of Nainital Lake, phosphorus settles down as carbonate flour apatite. However, Golterman (1988) observed that even very little amount of iron in the sediment may transform the phosphorus, which is precipitated as calcium bound to the iron bound fraction. In the Bhimtal, Sattal, and Naukuchiatal lakes (Fig. 3.7) where the iron concentration is much higher than the calcium and carbonate, may influence the calcium bound fraction and transform the calcium carbonate bound phosphorus fraction to the reducible fraction, thus causing retention of oxides in the sediments.

3.4.7 Biogenic silica and sulfur as potential competitors for phosphorus mobilization

3.4.7.1 Phosphorus and Silica

The silicate and phosphate both can be specifically adsorbed onto the surface of iron and aluminum oxide through a specific ligand exchange mechanism (Meyer and Gloss, 1980; Brinkman, 1993; Hartikainen et al. 1996). Additions of Si into the system results in the increase in the concentration of dissolved P in laboratory experiments (Tuominen et al. 1998; Koski- Vahala et al. 2001; Tallberg and Koski-Vahala, 2001). Silica in the sediments consists of large amounts of biogenic and amorphous silica, which is partly reactive (Tallberg et al 2008). The correlation between phosphorus and biogenic silica in the exchangeable fraction and easily reducible fractions were studied presently, as these two fractions are redox sensitive and easily available for the algae. Phosphorus shows very low correlation with biogenic silica (Fig. 3.10) in Nainital and Bhimtal (R^2= 0.17 and 0.41) and negative correlation in the Sattal and Naukuchiatal (R^2= 0.19 and 0.56) in the exchangeable fraction. Similarly, the easily reducible fraction shows (Fig. 3.10) very good negative correlation between silicate and phosphate in Nainital and Bhimtal (R^2= 0.67 and 0.69) and very low positive correlation in the Sattal and Naukuchiatal (R^2= 0.09 and 0.0002). The correlation clearly supports that the silica and phosphorus do not coexist in the iron and aluminum oxides and compete with each other for the sorption sites. The correlation in the exchangeable fraction also shows similar behavior to that of the easily reducible fraction. Because, this fraction consists of the elements that are adsorbed on to the sediment particles, the competition between the silica and phosphorus for sorption sites can play a major role in the mobilization of phosphorus.

3.4.7.2 Phosphorus and Sulfur

Sulfur in the lake as SO_4 is found to inhibit phosphorus sorption to sediment particles (Caraco et al. 1989). Sulfate can influence phosphorus mobilization due to, (i) SO_4 competing with PO_4 for anion sorption site, (ii) sulfate reduction to bind with iron and thus forming iron sulfide preventing the adsorption of phosphate on iron oxide sites, and (iii) increase in pH due to sulfate reduction inhibiting P- sorption (Curtis, 1989). In the present study, phosphorus and sulfur in the exchangeable fraction and easily reducible fraction (Fig. 3.11) show negative correlation in all the lakes (except Bhimtal in exchangeable and Nainital in easily reducible fraction (R^2= 0.4). The correlation (negative and low positive), shows that sulfur does not coexist with phosphorus in these fractions, resulting in a possible competition between each other for the sorption sites, and release of phosphorus from these sites.

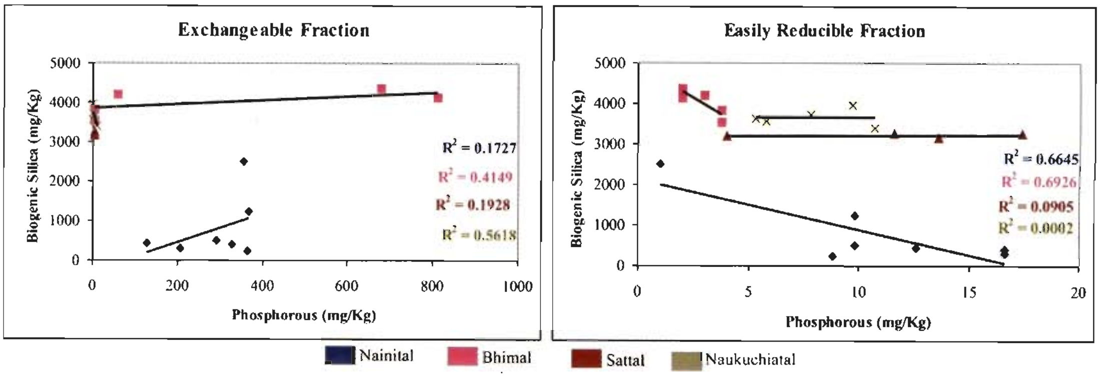


Figure 3.10 Relationship between phosphorus and biogenic silica in different fractions

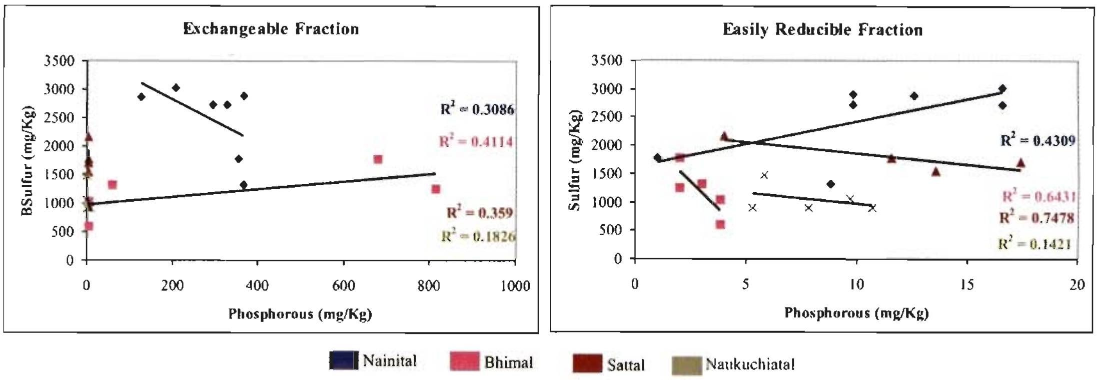


Figure 3.11 Relationship between phosphorus and sulfur in different fractions

3.5 Summary- Nutrients

The major water and sediment geochemistry of the lakes resembles the composition of the lithology in the catchment area. The Ca+Mg: Na+K ratio in the water, CIA and Al_2O_3/K_2O ratios in the sediments, indicate the dominance of weathering and the soil erosion in the catchment area. The over-saturation of carbonate minerals calcite, dolomite and aragonite in the water column of Nainital Lake and their presence in the sediments indicates a possible precipitation. The high concentration of chloride in the anoxic layer above the sediment column indicates the breakdown of chloride complexes and formation of mono- and bi- sulfides. The increasing concentration of ammonium in water indicates denitrification process in the lakes. The high concentration of the mineralisable nitrogen in the top layer of the sediment may be due to the adsorption of ammonia and free nitrogen onto the sediment surfaces. The high concentration of sulfate in the water column indicates oxidation of the sulfides by the reduction of nitrate and can also be attributed to the dissolution of sulfate minerals. Dissolved phosphate shows high concentration in the water column of the Nainital Lake compared to the other lakes. The over-saturation of minerals, hydroxyl- apatite (in Nainital) and carbonate flour apatite (in other lakes) in the water column indicates precipitation of phosphorus onto the sediments. The phosphorus concentration in interstitial water shows that very low amounts of phosphorus is released from the sediments in Nainital Lake, compared to the other lakes. This may be due to the sequestration of phosphorus by calcium, however, the dissolution of Fe-Mn oxides may be a good reason for the high concentration of phosphorus in other lakes; high concentration of phosphorus in the water column of Nainital Lake, thus, indicates the dominance of anthropogenic source. The relationship between the total phosphorus and the major elements in the sediment geochemistry and the phosphorus faction studies support that phosphorus is sequestered more by calcium than iron and aluminum oxides, as carbonate flour apatite. The correlation of phosphorus with sulfur and silica shows that these elements compete for the sorption site of the iron oxides and also in the adsorption site, resulting in subsequent release of phosphorus from the sediments.

Chapter 4

HEAVY METALS

4.1 Objective: Assessment of Metal Fractionation in the Lakes

4.1.1 Metals in Aquatic Environment

The study of metal behavior in aquatic environment is of great interest due to their potential detrimental effects on the aquatic ecosystems. The metals can exist in the aquatic environment in a variety of forms (Forstner and Wittman, 1983), and not all the forms are equally toxic or bio-available (Hare, 1992). The metal concentrations in the sediments depend on the weathering in the catchment area (Ramesh et al. 1995). Audry et al. (2006b) observed that these metal forms differ within an aquatic system due to variations in the source, aging of particles and due to slight changes in the physico-chemical conditions. The determination of total concentration in both the sediment and water do not make much sense, unless metal speciation studies have been carried out (Forstner and Wittman, 1983; Campbell and Tessier, 1989; Tack and Verloo, 1995; Wang et al. 2003). A clear understanding of metal behavior is possible only when different forms are identified and their interactions with the surrounding materials are understood. The reactions occurring at the solid surfaces play an important role in the partitioning of metals in to solid and solution phases (Warren and Haack, 2001). The factors affecting metal behavior at a given time are, (i) physical and chemical properties of an aquatic environment (such as, ionic strength, Eh, pH, biological activity), (ii) composition of the solution phase, (iii) types and densities of solid sorbent, and the kinetics of relevant reactions e.g. the influence of biological activities and temperature (Sheintuch and Rebhun, 1988; Tessier et al. 1989; Johnson, 1990; Warren and Zimmerman, 1994; Warren and Ferris, 1998;

Warren et al. 1998; Small et al. 1999; Warren and Haack, 2001; Mahanta, 2003; Callender 2004; Sparks, 2005; Demile et al. 2007).

The sorption of metals onto clays, iron and manganese oxides, and organic matter is the most important process controlling the fate and mobility of metals in aquatic environment (Sparks, 2005; Viers et al. 2007). Veeresh et al. (2003) observed that the formation and sorption of metal hydrolysis productivity is the dominant mechanism in sorption, and is dependent on the concentration of the metals in the solution. The redox potential of the system influences the metal behavior, since, dissolution and precipitation of iron and manganese oxides and organic matter takes place in changing oxic status. The metals with more than one oxidation state in natural waters are differently mobile, soluble, toxic and reactive (Ahmann et al. 1997; Losi and Frankenberger 1997; Newman et al. 1998; Brown et al. 1999; Wang 2000). Bacterial activity also reduces the metal mineral phases, such as Fe and Mn oxy-hydroxides (Lovely, 1995). The bacterial reduction ma y be given as (Ehrlich, 1996),

$$FeS_2 + 3.50_2 + H_2O \rightarrow -{*}Fe^{2+} + 2H^+ + 2SO^{2-} \qquad (4.1)$$

$$2Fe^{2+} + 0.50_2 + 2H^+ \rightarrow 2Fe^{3+} + H_2O \qquad (4.2)$$

The metal fractionation, as it is generally known for speciation studies, provides an insight in to the distribution patterns of metals in the aquatic environment and their potential bioavailability. The metal speciation studies are generally carried out using a multi-step sequential extraction procedure, in which reagents with different strengths and pH are used to leach the chemical forms of interest. There are some experimental uncertainties which persist with sequential extraction methods. The effect of pH (Bermond, 2001) and the concentration of the reagents (Sahuquillo et al. 1999) used in the extraction procedures have been extensively studied and are recommended for their usefulness in understanding the mobility of metals in sediments. The role of biogeochemical cycle of iron and sulfur, oxy-hydroxides and organic matter in metal sorption and bioavailability and mobility in sediments is well understood from the numerous metal fractionation studies in various environments. Zhang et al. (2001) and Hjorth (2004) studied the effects of drying of sediments in the chemical phases of different metals and nutrients. Wang et al. (2003) observed that the particle size of the sediments influences sorption of metals. Gambrell et al. (1991) observed that the trace metals behave differently under differing pH, redox and salinity conditions. They observed that the release of cadmium increases with change in pH, redox and higher salinity, whereas, chromium shows negligible variation. They also observed that the metals, copper, nickel and zinc are released with increasing anoxic condition, where as lead showed no effect of redox potential. The redox potential was found to influence the release of most of the metals in fresh and marine environments (Rippey and Jewson, 1982; Guo et al. 1997; Boyle, 2001). Jacobs et al. (1985), and Krauskopf and Bird (1995) observed that the metals show specific class behaviour i.e., the transition metals prefer both the sulfide and oxides, where as, the Group-B metals (in periodic table) prefer sulfide bonding. The sulfides are thought to be one of the potential scavengers for the trace metals in the anoxic environment. The trace metal sequestration along with authigenic pyrite and their kinetics were studied by many workers (Huerta- Diaz and Morse, 1990, 1992; Morse, 1991, 1994; Cooper and Morse, 1998; Morse and Luther, 1999; Scholz and Neumann, 2007) and are observed to be stable over a wide range of redox conditions. The formation of sulfides in anoxic condition can be depicted in a general equation as (Morse and Luther, 1999),

$$M(H_2O)_6^{2+} + Cl^- \rightarrow M(H_2O)_5(Cl)^+ + H_2O \quad \text{(Cl complexation)} \quad (4.3)$$

$$M(H_2O)_5(Cl)^+ + HS- \rightarrow M(H_2O)_5(HS)^- + Cl^- \text{ (Bi-Sulfide Complextaion)} \quad (4.4)$$

$M(H_2O)_6^{2+} + HS^- \rightarrow M(H_2O)_5(HS)^- + H_2O$ (Bi-Sulfide Complextaion) (4.5)

where, M is the Metal ion.

It is observed that the acid volatile sulfides (AVS) such as amorphous FeS, mackinawite and greigite act as scavengers for trace metals in anoxic environment, whereas iron and manganese oxides are found to sequester trace metals in oxic environment. Bebie et al. (1998) observed that the interaction between sulfate and pyrite is sorption-site specific rather than electrostatic forces. They also observed that the interaction between the dissolved metals and organic matter get enhanced due to the presence of iron groups and thiols. Kao et al. (2004a) observed that lack of organic matter and abundant reactive iron supply cause formation of intermediate sulfides preventing pyritization. Significant studies have been carried out in understanding the kinetics of metal sorption on to the iron oxy-hydroxides (Tessier et al. 1985; Suter et al. 1991; Stumm and Sulzberger, 1992; Tessier et al. 1996). Tessier et al. (1996) observed that in acidic conditions, the trace metals are adsorbed on to organic matter on iron oxy-hydroxides and directly on to the iron oxy-hydroxides at circum neutral conditions. The organic matter was also found to be associated with copper, zinc and cadmium (Calvert and Pederson, 1993; Bruland and Lohan, 2003; Morel and Price, 2003). The metals bound to organic matter were found to behave differently with age of the organic matter (Burba, 1994). Koschinsky et al. (2003) observed that hydrated cations and chloride complex metals such as, Mn^{2+}, $MnCl^-$, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and $PbCl^-$ are adsorbed onto manganese oxides, whereas, the neutral or negatively charged complexes, $HAsO_4^2$ and $PbCO_3^0$ are associated with iron oxy-hydroxides.

4.1.2 Selected Global Studies – Heavy Metals

Hoffman et al. (1981) studied the geochemistry of metals in the lakes of British-Columbia. Tessier et al. (1985, 1989) observed that pH and iron oxy-hydroxides play a significant role in the mobilization of zinc. Carroll et al. (2002) studied the effect of oxidizing and reducing conditions in the speciation of metals in a lagoon. They observed that oxidization of the metals in marine environment acts as a potential hazard. Mannio et al. (1995) observed significant atmospheric contribution to the total metal concentrations in the lake waters of Finland. Mogollon and Bifane (1996) studied the metal geochemistry in a trophic lake of Venezuela. Birch et al. (1996) studied the anthropogenic effects of heavy metals in an Alpine Lake. Szymanowska et al. (1999) studied heavy metals in the lakes of Western Poland and observed that the behavior of metals differed considerably between plants, water and the sediments in the lake bottom. They suggested that iron increased in plants with increase in water column, manganese and lead showed a negative correlation between water and sediment column, whereas chromium and cadmium showed a positive correlation between water, sediments and plants. Birch et al. (1996) and Motelic-Heino et al. (2003) observed release of metals along with the sulfides, by sulfate reducing bacteria. van Griethuysen et al. (2005) observed the sulfide minerals playing an important role in the adsorption and sequestration of minerals at the anoxic bottom of the lake. Koretsky et al. (2006) concluded that redox stratification in the Asylum Lake plays an important role in the bioavailability of trace elements. Audry et al. (2006a) observed that the metals were released during diagenesis and found that a minor change in the chemical conditions affects the speciation of the metals. Audry et al. (2007b) from their studies on the budget of manganese, copper and cadmium in the Gironde Estuary, concluded that metals which were released during reduction, co-precipitated again with iron and manganese oxy-hydroxides, which were later scavenged by the organic matter. They also observed that (Audry et al. 2005; 2007a), even though, the metals U and Mo are sequestered by the sulfides in the anoxic condition, the oxidation of sulfides by the reduction of Fe- and Mn- oxides and bacterial nitrate reduction, release back the metals again into the water column.

4.1.2.1 Metal Fractionation Procedures

Following the studies of Chang and Jackson (1957), many workers have formulated fractionation procedures for the determination of metal speciation in sediments. The methods formulated by Tessier et al. (1979) and its modified version, SM&T (Ruban et al. 2001), are the most used methods world wide. Williamson and Parnell, Jr. (1994) observed in East Central Arizona Lake that copper preferred organic matter and zinc preferred iron oxide sorption sites. Morse and Arakaki (1993) studied desorption and precipitation of the metal with sulfide minerals using the fractionation method. Harrington et al. (1998) and Ng et al. (2004) studied the geochemistry of the elements in lake sediments using metal fractionation. Dollar et al. (2001) from their studies on the Indiana Dunes lakeshore observed that the fractionation methods are very useful in understanding the metal behavior and restoration of lakes. Wu et al. (2001) studied water-sediment interaction and regeneration of N, P, and Si in the Lakes of South China. Gleyzes et al. (2002) on their review on the metal fractionation of the sediments and soils discussed various advantages and disadvantages associated with the different extraction procedures. Chen and Wann (2004) observed that metals in the sediments of Great Ghost Lake of China were bound to the lithogenic materials, and the labile forms of metals were found to be bound to iron oxides and organic matter. Bhattacharya et al. (2008a & b) on their study on the fractionation and bioavailability of metals on soils observed the metals to have been associated with iron and aluminum oxides and that the exchangeable fraction exhibits inhibitory nature of the metal adsorption by organic matter.

4.2 Methodology

4.2.1 Sample Collection

Water samples were collected from the surface of the lake and deep water samples at three depth intervals during 2008. The interstitial water samples were collected by centrifuging the sediments at 7500rpm for 1hr. The water samples were filtered through 0.45µm 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. The cores were segmented into sub-samples of 2 cm and 5cm thickness in the field immediately. The samples were stored in refrigerated condition in clean air-tight polythene bags.

4.2.2 Sample Analysis

Fig. 4.1 shows the different analysis carried out in the samples. The initial measurements of pH, Eh and temperature were carried out in the water and sediment samples immediately after sample collection in the field. 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.

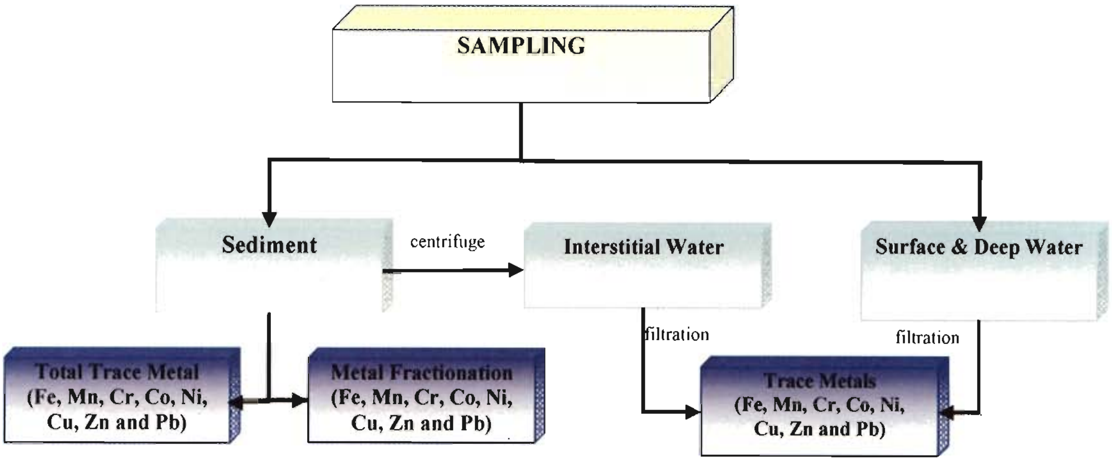


Figure 4.1 Flow-chart showing sampling and analysis of metals in water and sediments

The core sediment samples were air dried and powdered after the organic matter in the sediments was removed by treatment with H_2O_2. The sediments were digested using tri-acid ($HCl+HNO_3+HF$) method. The digested samples were analyzed for trace metals 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) analysis.

4.2.2.1 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 4.1) developed by Leleyter and Probst, (1999). The seven step procedure extracts the water soluble, exchangeable, carbonate bound, manganese oxide bound, amorphous iron oxy hydroxide bound, crystalline oxide bound and organic matter bound. The residue was digested using tri-acid method to determine the residual phase.

Table 4.1 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	1M Magnesium Nitrate	2 hrs. + Shaking	20
Bound to Carbonates	Sodium Acetate at pH-4.5 (HoAc)	5 hrs. + Shaking	20
Bound to Mn Oxides	0.1 M Hydroxyl Ammonium Chloride	30 min. + Shaking	20
Bound to Amorphous Fe Oxides	0.2M Ammonium Oxalate- 0.2M Oxalic Acid	4 hrs (in dark) + Shaking	20
Bound to Crystalline Fe Oxides	0.2M Ammonium Oxalate- 0.2M Oxalic Acid- 0.1M Ascorbic, Acid	30 min. + Shaking	80
Bound to Organic Matter	0.02M HNO_3, 35% H_2O_2 3.2M Ammonium Acetate (pH 2 with HNO_3)	30 min. + Shaking	85
Residual	Aqua regia + HF (Digestion)		89

4.3 Results

4.3.1 Dissolved Metals

The trace metal concentration in the Nainital is different with in 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 4.2; Fig. 4.2) where as, in the Bhimtal Lake, decreasing trend up core is observed. The Sattal lake shows high iron (Table 4.2; Fig. 4.2), lead and zinc (Table 4.2; Fig. 4.3) concentration in the water column and they show decreasing trend up core. The other metals show decreasing or no variation in concentration with depth. The trace metals in the Naukuchiatal lake show decreasing concentration up core. The metal concentration in the lakes at the sediment-water interface and the top 10cm of the interstitial water increases many folds (Table 4.2; Fig. 4.2 & 4.3), the concentration of the metal decreases with depth there after in the interstitial water column.

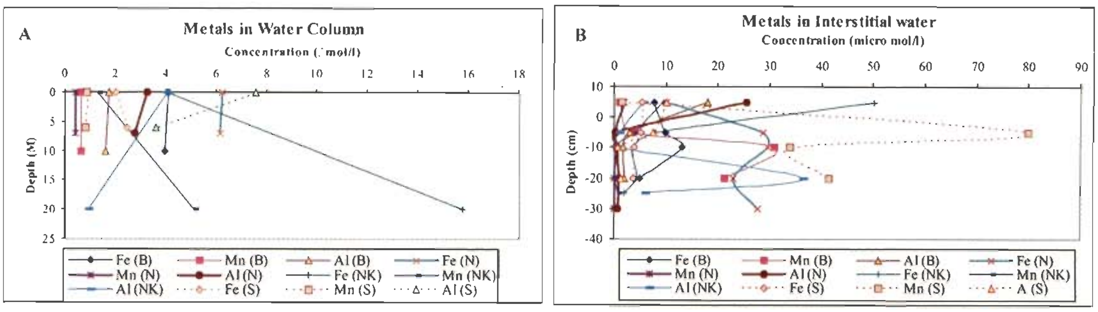


Figure 4.2 Metals (Fe, Mn and Al) in the water and interstitial water in the lakes (the letter in the parenthesis refers to Bhimtal (B), Nainital (N), Naukuchiatal (NK) and Sattal (S) lakes)

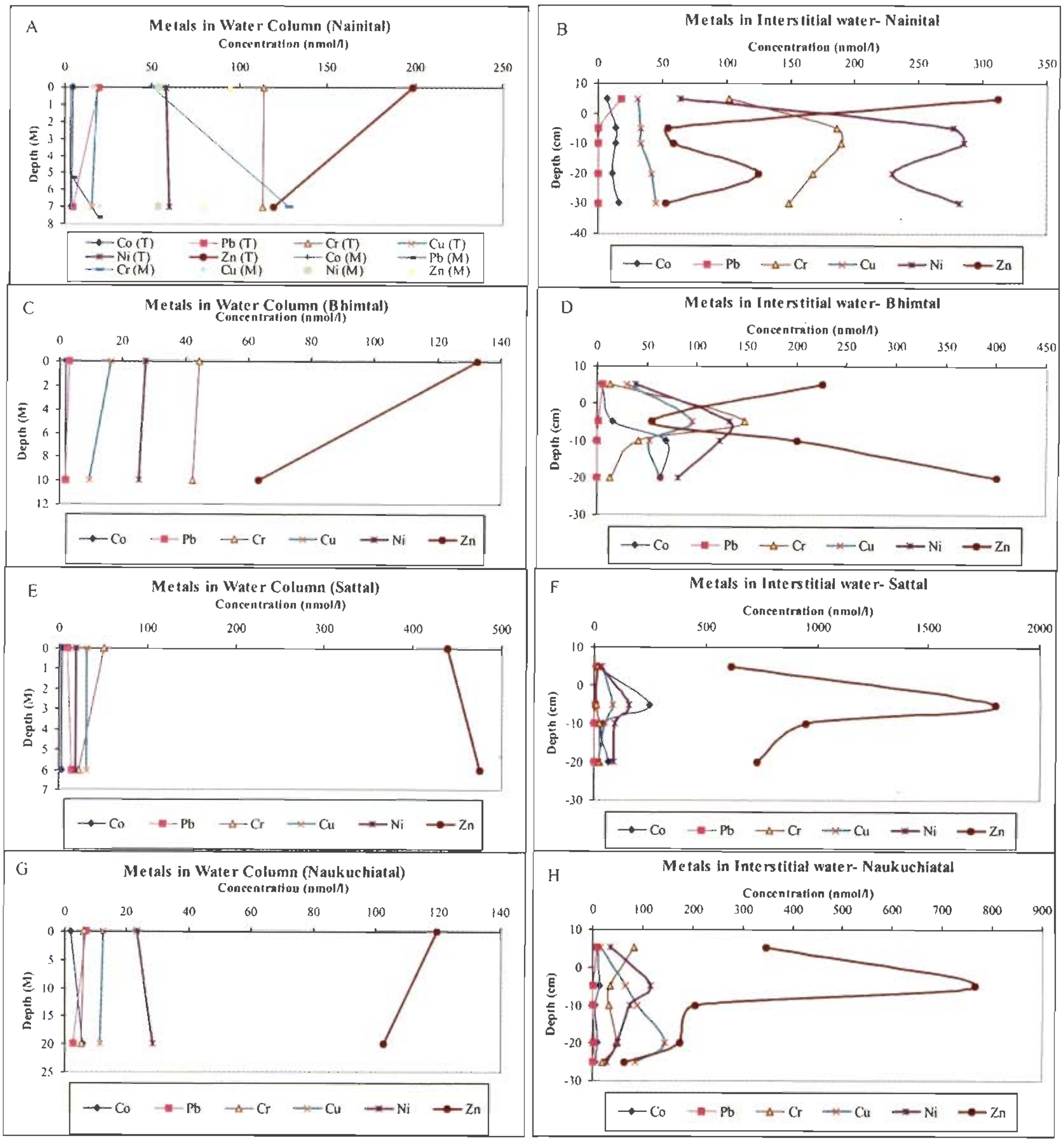


Figure 4.3 Metals in the water column and interstitial water in the lakes

Table 4.2 Water Chemistry of the Lakes- Dissolved trace metals

Sample ID	Fe (µM)	Mn (µM)	Al (µM)	Co (nM)	Cr (nM)	Ni (nM)	Cu (nM)	Pb (nM)	Zn (nM)
				Nainital					
Surface	7.0	0.5	3.4	4.2	113.8	57.7	18.2	18.8	198.1
14m	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
Above Sediment	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
				Bhimtal					
Surface	4.1	0.6	1.7	1.8	44.2	27.0	16.1	2.9	132.6
10m	4.0	0.6	1.6	1.8	42.0	24.9	9.1	1.7	63.3
Above Sediment	7.7	1.0	17.9	3.9	13.2	37.9	29.6	5.9	225.9
PW 0-5 cm	9.9	3.7	3.0	15.8	148.0	132.2	95.4	0.6	55.1
PW 5-10 cm	13.1	30.9	1.6	69.3	41.2	122.5	52.3	0.5	200.9
PW 15-20 cm	5.0	21.2	1.9	63.6	13.0	80.7	63.8	0.2	400.5
				Sattal					
Surface	2.0	0.8	7.6	2.4	50.0	18.9	30.9	8.0	438.8
6m	2.5	0.8	3.6	1.9	22.1	18.1	30.9	13.6	475.4
Above Sediment	5.4	1.5	10.0	3.1	13.0	25.9	34.0	9.2	615.3
PW 0-5 cm	5.2	79.9	7.5	250.4	10.0	153.8	84.0	5.7	1800.6
PW 5-10 cm	3.9	33.8	0.7	40.9	23.4	93.2	50.9	0.2	949.6
PW 15-20 cm	3.7	41.4	1.3	62.3	23.4	88.7	21.4	0.3	728.8
				Naukuchiatal					
Surface	4.0	1.3	4.1	1.8	5.9	23.0	12.0	6.5	119.3
20m	15.8	5.1	0.9	5.5	5.4	28.3	11.0	2.3	102.2
Above Sediment	50.1	9.2	5.6	8.1	83.6	34.0	15.9	7.7	346.8
PW 0-5 cm	8.0	3.8	1.1	13.5	35.3	114.8	66.2	0.1	765.9
PW 5-10 cm	3.7	0.3	0.6	4.1	32.0	75.1	89.6	0.1	204.2
PW 15-20 cm	4.3	0.2	36.5	9.3	48.8	49.7	143.0	1.6	173.4
PW 20-25 cm	1.9	0.6	6.0	4.5	20.5	29.3	84.4	0.2	64.0

N.A- Data Not Available/ below detection limit; PW- interstitial (Pore) water, T= Tallital; M= Mallital

4.3.2 Metals in Sediments

4.3.2.1 Total Metal Concentration

The concentration of aluminum is uniform in all the lakes with the concentration ranging between 4 - 7% (Table 4.3; Fig. 4.4). The metal iron, dominates the trace metal concentration in all the lakes (12- 3%) with high concentration in the Bhimtal (10- 12%) and low in the Nainital (~3%). Manganese is the next abundant metal with concentration ranging from 600mg/kg (Bhimtal) to 1100mg/kg (Naukuchiatal). The total trace metals concentrations in the lakes vary widely with each other (Table 4.3 (A-D); Fig. 4.4 (A-D)). The concentration of cobalt is high in the Naukuchiatal and Sattal (>50mg/kg) and least in the Nainital lake (<15mg/kg). Chromium is dominant in the Bhimtal followed by Nainital with the concentration ranging between 11- 70mg/kg, whereas it ranges between 15- 25mg/kg in Naukuchiatal and Sattal. The Nainital and Sattal have high concentration of nickel of 30- 63mg/kg and 50- 80mg/kg respectively. These metals show increasing up core trend in all the lakes.

The concentration of copper ranges from 18-40mg/kg; 40-58mg/kg; 35-53mg/kg and 80- 120mg/kg from top to bottom of the cores in Nainital, Bhimtal, Sattal and Naukuchiatal respectively. The concentration of lead does not vary much with depth, with concentrations not exceeding 20mg/kg, 125mg/kg, 75mg/kg and 70mg/kg respectively in Nainital, Bhimtal, Sattal and Naukuchiatal lakes. Zinc is the dominant metal in Nainital and Naukuchiatal, ranging from 70- 100mg/kg and 60-150mg/kg respectively and 44- 70mg/kg and 23- 53mg/kg in the Bhimtal and Sattal lakes respectively.

Table 4.3 Total metal concentrations (mg/kg) at different depths in the lake sediments

(A) Nainital

Depth(cm)	Cobalt	Copper	Chromium	Lead	Nickel	Zinc
0-2	7.1	39.4	37.5	16.0	63.9	90.5
2-4	33.2	32.7	37.5	20.3	48.7	83.0
4-6	16.9	32.4	11.0	21.3	57.2	31.0
6-8	12.6	29.6	32.0	15.7	41.2	104.8
8-10	11.0	29.7	28.0	15.5	41.2	96.5
10-12	10.9	25.9	29.0	15.7	46.2	99.5
12-14	10.0	26.0	n.a	16.4	36.3	93.2
14-16	16.8	22.9	75.0	18.8	31.5	73.8
16-18	12.3	23.0	59.0	20.6	32.5	91.3
18-20	9.7	22.6	24.5	15.9	33.3	87.2
20-22	14.7	21.0	57.5	20.3	29.9	87.8
22-24	6.9	19.8	58.5	6.1	30.3	87.4
24-26	24.1	20.8	36.5	19.1	29.3	74.4
26-28	16.3	20.0	29.0	19.4	29.2	81.8
28-30	10.4	18.0	33.5	19.5	31.4	84.0
30-32	9.9	18.8	28.5	18.0	34.2	79.3

(B) Bhimtal

Depth(cm)	Cobalt	Copper	Chromium	Lead	Nickel	Zinc
0-2	17.4	40.1	70.7	178.7	42.7	73.4
2-4	13.2	33.5	47.5	64.0	26.7	41.5
4-6	20.3	39.4	63.5	45.1	33.3	52.7
6-8	23.5	47.7	55.6	132.3	37.0	56.2
8-10	20.6	46.0	62.8	125.6	32.0	55.8
10-12	21.1	47.7	63.3	127.1	32.3	52.7
12-14	22.8	54.3	63.7	112.1	33.5	53.4
14-16	19.9	56.8	61.1	114.6	30.3	49.8
16-18	19.2	50.9	62.3	104.5	30.0	49.6
18-20	19.3	58.9	62.2	119.1	30.0	50.0
20-22	20.5	53.2	57.7	116.5	33.2	49.2
22-24	17.8	52.6	58.9	115.0	28.2	44.5
24-26	18.7	59.9	60.3	110.5	29.0	45.3
26-28	19.6	58.7	58.0	114.0	29.6	68.9

(C) Sattal

Depth(cm)	Cobalt	Copper	Chromium	Lead	Nickel	Zinc
0-2	50.6	52.6	24.8	72.0	80.3	34.2
2-4	47.5	100.8	28.3	74.4	76.1	33.8
4-6	64.1	33.6	12.6	72.1	71.6	30.0
6-8	56.7	38.1	26.3	76.6	72.3	31.4
8-10	61.0	24.1	17.0	80.0	67.2	33.8
10-12	53.2	32.7	16.6	68.0	71.2	46.6
12-14	63.4	19.6	24.0	70.1	73.3	37.0
14-16	52.8	31.1	20.1	66.8	69.9	33.1
16-18	80.5	35.6	15.6	73.0	79.9	31.6
18-20	64.8	26.3	13.3	68.0	72.7	31.5
20-22	55.1	33.6	8.9	66.8	60.9	27.3
22-24	79.9	35.0	17.1	64.6	77.6	25.5
24-26	66.1	25.4	26.7	61.8	69.5	25.5
26-28	53.5	28.6	17.3	66.9	64.7	23.4
28-30	67.8	42.2	21.2	72.3	57.2	25.1
30-32	57.8	35.2	17.7	62.5	65.8	31.4

(D) Naukuchiatal

Depth(cm)	Cobalt	Copper	Chromium	Lead	Nickel	Zinc
0-2	87.1	91.5	46.5	61.7	40.8	150.0
2-4	66.1	120.2	21.0	60.8	48.1	143.0
4-6	21.5	81.8	17.5	60.1	42.6	126.8
6-8	44.4	72.7	14.8	47.8	46.5	117.1
8-10	40.9	87.1	12.0	63.1	35.8	158.8
10-12	63.5	85.2	29.4	60.0	42.6	100.8
12-14	54.6	78.5	35.0	64.4	46.0	86.8
14-16	71.2	95.1	25.3	61.3	34.0	81.8
16-18	50.2	81.8	23.0	73.2	28.0	83.7
18-20	63.9	70.2	21.1	60.3	25.9	79.9
20-22	47.7	76.6	28.2	63.3	49.6	95.3
22-24	51.7	79.4	28.0	58.3	45.6	82.6
24-26	54.7	80.9	30.6	62.8	50.7	85.6
26-28	55.8	110.7	25.9	60.8	47.5	76.4
28-30	40.5	84.7	29.0	55.0	46.4	66.8
30-32	66.0	81.5	29.4	56.9	47.3	66.3

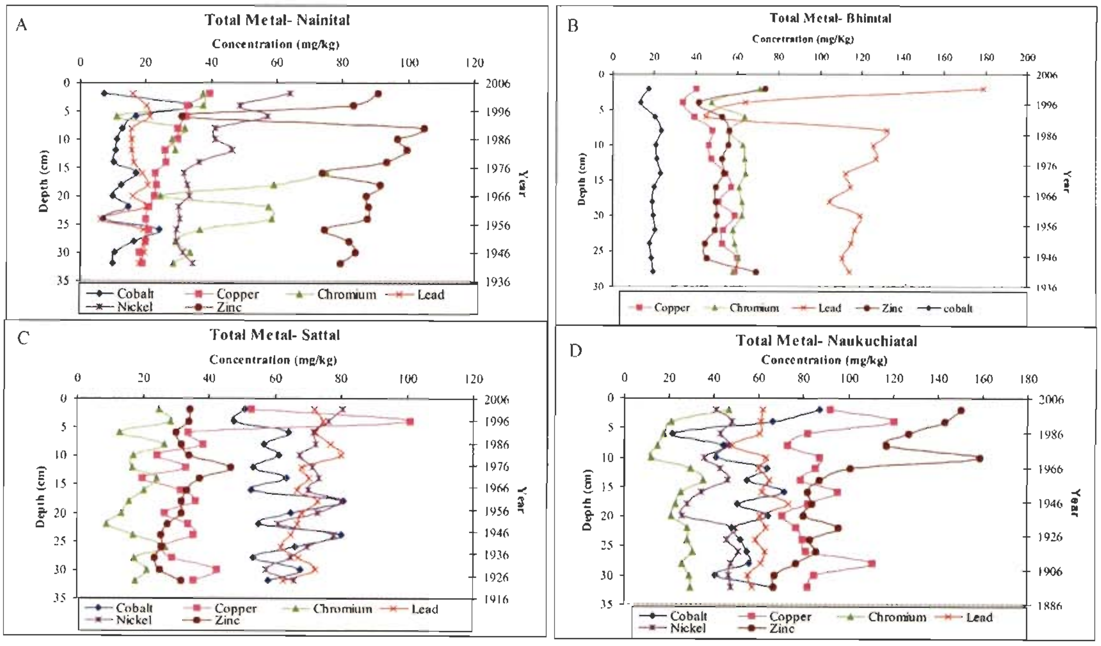


Figure 4.4 Variations in total metal concentrations in the sediments of different lakes

4.3.2.2 Heavy Metal Fractionation

4.3.2.2.1 Iron

Iron in residual fraction is dominant among all the fractions in all the lakes constituting >50% of total iron. The lakes show different behavior among the chemical phases, with the Nainital (Fig. 4.5A) showing high concentration in the carbonate and amorphous phases and Bhimtal (Fig. 4.6 A) shows high concentration in the amorphous iron oxides and the organic phase. Sattal (Fig. 4.7 A) and Naukuchiatal (Fig. 4.8 A) show high concentration of iron in organic bound phase. The crystalline iron oxide bound fraction also contains significant amounts of iron in all the lakes.

4.3.2.2.2 Manganese

The carbonate phase contains higher manganese in the Nainital (Fig 4.5 B) and Bhimtal (Fig. 4.6 B), where as the water dissolvable and easily exchangeable phases have high percentage of manganese in the Sattal (Fig. 4.7 B) and Naukuchiatal (Fig. 4.87 B). The manganese oxide bound fraction contains high concentration of manganese in Nainital and the organic matter bound and crystalline fraction show high concentration of manganese in all the other lakes.

4.3.2.2.3 Cobalt

The carbonate phase shows high concentration of cobalt in the Nainital (Fig 4.5 D) lake sediments followed by manganese and iron oxide phases, where as the other three (Fig 4.6-8 D) lakes show high concentration of cobalt in the iron oxide fraction (amorphous and crystalline) and organic matter fraction. The other fractions show very low cobalt concentration.

4.3.2.2.4 Chromium

The residual fraction contains considerable amounts of chromium in all the lakes. The crystalline iron oxide bound fraction dominates the Nainital (Fig 4.5 C) and Sattal lake (Fig 4.7 C) sediments and the amorphous iron oxide fraction dominates the Bhimtal Lake (Fig 4.6 C). The organic fraction also contains considerable amount of chromium in all the lakes especially in the Sattal (Fig 4.7 C) and Naukuchiatal Lakes (Fig 4.8 C).

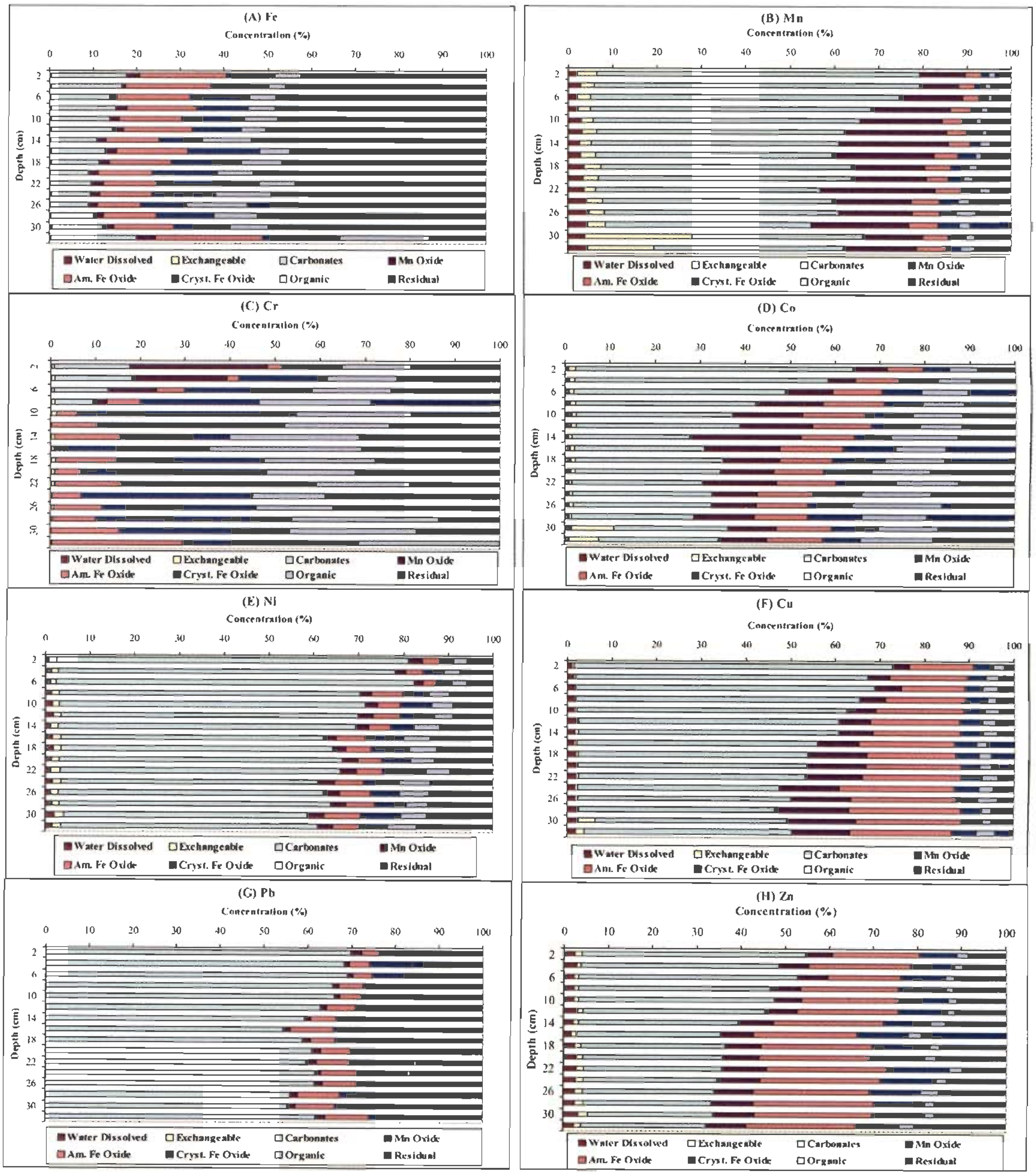


Figure 4.5 Percentage abundance of metals in different chemical fractions in Nainital lake sediments

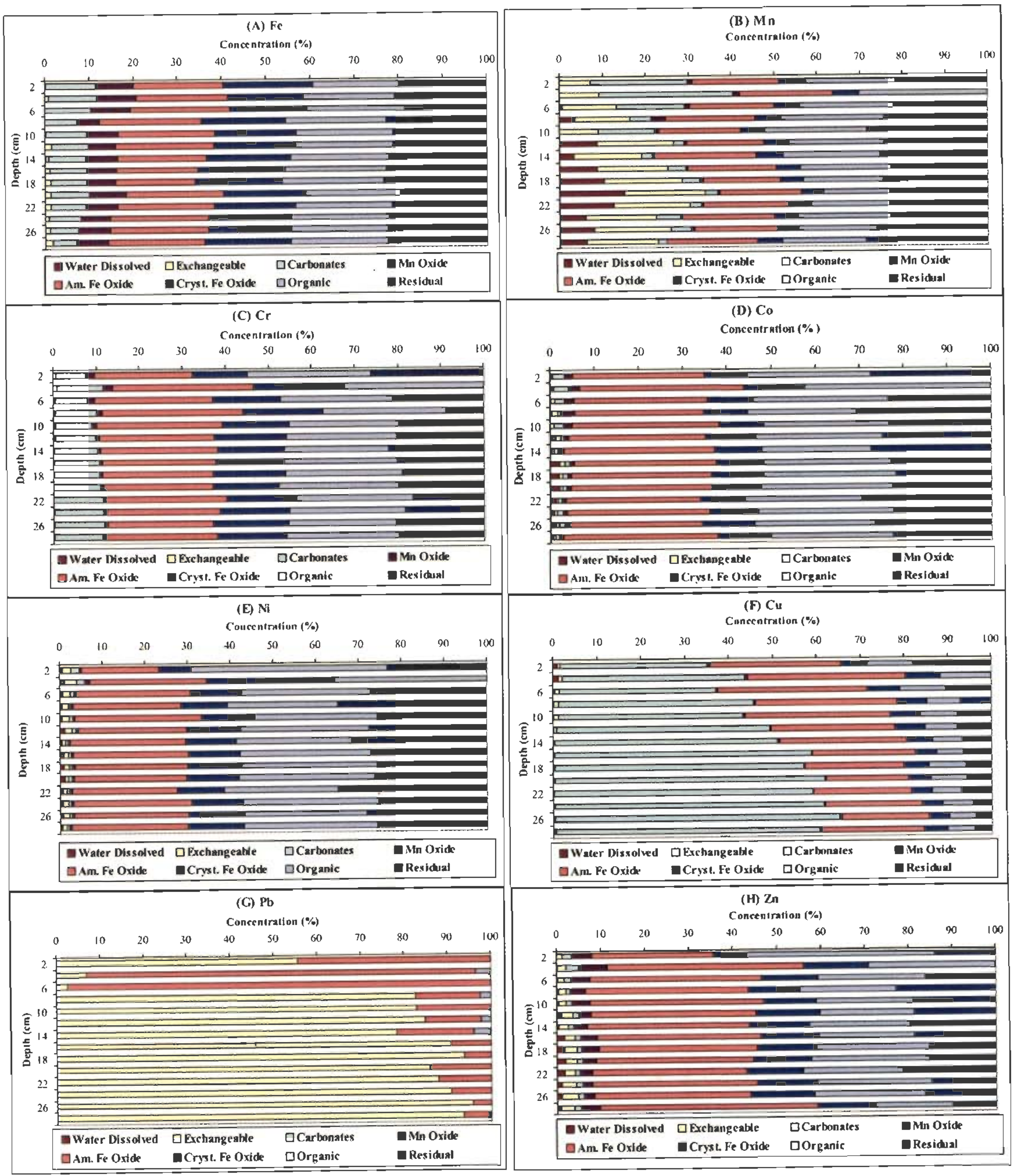
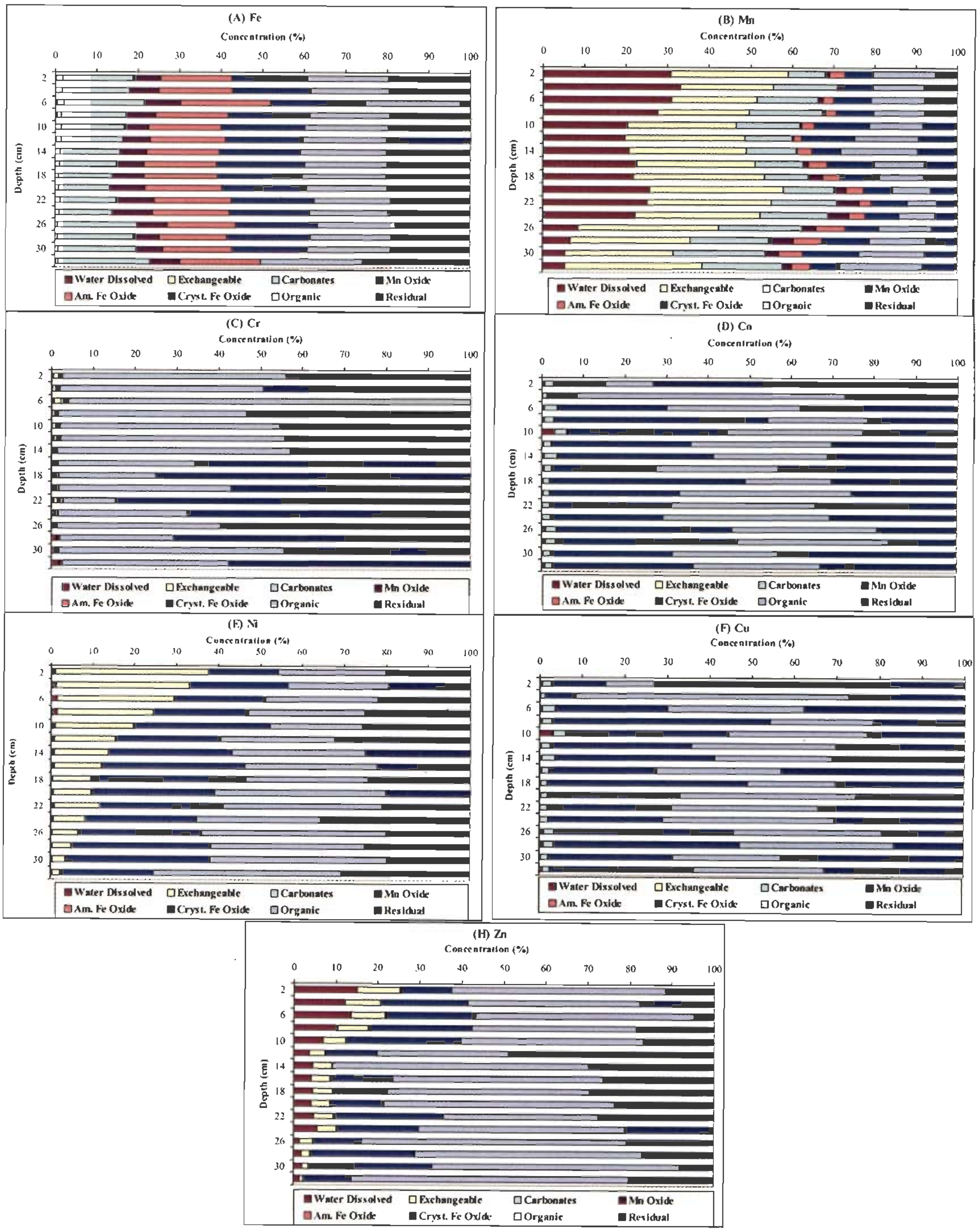


Figure 4.6 Percentage abundance of metals in different chemical fractions in Bhimtal lake sediments



(A) Fe

(B) Mn

(C) Cr

(D) Co

(E) Ni

(F) Cu

(H) Zn

Figure 4.7 Percentage abundance of metals in different chemical fractions in Sattal lake sediments

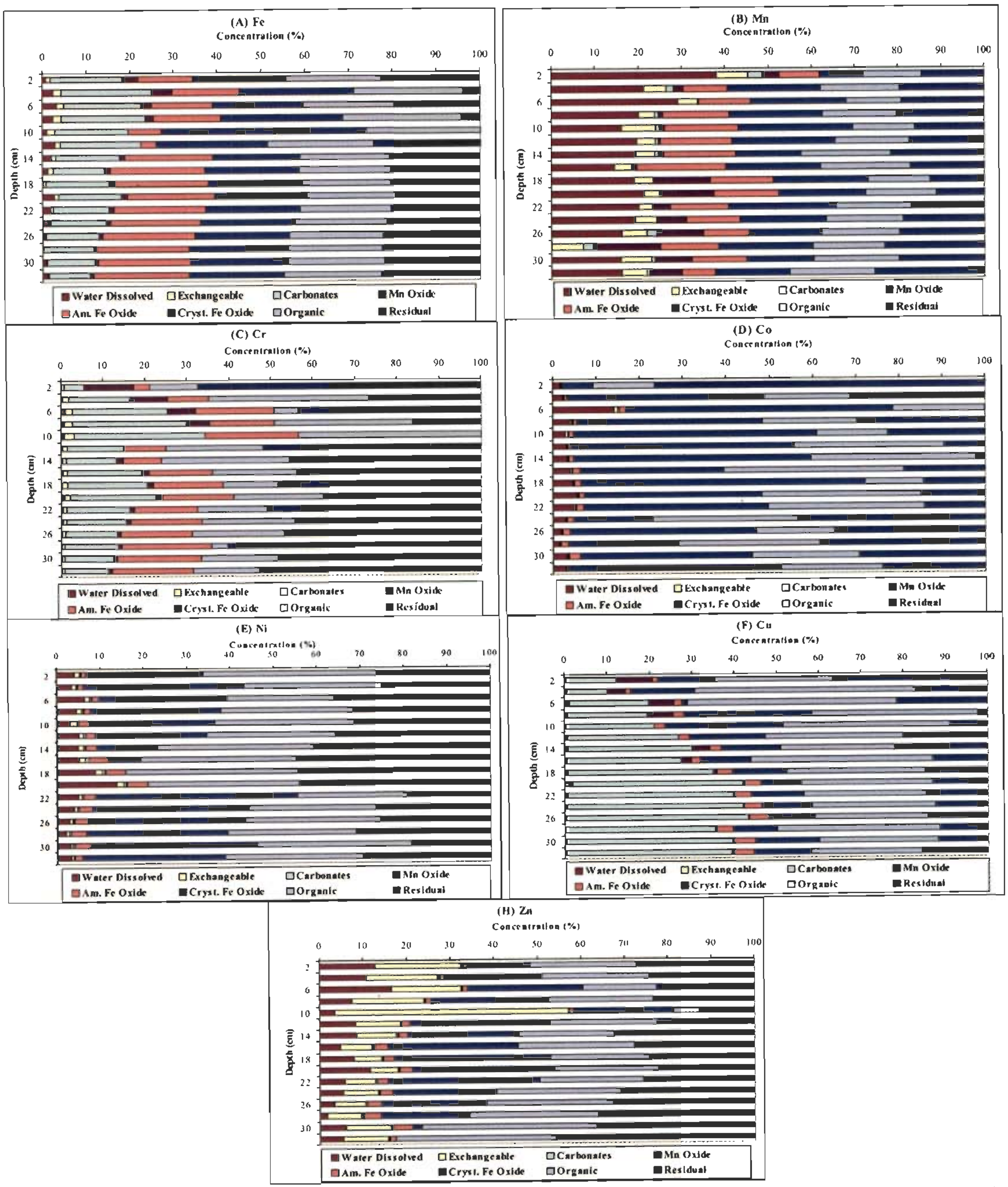


Figure 4.8 Percentage abundance of metals in different chemical fractions in Naukuchiatal lake sediments

4.3.2.2.5 Nickel

The residual fraction contains considerable amount of nickel in all the lakes. The carbonate bound fraction dominates the Nainital (Fig. 4.5 E) lake sediments and the organic matter fraction dominates the Bhimtal, Sattal and Naukuchiatal Lakes (Fig. 4.6-8 E) after residual fraction. The crystalline iron oxide and amorphous iron oxide bound fractions are the other fractions which have considerable concentartions of nickel.

4.3.2.2.6 Copper

Copper is predominant in the carbonate fraction in the Nainital (Fig. 4.5 F), Naukuchiatal (Fig. 4.8 F) and Bhimtal lake (Fig. 4.6 F) sediments followed by the amorphous iron oxide fraction in the Nainital and Bhimtal and by the organic matter bound fraction in the Naukuchiatal. The Sattal (Fig. 4.7 F) shows high concentration of copper in organic bound fraction followed by residual fraction. The other fractions show considerable amount of copper in all the lakes.

4.3.2.2.7 Lead

Lead is dominant in the carbonate fraction in the Nainital lake (Fig. 4.5 G) sediments followed by the amorphous iron oxide fraction. The residual and crystalline iron oxide fractions have considerable amounts of lead in this lake. The other lakes have high concentration of lead in the exchangeable fraction. The Bhimtal lake (Fig. 4.6 G) contains considerable lead in the amorphous iron oxide and organic fractions, where as the Sattal and Naukuchiatal lakes have lead only in the easily exchangeable fraction.

4.3.2.2.8 Zinc

A sizeable amount of zinc is present in the amorphous iron oxide fraction in the Nainital (Fig. 4.5 H) and Bhimtal lakes. The sediments in these lakes have high amounts of zinc in the carbonate (Nainital) and organic (Bhimtal) fractions as well. The other fractions also contain considerable amounts of zinc in these lakes. The Sattal and Naukuchiatal (Fig. 4.7 & 4.8 H) have high concentration of zinc in the organic fraction followed by the crystalline iron oxide fractions.

4.4 Discussion

4.4.1 Metals in Water

The trace metals concentrations in the Kumaun Himalayan lakes differ widely. The metal concentration in the water column of the Nainital Lake (Table 4.1A; Fig. 4.2& 4.3) 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 (Table 4.1A; Fig. 4.3) in the water column may be due to the sewage draining into the water and the vehicular and the scrapheap wasteages being drained into the water (Sparks, 2005). The other lakes generally do not show much variation in the trace metal concentration in the water column, high concentration of metals such as, chromium (Table 4.1 B-D; Fig. 4.3) may be due to the influence of the weathering of catchment rocks which have high concentration of chromium (Bhat and Ahmad, 1987). The metals are present in very high concentration in the sediment-water interface and at the top 10cm of the interstitial water in all the lakes. 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 concentration of manganese is very high in the interstitial water of the Sattal and Naukuchiatal (Table 4.1 C& D; Fig. 4.3), which may be due to the release of manganese in the anoxic layer due to the presence of organic matter (Davison, 1993). The manganese concentration is low in the interstitial water of Nainital Lake (Table 4.1A; Fig. 4.2), 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 4.1 B- D; Fig. 4.3) show increased concentration indicating the dissolution of oxide minerals. The metals aluminum (Table 4.1; Fig. 4.2), copper, lead and zinc (Table 4.1; Fig. 4.3) 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; Bruland and Lohan, 2003; Morel and Price, 2003).

4.4.1.1 Saturation of minerals in the water column and interstitial water

The metals are present in the lake water column mainly as free metal ions and as metal oxides in all the lakes, where as iron also occurs as carbonate (siderite) in Nainital lake. The presence of metal ions in the lake water column and the interstitial water enhances the formation of metal ligands due to the presence of high amounts of organic matter. The oxide minerals ferrihydrite, goethite, hematite, magnetite and manganese hydroxides show oversaturation in the water column (Table 3.7), indicating their precipitation. However, when they reach the sediment-water interface and the interstitial water, dissociation starts because of the prevailing anoxic conditions (Table 3.8). This is clearly visible from the undersaturation of the oxide minerals in the anoxic conditions. The aluminohydroxide minerals, i.e clay minerals such as illite, montmorillonite and kaolinite, are over saturated through out and precipitate in the sediments.

4.4.2 Metals in Sediments

4.4.2.1 Total Metals

The trace metal concentration of the Kumaun Himalayan lakes are high compared to some other global lakes (Table 4.4).

Table 4.4 A comparison of metals in sediments (mg/kg) of Kumaun Himalayan Lakes with some of the world Lakes and Rivers

	Country	Co	Cr	Ni	Cu	Pb	Zn
Lake Wielkie[a]	Poland	2.3	1.15	1.6	2.05	9.7	571
Lake Bosekowo[a]	Poland	4.2	1.85	2.95	2.95	13.4	1100
Lake Dominicke[a]	Poland	2.25	1.3	2.05	2.65	12.9	475
Blue Mountain Lake[b]	USA	-	-	-	-	64-80	235-287
Catfish Pond[b]	USA	-	-	-	-	132-177	106-182
Crater Lake[b]	USA	-	-	-	-	150-167	129-165
Lake Success[b]	USA	-	-	-	-	165-179	159-186
Long Pine Pond[b]	USA	-	-	-	-	114-134	71-30
Sunfish Pond[b]	USA	-	-	-	-	36-12	57-77
Chilika Lake[c]	India		4-74	52-143	10-101	28-59	21-63
Clear water Lake[d]	Ontario, Canada	-	-	1133	800	190	95
Fairbank Lake[d]	Ontario, Canada	-	-	45	21	16	88
Joe Lake[d]	Ontario, Canada	-	-	85	56	34	59
Agricultural Soil[e]	Spain	14	115	35	230	69	500
Ell-Ren River[f]	China	-	-	11-215	15-1200	32-460	45-1600
Oka River[g]	Spain	15-50	20-180	25-130	40-150	25-110	100-360
Seaplane Lagoon[h]	USA	14-48	100-1730	108-150	19-240	73-1270	108-580
Severn Estuary[i]	Britain	-	-	-	<1.5	<0.5	2-6
Nainital[j]	**India**	**7-33**	**11-59**	**30-64**	**18-40**	**6-21**	**31-105**
Bhimtal[j]	**India**	**13-20**	**47-71**	**26-42**	**34-60**	**45-178**	**42-73**
Sattal[j]	**India**	**48-80**	**9-28**	**57-80**	**20-101**	**62-80**	**26-47**
Naukuchiatal[j]	**India**	**41-87**	**12-47**	**26-51**	**80-120**	**48-73**	**66-159**
Crustal Avergae[k]		25	100	75	55	12.5	70
Upper Crust[k]		10	35	20	25	20	71
Carbonate Rocks[l]		0.1	11	20	4	9	20
Average Shale[l]		19	90	68	45	20	95

a- van Griethnysen et al. 2005; b- Szymanowska et al. 1999; c- Yu et al.- 2001; d- Sprenger and McIntosh 1989; e- Irabien and Velasco- 1999; f- Carroll et al. 2002; g- Mortimer and Rae 2000; h- Panda et al. 1995; i- Tessier et al. 1985; j- Present Study; k- Taylor and Mclennan 1985; l-Forstner and Wittmann, 1983

The metals enter the lake through the weathering of the catchment rocks (Ramesh et al. 1999). The manganese concentration (Table 3.5; Fig. 3.5) is almost similar to that of the average carbonate rock (Table 4.4). The trace metal (Table 4.3 A; Fig. 4.4) concentration of the Nainital 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 (Table 4.3 A; Fig. 4.4) is due to reduction of iron and manganese oxides and simultaneous release of these metals into the interstitial water (Gambrell et al. 1991; Carroll et al. 2002; 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 concentration of the trace metals in the Bhimtal lake is much less than the average shale concentration, except for copper and lead (Table 4.3 B; Fig. 4.4), which are added to lake systems through vehicular pollution (Sparks, 2005).

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 the lakes are 50mm, 48mm, 40mm in the Nanintal, Bhimtal and Sattal Lakes (Choudhary, 2008) and 30mm in Naukuchiatal Lake (Das, 1994) respectively. The increasing concentration of the metals from depth to the surface shows that, there is increasing pollution in and around the lakes. The metals copper, zinc, nickel and lead in the Nainital Lake (Table 4.3 A; Fig. 4.4) show maximum concentration up core. The Bhimtal Lake shows almost constant concentration of metals below 5-10cm. The high concentration of metals in the top 10cm may be due to the rapid industrialization taking place in and around the lake. The Sattal and Naukuchiatal Lakes (Table 4.3 C, D; Fig. 4.4) show high fluctuations in the metals concentration through out the core irrespective of the metals. 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,

$$I_{geo} = \ln [C_n / (1.5 \times B_n)] \quad (4.6)$$

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 0-6, 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- moderately contaminated nature throughout the core indicating vehicular pollution. The metal chromium and nickel with moderately contaminated (Table 4.5) 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 (Table 4.5) nature of the sediments. All other lakes show uncontaminated nature for almost all metals except, cobalt in Sattal and Naukuchiatal, showing uncontaminated to moderately polluted (Table 4.5) character and lead in Bhimtal and Naukuchiatal showing uncontaminated- moderately polluted to moderately polluted nature.

Table 4.5 Geo-accumulation (I_{geo}) index of the metals in the lake sediments

Metal	Nainital	Bhimtal	Sattal	Naukuchiatal
Cobalt	Strongly Contaminated	Uncontaminated	Uncontaminated - Moderately Contaminated	Uncontaminated - Moderately Contaminated
Chromium	Moderately Contaminated (0-15cm) / Uncontaminated - Moderately Contaminated (15-32cm)	Uncontaminated	Uncontaminated	Uncontaminated
Nickel	Moderately Contaminated (0-15cm) / Uncontaminated - Moderately Contaminated (15-32cm)	Uncontaminated	Uncontaminated	Uncontaminated
Copper	Moderately Strongly Contaminated (0-15cm) / Moderately Contaminated (15-32cm)	Uncontaminated	Uncontaminated	Uncontaminated-Moderately Contaminated
Lead	Uncontaminated-Moderately Contaminated	Moderately-Strongly Contaminated (0-15cm) / Moderately Contaminated (15-28cm)	Moderately Contaminated	Uncontaminated-Moderately Contaminated
Zinc	Moderately Contaminated	Uncontaminated	Uncontaminated	Uncontaminated

4.4.2.2 Metal Fractionation

4.4.2.2.1 Iron

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 iron present in the aquatic environment settles down as the amorphous iron oxy-hydroxides, and dissolution takes place at the anoxic sediment-water interface. 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). Previous studies on the behavior of iron oxides in the anoxic environment (Davison 1993) indicate that all of the iron present as iron oxide do not dissolve and remain as the oxides even at high anoxic condition. The high concentration of iron in the oxide fractions (amorphous, crystalline and manganese bound fractions) in the Kumaun Himalayan lakes may be due to the above discussed processes. The dissolution of iron oxides is predominantly dominated by microbial activity at high anoxic condition (Eh> -130mv) (Guo et al. 1997). In the presence of sulfides, the dissolution of these oxides enhances the formation of iron sulfides, mostly of mackinawite (Huerta- Diaz and Morse, 1990, 1992; Morse, 1991, 1994; Coopper and Morse, 1998; Morse and Luther, 1999). Iron abundance in different fractions in the lakes are,

Nainital (Fig. 4.5A)

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

Bhimtal(Fig. 4.6A)

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

Sattal(Fig. 4.7A)

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

Naukuchiatal(Fig. 4.8A)

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

4.4.2.2.2 Manganese

Manganese occurs as carbonate at lower anoxic/suboxic condition and sulfides at higher anoxic condition (Davison, 1993). The dominance of the carbonate fraction may be due to the precipitation of manganese as rhodochrosite or along with calcite (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 (Davison, 1993). The dissolution of manganese gets enhanced in the presence of organic matter (Davison, 1993), causing its release into the water column. The released manganese gets adsorbed onto the settling clay particles and mineral surfaces and also gets adsorbed onto the carbonates. The manganese oxides which have escaped dissolution might have transformed to the most stable forms with aging at depth. Manganese abundance in different fractions in the sediments are,

Nainital (Fig. 4.5B)

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

Bhimtal (Fig. 4.6B)

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

Sattal (Fig. 4.7B)

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

Naukuchiatal (Fig. 4.8B)

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

4.4.2.2.3 Chromium, Nickel and Cobalt

Chromium, cobalt and nickel show similar characteristics in chemical forms. They prefer manganese and iron oxy-ohydroxide forms, over the other forms (Scholz and Neumann, 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. This is because nickel has an affinity to form sulfides (Jacobs et al. 1985). These metals have been found to be associated with the carbonates and organic matter at high anoxic condition (Yu et al. 2001).

(A) Cobalt

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, followed by the organic fractions (Koretsky et al. 2006). At lower Eh, cobalt prefers to associate with the oxides and organic matters. Cobalt adsorbed on to the amorphous iron oxides on aging, converts to crystalline iron oxides, and the cobalt bound to the manganese oxides are released into solution, whenever the manganese oxides are reduced at high anoxic condition. The released cobalt in the presence of organic matter complexes with the mineral surfaces forms mono-sulfides and settles down (Davison, 1993). The cobalt association in the lakes are,

Nainital (Fig. 4.5D)

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

Bhimtal (Fig. 4.6D)

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

Sattal and Naukuchiatal (Fig. 4.7& 4.8D)

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

(B) Chromium

Chromium may enter an aquatic system anthropogenically through the landfills, scrapheap in the form of oxides and organic and inorganic ligands. Chromium, generally, is sorbed 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 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; Carroll et al. 2002; 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). The association of chromium to different chemical forms in the lake sediments is,

Nainital (Fig. 4.5C)

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

Bhimtal (Fig. 4.6C)

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

Sattal (Fig. 4.7C)

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

Naukuchiatal (Fig 4.8. C)

Residual> Organic> Carbonate> Amorphous iron oxide> Manganese oxide> Exchangeable> Water dissolvable> Crystalline iron oxide

(C) Nickel

In general, nickel is found to be present in the organic and residual fraction (Panda et al. 1995; Stalenes 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 gets 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 correlation coefficient indicates that cobalt shows negative correlation with nickel in almost all the fractions (water dissolvable, exchangeable, crystalline iron oxide and organic fraction), in all the lakes indicating a possible competition between these elements for the sorption sites. These metals also show negative correlation in the carbonate fraction, indicating their competition for carbonate sorption sites in the sediments. The association of nickel in the lake sediments are,

Nainital (Fig. 4.5E)

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

Bhimtal (Fig. 4.6E)

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

Sattal (Fig. 4.7E)

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

Naukuchiatal (Fig. 4.8E)

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

4.4.2.2.4 Copper, Lead and Zinc

These metals are chalcophilic in nature; copper and zinc are micronutrients and get settled along with the readily oxidisable organic matter. These metals at high anoxic conditions, generally are associated with the carbonate and organic matter and are not affected by the redox conditions (Yu et al., 2001).

(A) Copper and (B) Zinc

Copper may enter and aquatic system through break linings, metal finishing, manure, pesticides, wood treatment; lead through automobile refineries sewage sludge, pesticides and zinc through sewage sludge, pesticides (Sparks, 2005). Under high anoxic conditions, these metals are bound to the carbonate and sulfides (Davison, 1993). This is a major reason for the dominance of the carbonate fraction in the highly anoxic Nainital lake sediments compared to the other lakes, where they are relatively less anoxic. These metals generally show high concentration in the organic and oxides phases. The high concentration of copper and zinc in the organic fraction may be due to their affinity towards the organic substance and their ability to form complexes (Guo et al. 1997; Koretsky et al. 2006). As these metals are less affected by the redox changes, they also occur in higher concentrations in the oxide fractions.

The associations of these metals to various chemical fractions in the lake sediments are,

Copper

Nainital (Fig. 4.5F)

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

Bhimtal (Fig. 4.6F)

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

Sattal (Fig. 4.7F)

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

Naukuchiatal (Fig. 4.8F)

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

Zinc

Nainital (Fig. 4.5H)

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

Bhimtal (Fig. 4.6H)

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

Sattal (Fig. 4.7H)

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

Naukuchiatal (Fig. 4.8H)

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

(C) Lead

Lead behaves similar to copper and zinc in the Nainital lake sediments, and generally occurs as carbonates in aquatic systems. The high concentration of lead in residual fraction shows its natural origin. The dominance of carbonates and the oxides in the sediments shows precipitation of lead from the overlying water column. The associations of lead to various chemical fractions in lake sediments are,

Nainital (Fig. 4.5G)

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

Bhimtal (Fig. 4.6G)

Easily exchangeable> Amorphous iron oxide> Organic

Sattal and Naukuchiatal

Easily exchangeable

Iron and manganese are the two elements which determine the fate of the metals in the sediments. Hence, the correlation of iron and manganese (Table 4.6) with other elements were studied to understand the association of these elements in different fractions using SPSS10. The behavior of elements with iron and manganese varies widely in different fractions.

Table 4.6 Correlation coefficient of metals in different fractions

(A) Nainital

	Positive		Negative	
	Good Correlation	Very Good Correlation	Good Correlation	Very Good Correlation
Water dissolvable	**Co**- Ni, Cu; **Ni**- Zn, Cu			
Easily Exchangeable	**Cr**- Mn	**Cu**-Co, Cr, Ni, Mn, Zn **Co**- Ni, Mn, Cr, Zn **Ni**- Mn, Zn, Cr **Mn**- Zn		
Carbonate	**Cr**- Fe, Ni, Zn, Pb **Fe**- Ni	**Co**- , Cr, Mn, Ni, Pb, Zn, Fe, Cu **Cu**- Cr, Fe, Mn, Ni, Pb, Zn **Fe**- Mn, Pb, Zn **Mn**- Ni, Pb, Zn **Ni**- Pb, Zn **Pb**- Zn		
Manganese oxide	**Cr**- Co, Mn **Ni**- Pb	**Co**- Mn **Cr**- Cu, Ni, Pb		
Amorphous iron oxide	**Co**- Mn	**Cu**- Zn		
Crystalline iron oxide	**Co**- Mn, Ni, Zn **Cr**- Ni **Cu**- Zn **Mn**- Fe, Ni			
Organic	**Co**- Fe, Mn **Mn**- Fe, Zn			
Residual	**Co**- Ni, Zn **Fe**- Pb **Zn**- Ni	**Co**- Mn		

Good Correlation: 0.6- 0.8; Very Good Correlation: >0.8

(B) Bhimtal

	Positive		Negative	
	Good Correlation	Very Good Correlation	Good Correlation	Very Good Correlation
Water dissolvable	**Mn** -Zn	**Co**- Mn, Zn **Cr**- Cu	**Cr**- Co, Zn, Mn **Cu**- Zn	
Easily Exchangeable	**Cu**- Cr, Ni **Fe**- Mn, Zn	**Cr**- Ni	**Cr**- Fe, Zn **Cu**- Fe, Mn **Fe**- Ni	**Cr**- Mn **Ni**- Mn
Carbonate	Co- Ni	Fe- Co, Ni **Cr**- Cu, Mn **Zn**- Ni	**Co**- Cr, Cu **Fe**- Cr, Mn **Mn**- Cu, Ni, Zn	**Co**- Mn **Cu**- Fe
Manganese oxide	**Co**- Ni **Cu**- Cr, Pb, Zn **Zn**- Cr, Pb **Mn**- Ni **Pb**- Fe	**Co**- Mn **Cr**- Pb		
Amorphous iron oxide	**Co**- Ni, Cu **Cr**- Cu	**Co**- Mn **Ni**- Cr, Cu		
Crystalline iron oxide	**Co**- Mn, Zn **Cu**- Mn, Zn	**Cu**- Co		
Organic	**Mn**- Fe, Pb	**Co**- Ni, Zn **Cu**- Mn **Ni**- Zn	**Cu**- Co, Ni, Zn	
Residual	**Mn**- Fe, Ni, Zn **Cr**- Co, Ni, Zn	**Fe**- Ni, Zn **Ni**- Zn		

Good Correlation: 0.6- 0.8; Very Good Correlation: >0.8

(C) Sattal

	Positive		Negative	
	Good Correlation	Very Good Correlation	Good Correlation	Very Good Correlation
Water dissolvable	**Mn-** Co, Ni, Zn **Fe-** Ni	**Co-** Ni, Zn **Ni-** Zn		
Easily Exchangeable	**Cu-** Fe	**Co-** Cu, Fe, Zn **Cr-** Cu, Fe, Zn **Cu-** Ni, Zn **Fe-** Ni, Zn **Ni-** Zn		
Carbonate	**Co-** Fe	**Co-** Cr, Cu, Ni, Zn **Cr-** Cu, Ni, Zn **Cu-** Ni, Zn **Ni-**Zn		
Manganese oxide	**Co-** Fe **Zn-** Cr, Cu, Ni **Fe-** Mn	**Co-** Mn **Cr-** Cu	**Co-** Cr, Cu **Cu-** Mn	
Amorphous iron oxide	**Co-** Cr, Mn, Ni **Cr-** Cu, Mn, Ni	**Co-** Cu		
Crystalline iron oxide	**Zn-** Mn			
Organic	**Mn-** Co, Fe, Zn		**Cr-** Cu	
Residual	**Fe-** Cr			

Good Correlation: 0.6- 0.8; Very Good Correlation: >0.8

(D) Naukuchiatal

	Positive		Negative	
	Good Correlation	Very Good Correlation	Good Correlation	Very Good Correlation
Water dissolvable	**Co-** Cr, Fe **Ni-** Cr, Fe	**Co-** Cu, Ni **Cr-** Cu, Fe **Cu-** Fe, Ni **Mn-** Zn		
Easily Exchangeable	**Co-** Fe, Ni **Cu-** Fe	**Cr-** Cu, Fe, Ni Ni Fe	**Cu-** Mn	
Carbonate	**Co-** Cr	**Ni-** Co, Cr	**Cu-** Zn, Fe **Ni-** Mn	**Cr-** Mn
Manganese oxide	**Co-** Cr, Cu **Cr-** Ni	**Co-** Fe, Ni, Zn **Cr-** Cu, Fe, Zn **Zn-** Fe, Ni, Cu **Cu-** Fe, Ni **Fe-** Ni		
Amorphous iron oxide	**Cr-** Fe, Ni **Cu-** Ni, Zn **Ni-** Fe, Zn	**Co-** Ni, Zn **Cr-** Cu		
Crystalline iron oxide	**Cu-** Fe **Mn-** Zn			
Organic	**Co-** Mn **Fe-** Cr, Ni	**Fe-** Mn		
Residual	**Co-** Cr, Cu **Cr-** Cu, Fe **Cu-** Zn			

Good Correlation: 0.6- 0.8; Very Good Correlation: >0.8

All the metals show very good - good positive correlation with iron in the carbonate phase (Table 4.6). At high anoxic conditions, the metals released from the metal oxides prefer to bond with the carbonate phase (Yu et al. 2001). The metals on the other hand show very different behavior in the other lakes. Cobalt and nickel show good positive correlation (0.6-0.8) with manganese (Table 4.6) in the Sattal and Naukuchiatal, as these metals prefer to bind with the manganese oxides. The positive correlation of chromium with iron in the residual fraction indicates chromium is chiefly introduced into these lakes from catchment lithology. The positive correlation of chromium (Table 4.6) with iron in the oxide and organic fraction is due to its preference for the iron oxides by formation of ligands, where as copper and zinc (Table 4.6) show positive correlation with iron in the exchangeable fraction. This may be due to the adsorption of the metals onto the surface sites as organic complexes. Overall, the carbonate fraction in the Nainital shows very good positive correlation with the metals and in the other lakes, the water dissolvable, exchangeable, manganese oxide and amorphous iron oxide fractions shows good correlation, especially in the Naukuchiatal Lake.

The metals also show different behavior with manganese in the lake sediments. Cobalt shows very good - good positive correlation (Table 4.6) with manganese in almost all the fractions. This shows its preference for manganese oxide than other phases. Chromium shows good negative correlation (Table 4.6) with manganese in the water dissolvable and exchangeable fraction, which may be due to the release of chromium from oxides in anoxic condition. Chromium also shows good positive correlation with manganese in the carbonate, amorphous iron oxide, and crystalline iron oxide fraction in Nainital and Bhimtal lake sediments and in amorphous iron oxide fraction in Sattal and carbonate fraction in Naukuchiatal. Nickel shows negative correlation (Table 4.6) with manganese oxide fraction in Nainital, residual fraction in Bhimtal and crystalline iron oxide fractions in Bhimtal, Sattal and Naukuchiatal. In general these metals show good correlation with manganese, indicating preferential bonding with manganese in sediments. Copper shows good positive correlation (Table 4.6) in the carbonate fraction in the Nainital and Bhimtal, but negative correlation in the other two lakes. Zinc shows negative correlation in the iron oxide fraction and positive correlation in the organic fractions in the Bhimtal, Sattal and Naukuchiatal lakes. These metals do not show any specific correlation with the manganese in these lakes.

4.5 Summary- Metals

The metals in the lakes show the major influence of the source rocks. The metal concentration in the water column shows that the Nainital Lake is highly polluted as compared to the other lakes. The high concentration of aluminum, manganese in the interstitial water column and the metals in the Sattal, and Naukuchiatal may be because of the dissolution of these metals from metal oxides. The high concentration of the metals in the organic and manganese and amorphous iron oxides also support the possible dissolution of these metals from oxides. The metal concentrations in the Nainital lake sediments are much less than the average shale value, but are very high compared to the metal concentration of common carbonate rocks. The other lakes show metal concentrations similar to that of the metals in the average shale. The general increasing up core trend of the metals in the Nainital and Bhimtal lakes indicate increasing anthropogenic activity in the catchment area and the absence of any trend in the Sattal and Naukuchiatal shows that, these lakes are least affected by anthropogenic activities. The I_{geo} values of metals in the lakes show that the metal lead shows unpolluted nature in the Nainital lake sediments, where as they show moderately polluted nature in the Bhimtal and Naukuchiatal lakes. The metal cobalt shows polluted nature in all the lakes. The metals chromium, nickel show moderately polluted nature in the Nainital lakes, indicating vehicular pollution. The moderate to strong polluted nature of copper and zinc in the Nainital lakes, indicate the influence of domestic wastes and agricultural wastes discharged in to the lakes. The Nainital lake sediments show the influence of carbonates, as the metals in the oxides and organic matter bound phases get reduced in the high anoxic condition and get adsorbed on to the carbonate phases. The metals in the other lakes show the influence of organic matter and mostly are present in the oxide and organic phases. The high concentration of metals in the residual fraction in the Sattal and Naukuchiatal shows their natural source/ input from the catchment area.

Chapter 5

LAKE PROCESSES AND REMEDIATION

A gist of the various lake processes in the study area, diffusive flux and suggested remedial measures are discussed here.

5.1 Chemical Processes in the Lakes

The various lake processes in brief are shown in the box model (Fig. 5.1). The chemistry of the lakes 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 aluminum and their saturation levels support possible formation of iron-manganese/aluminum 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 decrease in concentration of phosphorus may also be due to co-precipitation with the calcium carbonate and iron-manganese oxy-hydroxides (Stumm and Sulzberger, 1992).

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 (Morse and Luther, 1999),

$M(H_2O)_5(Cl)^+ + HS^- \rightarrow M(H_2O)_5(HS)^- + Cl^-$ (Bi-sulfide complexation) - where, M denotes the metal ion.

The presence of significant amounts of iron oxides and sulfides act as major regenerators of these elements into the water column. The mono-sulfides which are formed in the anoxic layer get oxidized due to denitirfiaction (Pauwels et al. 2000; Schwientek et al. 2008) and microbial processes (Lovely, 1995). The dissolution of sulfate minerals such as gypsum in the anoxic layer results in increasing sulfate concentrations in the interstitial waters.

Manganese released due to the decomposition of organic matter and also by the reduction of sulfides in the anoxic layer may be scavenged by the carbonates in the sediments (in Nainital). The iron sulfide that is reduced by the manganese oxide forms iron-hydroxides (Canfield et al. 1993). Silica which is used as a nucleus by the metal complexes shows reduced concentration with depth, indicating possible precipitation of the amorphous silica in the bottom sediments. The high concentration of silica and sulfate in the interstitial water column may act as a possible competitor for the sorption sites of iron oxy-hydroixde, as silica is the main component required for the formation of ferrihydrite, and sulfide for the formation of mackinawite (amorphous iron sulfide). However, sulfidisation of zinc and cobalt are faster than that of iron, thus preventing the pyritization of iron (Davison 1993). The formation of iron ferrihydrite acts as a possible scavenger of the metals in the sediments. All the oxides formed are not reduced even at high anoxic condition, resulting in the dominance of the oxide phase in the sediments.

Phosphorous is dominantly associated with the carbonate flour apatite, indicating carbonate as the chief sequester of these elements. The dissolution of iron oxides in the anoxic layer may be a potential source for phosphorous in the interstitial water. The sediments in the Nainital lake act as a good scavenger of phosphorous from the water; the high concentration of phosphorus in the water may also be due to the increased anthropogenic activity around the lake.

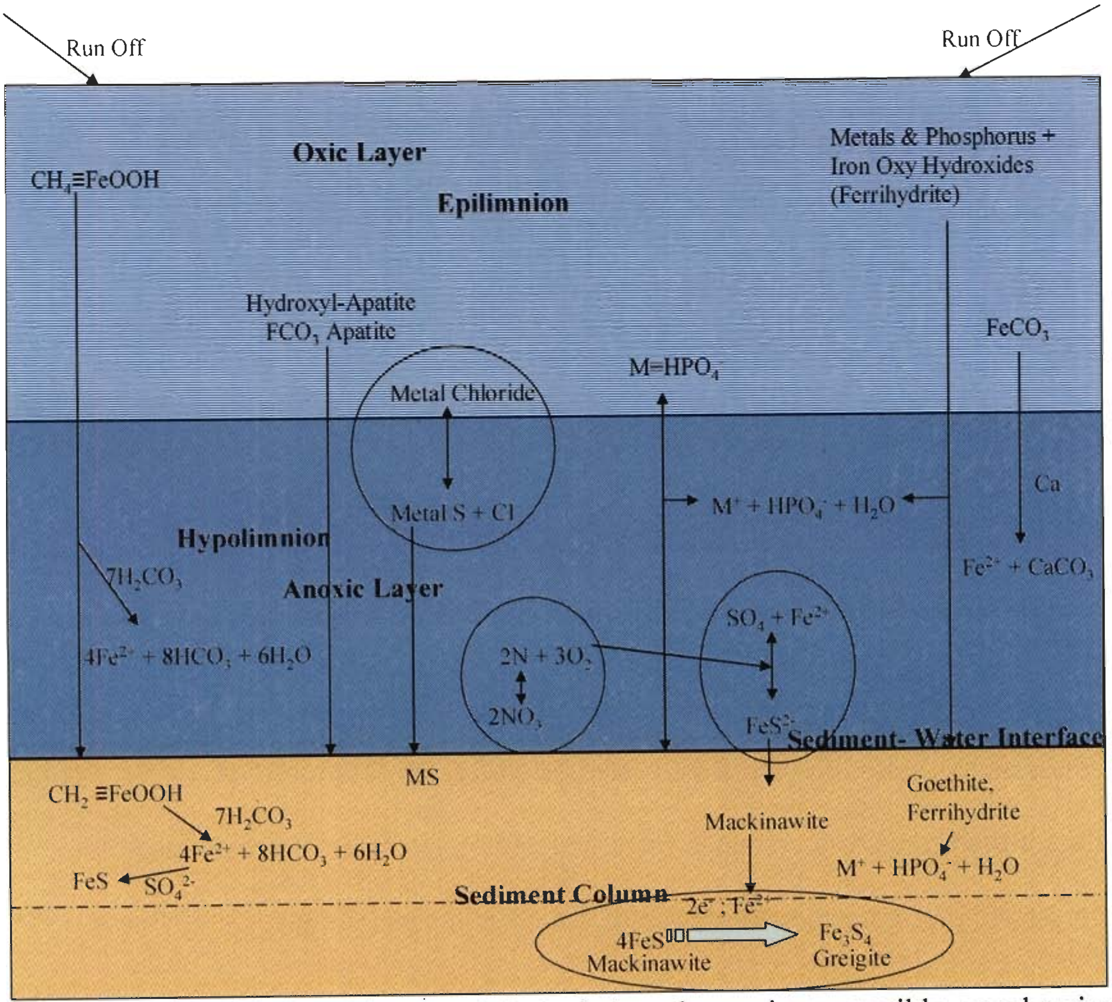


Figure 5.1 An idealised box model depicting the various possible geochemical processes in the Kumaun Himalayan Lakes. The limnetic layers are drawn arbitrarily.

5.2 Diffusive Flux of Metals in Nainital Lake

The sediments are repositories for the materials from the lake catchment and in-lake processes. The flux of constituents from the sediments into the water, and vice versa is an important controlling factor of lake compositions. The flux of the metal at the sediment-water interface and along depth gives an idea about the physico-chemical processes taking place at the lake bottom. The diffusive flux of the elements in the Nainital Lake has been estimated to understand the diffusivity of the elements to the overlying water column. The diffusive flux was calculated using the formula (Stumm and Morgan, 1996),

$F= \Phi\ [-D.\ dc/dz + U\ (K+1)\ C]$ Where, F= Flux; Φ= Porosity (Data for the Nainital lake obtained from Choudhary, 2008); D= Diffusion Coefficient (present study); dc/dz= Concentration gradient; U= Sedimentation rate (Data for the Nainital lake obtained from Choudhary, 2008); K= Distribution coefficient (From Last and Smol (Ed.), 2001); C= Dissolved concentration.

Table 5.1 Metal diffusion flux (mg $cm^{-2}\ yr^{-1}$) at three different depths in Nainital lake sediments

Depth (cm)	Fe	Mn	Pb	Cu	Ni	Zn
0-5	9.29	0.045	0.00015	0.012	0.054	0.021
5-10	9.60	0.14	0.000012	0.012	0.056	0.022
15-20	6.86	0.023	0.00011	0.014	0.041	0.044

The positive flux of the metals in the Nainital lake sediments shows the dominance of release of the metals from the sediments (Blasco et al. 2000). The high flux of the metals may be due to increased anthropogenic activities, in addition to the diagenetic processes in operation in the lake sediments (Carignan and Nriagu, 1985). The flux of the redox sensitive elements (Fe, Mn, Ni) are higher compared to the less sensitive elements (Cu, Zn, Pb).

5.3 Remediation Methods for Phosphorus and Metals

The remediation of the aquatic system becomes an important task after the study on the toxicity or bioavailability of the nutrients and metals in the sediments and water column are completed. The speciation/ fractionation study of the nutrients and metals helps us to understand the nature of these elements in the sediments and to suggest appropriate remediation methods. The remediation technologies involve two different approaches, in-situ, which include, amendments (Shrestha et al. 2003; Raicevic et al. 2005, 2006), sand caps (Theofanis et al. 2001) and phytoremediation (Battacharyra et al. 2006) and ex-situ, which include, washing, electro-chemical and floatation methods (Peng et al. 2008). The in-situ method mainly involves the immobilization of metals from the sediment particles by enhancing adsorption, complexation and precipitation. The ex-situ methods involve the removal of mobile metals from the sediment particles using chemical, physical and biological methods (Peng et al. 2008). The in-situ methods are cheaper and hence are widely used. However, the main disadvantage with the in-situ method is that it does not remove the metals from the sediments and can be remobilized with changes in physico-chemical conditions.

5.3.1 Recommended Remediation - Kumaun Himalayan Lakes

The Kumaun Himalayan Lakes show almost unpolluted- moderately polluted characteristics in sediments. The usage of in-situ remediation will be a good method for removal of metals from the water column and immobilization of metals from the sediments.

5.3.1.1 Phosphorus Remediation

The Nainital Lake shows high concentration of phosphorus in the water column but low concentration in the interstitial waters, since they are precipitated as carbonate flour apatite (i.e. in calcium carbonate bound and biogenic apatite fraction). Driscoll et al. (1993) observed that oxygenation (aeration) of the lake system results in the decrease in pH and increases the dissolution of calcium phosphate. Thus, the oxygenation of the water column in due course of time may result in the dissolution of calcium phosphate with decrease in pH and increase the phosphorus concentration further in the water column. The usage of alum-amendment may be a good choice as the addition of these amendments will not cause much change in pH or Eh. The addition of alum helps in reducing the release of phosphorus from the sediments and also reduces the phosphorus concentration in the water column. However, a temporary change in phosphorus levels in the sediments may alter the requirements of organisms and hence need to be studied for its suitability before implementing such artificial methods.

5.3.1.2 Metal Remediation

Most of the metals in the Nainital Lake sediments are associated generally with the carbonate phase. The carbonate phase which is very much susceptible to the pH changes, can release metals with slight change in the pH condition. Hence, a proper remediation method should be adopted to reduce the metal concentration from the water without changing the pH and Eh of the lake. A good and possible method of remediation should be usage of the amendments which can precipitate the metals from the water column. A better method of remediation is the usage of two or more methods, which can effectively reduce the metal and phosphorus concentration from the water column. The usage of sand cap and amendments methods together will be more effective than a single usage of amendments. The sand cap which covers the sediments may prevent the release of metals into the water column, and the amendment used at the same time may precipitate phosphorus and metals from the water column.

The other three lakes (Bhimtal, Sattal, and Naukuchiatal) are less polluted in terms of both phosphorus and metals. However, the metals in these lakes are generally bound with the oxide and organic phase, which are very much sensitive to changes in Eh condition. The sand cap method is a good remediation method as this method reduces the sediment-water interaction. This may reduce the dissolution of oxides and organic matter in sediments and, thereby, release of metals from sediments will also be reduced.

Chapter 6

CONCLUSIONS

- The water composition, Ca+Mg: Na+K, CIA and Al_2O_3/K_2O show the major influence of carbonate rock weathering in water chemistry of the lakes. The increasing concentration of chloride in the anoxic layer shows formation of mono- and bi-sulfides in the anoxic condition. The increasing concentration of ammonia shows denitrification process. The high dissolved sulfate concentration in the Nainital Lake may be due to the oxidation of mono- and bi- sulfides.
- The Nainital Lake also shows high dissolved phosphate compared to the other three lakes. Dissolved phosphate precipitates from the water column as carbonate flour apatite, resulting in low concentration in the interstitial water. The high concentration of phosphorus in the sediments of Nainital and Sattal lakes may be due to the weathering of apatite bearing calcareous rocks in the catchment.
- Phosphorus in sediments prefers to bind with calcium, evidenced from high abundance (>90%) of phosphorus in the calcium carbonate, biogenic apatite fraction. The negative correlation between biogenic silica and sulfur shows that these elements compete for the iron oxide sorption sites with phosphorus.
- The heavy metal concentration show that the Nainital Lake is more polluted compared to the other three lakes. The increasing concentration of metals in the Tallital end of the lake may be due to the presence of a bus station, discharging vehicular pollution waste in to the lake. The metal oxides dissolve at the anoxic layer resulting in the high concentration in water. The high

concentration of manganese at the interstitial water may be due to the enhanced dissolution of manganese in the presence of organic matter. The low concentration of manganese in the interstitial water column is Nainital Lake is because of its precipitation with the carbonates in the lake.

- The total metal concentration shows high concentration of copper, zinc, chromium zinc nickel in the Nainital Lake, caused mainly by discharging domestic and industrial wastes and increased vehicular pollution. The geo-accumulation index also shows that the metals copper, chromium, nickel, cobalt show moderate-strong contamination in the Nainital Lake.
- The metals behave differently in the different lakes. The metals in high anoxic condition prefer association with the carbonate phase in the Nainital lake sediments. The metals cobalt and chromium prefer binding with manganese oxide, whereas nickel and zinc prefer residual and organic fraction.
- The overall chemical processes in the lakes show precipitation of metals and phosphorus with oxy-hydorixes. These metals are released onto the water column with reduction in the anoxic layer. The metals in the Nainital Lake are mainly sequestered as carbonate and in the other three lakes as organic complexes and oxide minerals, where as phosphorus is sequestered as carbonate in all the lakes.
- The diffusive flux in the Nainital Lake shows that the metals are released onto the water column. This may be due to the digenetic processes taking place in the lake sediments, although increasing anthropogenic activities also can not be ruled out.
- The possible remediation suggested for removing excess metals and phosphorus from the Nainital Lake includes sand capping and suitable

amendments such as alum for phosphorus. The other three lakes are relatively unpolluted and hence, may be preserved as such.

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