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ORIGINAL PAPER

Biogeochemical records of paleoenvironmental changes in Nainital Lake, Kumaun Himalayas, India

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Abstract Rapid urbanization and increased tourism around Nainital Lake in the Kumaun Himalayan region in north India has raised concerns about sediment and water pollution. Lead-210 dated sediment cores from the lake represent ~95 years of accumulation and yield a mean sedimentation rate of ~4.7 mm year^{-1}. Total organic carbon (TOC), percent N and S and their atomic C/N and C/S ratios, stable isotopes (δ^{13}C, δ^{15}N, and δ^{34}S), and specific biomarkers (*n*-alkanes and pigments) were measured in the core. Organic matter is primarily derived from in-lake algal production and TOC flux varies from 1.0 to 3.5 g m^{-2} year^{-1}. Sediments are anoxic (Eh −328 to −187 mV) and have low (0.10–0.30 g m^{-2} year^{-1}) N, but high (0.37–1.0 g m^{-2} year^{-1}) S flux. Shifts in δ^{13}C, δ^{15}N, and δ^{34}S suggest in-lake microbial processes dominated by denitrification and sulfate reduction. The sediments are dominated by short-chain hydrocarbons with low Carbon Preference Index values. The pigments indicate a gradual shift to cyanobacterial domination of the phytoplankton community in recent years. Despite an increase in external input of nutrients, the trophic state of the lake has remained largely unchanged, and the perceived human-induced impacts are limited.

Keywords Lake sediments · Paleoproductivity · Organic matter · Stable isotopes · Hydrocarbons · Pigments

Introduction

Environmental changes leave distinct geochemical signals in sediments, which can be used to infer paleoecological and paleoenvironmental histories in lacustrine environments (Schelske and Hodell 1991; Bernasconi et al. 1997; Tenzer et al. 1999; Routh et al. 2004). Organic matter (OM) characteristics, trace elements, and stable C and N isotope compositions are widely used as indicators of watershed disturbance and primary productivity changes (for reviews see Meyers and Lallier-Vergès 1999; Boyle 2001; Meyers 2003). Although some of these paleoenvironmental proxies are relatively conservative, others may be influenced by sediment–water interactions, biological processes, and anthropogenic activities. Nevertheless, these geochemical proxies can provide reliable records of environmental change in lakes over multi-million-year periods, even for

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sediments in which only a small fraction of OM is preserved (Meyers 1994; Meyers et al. 1995).

Sediment OM in lacustrine environments provides information about the origin of OM and the kinds of biota that produce it. This information provides a better understanding of various biogeochemical processes, trophic state shifts, and natural and/or human-induced effects in lacustrine environments (Meyers 1997; Tenzer et al. 1999; Meyers 2003; Das et al. 2008; Routh et al. 2008; Choudhary et al. 2008). Notably, periods of high sedimentation rate and greater primary productivity can preserve evidence of processes that affect OM delivery and burial in lacustrine sediments. Hence, lakes offer special opportunities to study the response of sediment geochemistry to environmental changes on short- (annual to decadal), and even long-term (centennial to millennial) time scales.

Lake Nainital, situated in the Kumaun Himalayan region of northern India, has been affected by urban development. In particular, water quality has deteriorated over the years (Ali et al. 1999; Gupta et al. 1999; Chakrapani 2002). We used various paleolimnological proxies to explore the recent history of environmental changes in Lake Nainital. Our multiproxy approach included elemental ratios (C/N, C/S), isotope signatures (C, N, and S), and specific biomarkers (hydrocarbons and pigments), and was used to characterize the OM in sediments. The results were related to nutrient dynamics, paleoproductivity, and probable anthropogenic effects. To the best of our knowledge, this is one of the first such studies in a Himalayan lake system. Hence, useful generalizations can be drawn based on the sediment OM records. Further, the study illustrates the potential of these types of proxy-based analyses to reconstruct trophic state changes in lakes in areas where hardly any water column data are available. These concepts can be extended to other lacustrine systems to understand biogeochemical processes, particularly the effects of human-induced activities in the catchment.

Study area

Nainital Lake (latitude 29°24′N, longitude 79°28′E) is situated at the center of Nainital city in Uttarakhand state, India (Fig. 1). The crescent-shaped lake, discovered in 1841 AD, is a warm monomictic, hyper-eutrophic water body situated at an altitude of 1,937 m (Pant et al. 1980; Singh and Gopal 1999; Gupta et al. 1999). The lake is 1.4 km long, 0.45 km wide, 27.3 m deep, and 0.46 km^2 in surface area. The catchment area is 4.9 km^2, of which 48.4% is covered by forests (oak and cypress), 18.3% is barren, 19.3% is human settlements, and 10.4% is water body. The catchment is home to over 700 plant species and 200 species of birds (Singh et al. 2001). The lake is the main source of water supply for the local population (~40,000 inhabitants; Singh and Gopal 1999). The average annual rainfall in the basin is 2,271 mm, and summer and winter temperatures average around 25°C and 10°C, respectively (Pant et al. 1980). The lake remains thermally stratified for 7–9 months of the year (March–October; Kumar et al. 2001).

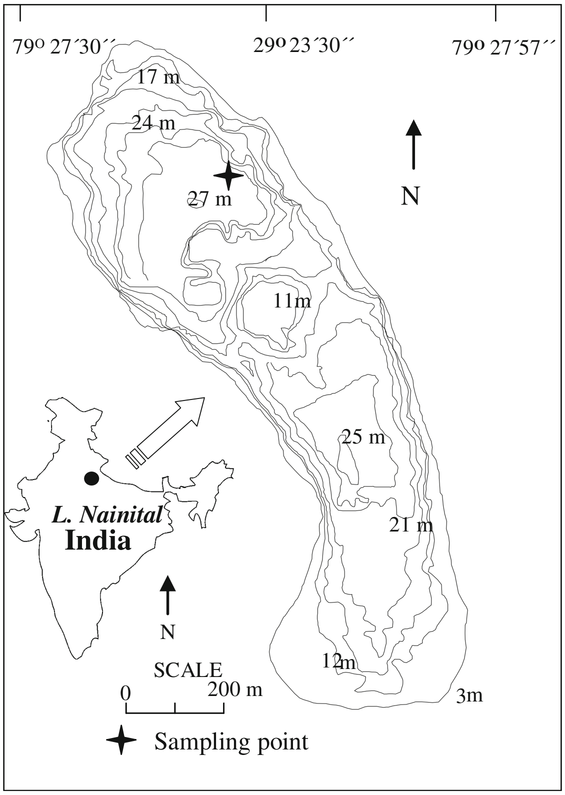


Fig. 1 Bathymetric map of Lake Nainital showing core location (modified from Nainital Development Authority)

There are 24 open drains in the catchment area. Nine of these drains are permanent (Das et al. 1995) and carry domestic waste, including town sewage, run-off water, and eroded sediments into the lake (Pant et al. 1980). The lake is essentially a flow-through system, with substantial groundwater inflow and seepage. The hydrologic budget of the lake shows that most of the lake water owes its origin to surface run-off (25%), sub-surface inflow (43%), and direct precipitation (15%) (Singh et al. 2001; Kumar et al. 2001). The groundwater age is <14 years and retention time is about 2 years (Kumar et al. 2001; Nachiappan et al. 2002). Isotope studies reveal that the slope of the δ^{18}O–δD water line in Nainital Lake (7.1) is close to the LMWL (7.5), implying that evaporation losses from the lake are insignificant (Nachiappan et al. 2002).

The Lake Nainital basin is made up of folded and faulted rocks of the Krol and Tal Formations (Valdiya 1988). The sub-rotational movements in the fault zone were responsible for blocking the Gaula River in its upper reaches, resulting in the formation of Nainital Lake. The lake is divided into two sub-basins separated by a 100-m wide, transverse underwater ridge, which crops out at depths of 7–20 m. Northeastern Sher-ka-dand-Naina ridge is made up almost exclusively of the Lower Krol Formation and south-western Deopatta–Ayarpatta ridge consists of the Middle and Upper Krol and Tal Formations (Valdiya 1988). The lithology consists of dolomites, argillaceous limestone, marlites, gypsum, and black carbonaceous slates, which are susceptible to extensive physical and chemical weathering (Das et al. 1995; Chakrapani 2002). Because of high tectonic activity, the region is prone to landslides (Valdiya 1988; Kumar et al. 2007). Seven major landslides were reported within the last century (Singh et al. 2001).

The idyllic setting of Lake Nainital attracts many tourists (~300,000–400,000 people annually) during summer (April–August). The population is spread over a small area of 11–12 km^2. Rapid urbanization in the catchment has increased the construction of buildings and roads, and human population has doubled since the 1950s (Singh et al. 2001). This has resulted in high input to the lake of heavy metals, phosphate, and nitrate (Das et al. 1995; Ali et al. 1999; Chakrapani 2002). In fact, several planktonic species commonly considered indicators of eutrophication are widely found in Lake Nainital, e.g., *Microcystis, Anabaena, Chlamydomonas*, and *Clostridium* (Pant et al. 1980). Nutrients such as phosphate, nitrate, and ammonium support luxuriant phytoplankton and algal growth (2.4–37.6×10^6 cells l^{-1}; Sharma et al. 1982; Ali et al. 1999). Previous studies also suggest that recent fish kills are a consequence of long-term anoxia and presence of toxic pollutants in the lake (e.g., Ali et al. 1999; Singh et al. 2001; Nagdali and Gupta 2002). However, these studies do not elucidate the actual source(s) of OM (or pollutants) in the lake, their effect on nutrient dynamics, or in productivity shifts affecting the lake's trophic state.

Methodology

Sediment cores were collected from the deepest part of the lake in December 2004. A gravity corer was used to obtain two relatively undisturbed sediment cores, 55 mm in diameter and 40–45 cm long (NT 1 and NT 2; Fig. 1). Each core was sliced into 2-cm sections in the field and Eh was measured immediately; the samples were packed into airtight plastic bags and refrigerated. Loss-on-ignition (LOI) was measured as described in Heiri et al. (2001). The bulk density of sediments was measured by estimating the water content (heating for 8 h at 105°C) and porosity. Grain size was measured by sieving the sediments.

In one of the cores (NT 1), sedimentation rate was estimated using ^{210}Pb. The measurement of ^{210}Pb was based on the α-measurement of ^{210}Po, which was assumed to be in secular equilibrium with its parent. The procedure involved adding ^{209}Po as a tracer and leaching the sediment sample with aqua regia (Kumar et al. 2007). The residual solid was filtered and treated with HCl. The Polonium nuclides (^{210}Po and ^{209}Po) were deposited on copper disks by adding ascorbic acid in HCl solution prior to alpha counting. The standard counting error was <10% in the upper section of the core and slightly higher in the deeper sections. The supported activity for ^{210}Pb was estimated from the asymptote, which was subtracted from the total ^{210}Pb activity to get the unsupported ^{210}Pb activity, i.e. excess ^{210}Pb (^{210}Pb$_{ex}$). To correct for the effect of sediment compaction, ^{210}Pb$_{ex}$ at each depth was multiplied by the dry density.

In the second core (NT 2), sediments were centrifuged at 10,000 rpm (3,023 *g*) for 30 min to extract the pore-water. Dissolved organic carbon (DOC) concentration was measured with a Shimadzu TOC 5000 analyzer. Reproducibility of duplicate analysis was within ±10%. The sediments were later freeze-dried and used for characterizing the OM. The C and N isotopic compositions of acid-treated samples were analyzed using a continuous flow system consisting of a Carlo Erba elemental analyzer coupled to a Finnigan MAT Delta Plus mass spectrometer. Data are reported in the conventional delta (δ) notation versus Vienna PeeDee Belemnite (V-PDB) for C and atmospheric N_2 for total N. The precision for C and N isotope analyses was ±0.18‰ and ±0.06‰, respectively. The sulfur isotopes were measured in the sulfate and sulfide fractions. Sulfate was extracted by treating the samples with hot (90°C) 6 M HCl for 2 h; the residue was filtered and washed with deionized water. Barium sulfate was then precipitated after addition of 0.25 M $BaCl_2$ to the solution, and the precipitate was dried and weighed. The remaining sulfide fraction was treated with HNO_3 and bromine, and the supernatant was oxidized to form $BaSO_4$. The S isotopes were analyzed by combusting $BaSO_4$ mixed with an equal amount of V_2O_5 at 1,020°C in a Carlo Erba elemental analyzer connected to a Finnigan MAT Delta Plus mass spectrometer. The values were expressed in the conventional $\delta^{34}S$ notation relative to the Vienna-Canyon Diablo Troilite (V-CDT) standard; the precision was ±0.2‰.

Approximately 1–2 g of freeze-dried sediment was extracted with a mixture of CH_2Cl_2 and MeOH (9:1 v/v) on a Dionex Automated Solvent Extractor 300 (three extraction cycles at 1,500 psi and 100°C). The total lipid extracts were reduced using a Büchli rotovapor and injected in pulsed splitless mode into an Agilent 6890 gas chromatograph with a DB5-MS column (30 m × 0.25 mm i.d. × 0.25 µm film). The oven temperature was held at 35°C for 6 min, increased to 300°C at 5°C min^{-1}, and held for 20 min. The chromatograph was interfaced with an Agilent 5973 mass spectrometer operated at 70 eV in full-scan mode (*m/z* 50–500 amu). External and internal standards (S-4066 from CHIRON, Norway and deuterated perylene from Cambridge Laboratory, USA) were used for quantification.

Pigments were extracted for 2 min by ultrasonication in acetone (2 ml g^{-1} sediment), and stored overnight. After filtration (0.02 µm), the samples were injected into a HPLC consisting of a Waters 2690 separation module coupled to a photodiode UV/VIS detector (set at 450 nm). The injector was connected to a RP-18 LiChroCART column (5 µm particle size, 250 mm × 4.6 mm i.d.). The gradient (1 ml min^{-1}) program began with 100% mobile phase A (80:20 MeOH:0.5 M ammonium acetate; Westman et al. 2003). This was followed by 100% mobile phase B (90:10 acetonitrile: water) for 4 min, and 25% B and 75% C (100% ethyl acetate) for 28 min. The program was changed to 100% B for 5 min with a final ramping to 100% A for 4 min. The pigment standards were obtained from DHI, Denmark. Chlorophyll (Chl) was analyzed colorimetrically on a Hitachi U-1100 spectrometer following the method by Dere et al. (1998; absorbance at 470, 645, and 662 nm). The pigment concentrations were calculated according to (Lichtenthaler and Wellburn 1985):

$$C_a = 11.75\ A_{662} - 2.350\ A_{645} \tag{1}$$

$$C_b = 18.61\ A_{645} - 3.960\ A_{662} \tag{2}$$

$$\text{Total carotene} = 1000\ A_{470} - 2.270C_a - 81.4C_b/227 \tag{3}$$

where C_a is Chl *a* and C_b is Chl *b*. Typical precision of duplicate runs was ≤2%.

Results

The cores were dominated by <45-µm size clay + silt fractions. Porosity varied from 40 to 69% (Fig. 2). The LOI content in samples ranged from 2.1 to 7.6%. The results were similar in both cores and reproducibility of duplicate runs was ca. ± 3%.

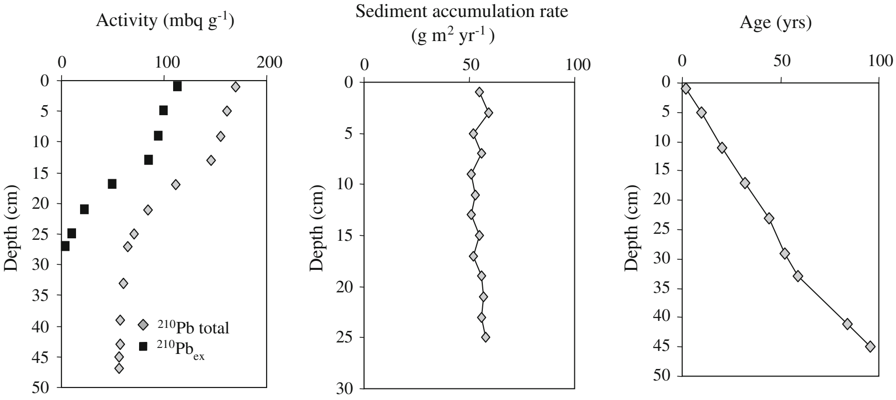
Sedimentation rates

The total activity of ^{210}Pb declined from a maximum of 169 mbq g^{-1} near the surface to 59 mbq g^{-1} at 45 cm depth. The CRS (Constant Rate of Supply) model was used to derive the sediment accumulation rate. The model assumes a constant ^{210}Pb flux, but variable sedimentation rate (Appleby and Oldfield 1978). The sedimentation rate was 4.7 ± 0.04 mm $year^{-1}$, and the sediment accumulation rate was 56 ± 0.3 g m^{-2} $year^{-1}$ (Fig. 3). Based on these values, the deepest part of the core was dated to be ~1908 AD.

Paleoproductivity

The rate of primary paleoproductivity (*PP*; g C m^{-2} $year^{-1}$) was originally calculated for marine sediments

Fig. 2 Depth distribution of ^{210}Pb and mass accumulation rate in sediment core collected from Lake Nainital. The dates were calculated by using ^{210}Pb activity and CRS model



(Muller and Suess 1979), but later, the principle was successfully applied to several freshwater lake systems (e.g. Williams et al. 1993; Ishiwatari et al. 2005; Das et al. 2008; Routh et al. 2008; Choudhary et al. 2008).

$$PP = (\%\mathrm{TOC} \times D)/(0.0030 \times S^{0.3}) \qquad (4)$$

where D is dry bulk density (g cm^{-3}) and S is sedimentation rate (cm kyr^{-1}). PP was also calculated based on the distribution of hydrocarbons (n-$\sum C_{15,17,19}$) representing in-lake algal production. Both profiles indicated a similar trend with the maximum value occurring at 33 cm depth (Fig. 4).

Geochemical analyses

The sediments were anoxic and Eh varied between −187 and −328 mV. Average DOC concentrations in pore water were 36–131 mg l^{-1}. TOC flux in sediments ranged between 1.0 and 3.5 g m^{-2} year^{-1} with a minimum value at 37 cm (Fig. 4). The total N flux was between 0.1 and 0.3 g m^{-2} year^{-1}; the values were maximum (0. 3 g cm^{-2} year^{-1}) between 31 and 33 cm. The total S flux was high and ranged from 0.37 to 1.0 g m^{-2} year^{-1}; the highest rate, 1.0 g m^{-2} year^{-1} S occurred at 29 cm. The atomic C/N ratio in sediments ranged between 11 and 15, and the atomic C/S ratio varied between 4.3 and 19 (Fig. 4).

The δ^{13}C of OM ranged from −26.5‰ to −27.7‰; the values were low around two depth intervals in the sediment core, 31–37 cm and 21–25 cm (Fig. 5). The δ^{15}N values varied between 3.1‰ and 9.2‰. The δ^{15}N values increased up-core to a maximum value of 9.2‰ at 35 cm. The δ^{15}N values decreased, followed by another increase

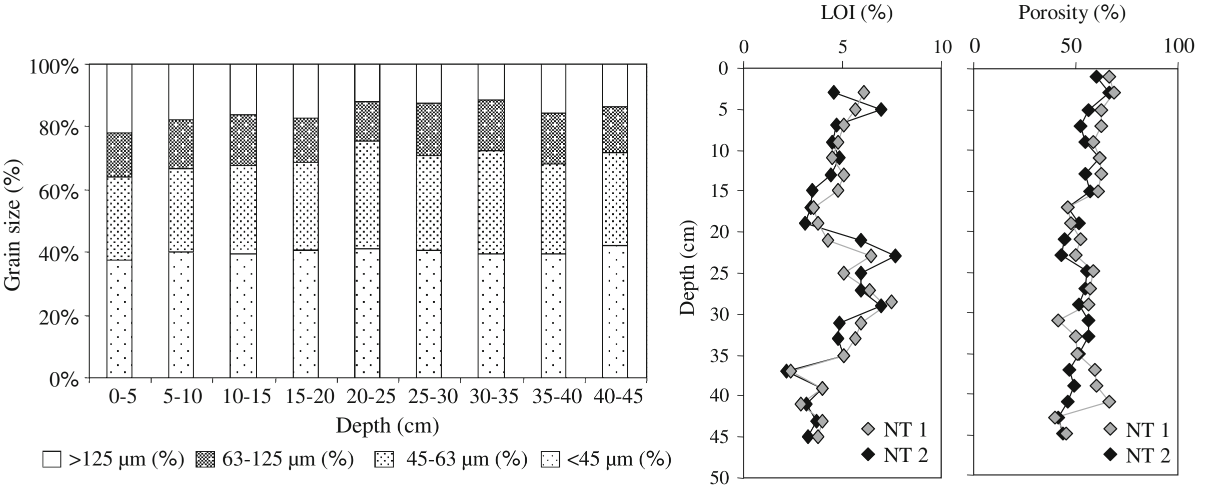


Fig. 3 Grain size, LOI, and porosity in Lake Nanital sediments

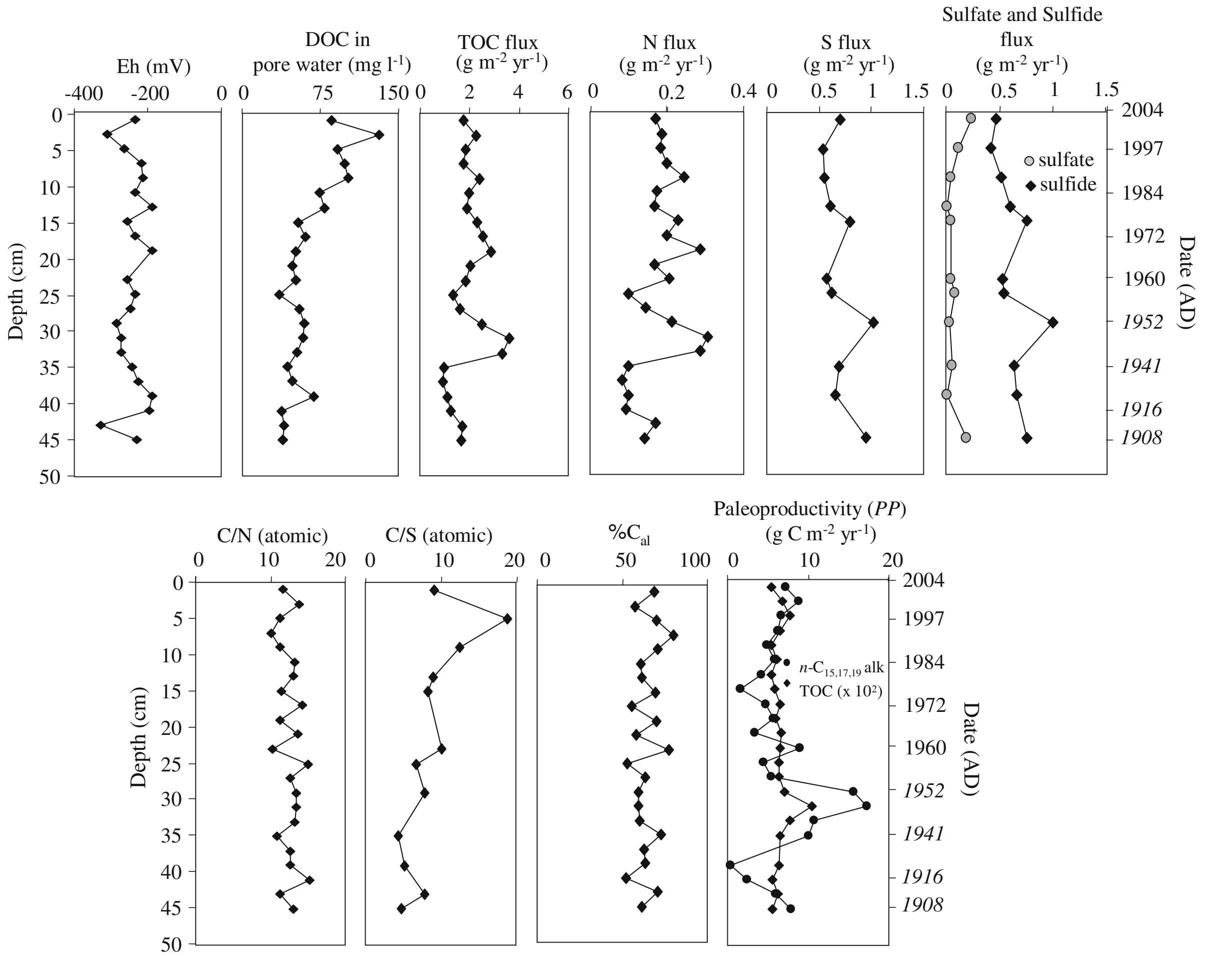


Fig. 4 Eh, dissolved organic carbon (DOC), total organic carbon (TOC), total nitrogen, total sulfur, sulfate and sulfide, C/N (atomic), C/S (atomic), algal organic matter (%C_{al}), and paleoproductivity in Lake Nainital sediments (Note that units for some indicate accumulation rates—not concentrations)

between 11 and 15 cm (up to 8.6‰). The $\delta^{34}S$ in sulfides ($\delta^{34}S_{red}$) between 24 and 45 cm depth was almost constant (~1.9‰); negative $\delta^{34}S$ values occurred at 23 cm (−0.9‰) and 1 cm (−6.3‰). The average value of $\delta^{34}S_{red}$ between 21 and 3 cm was ~3.6‰. The $\delta^{34}S$ in sulfates ($\delta^{34}S_{oxi}$) from 27 to 45 cm was between −0.01‰ and −0.9‰. In contrast, the $\delta^{34}S_{oxi}$ values above 26 cm ranged from 0.3‰ to 3.8‰. In two samples, the amount of sulfate extracted was too little to obtain reliable results.

The hydrocarbon concentrations in sediments were normalized to TOC to compensate for depositional variations, and to express the enrichment or depletion of hydrocarbons relative to TOC (Fig. 6). Total hydrocarbon concentrations varied from 1.8 to 5.9 µg mg^{-1} of TOC; the concentrations were high in the 30–40 cm interval. The total concentration of low, odd numbered *n*-alkanes (*n*-$C_{15,17,19}$) exhibited variations with depth. Higher concentrations, 0.66–0.80 µg mg^{-1} of TOC, occurred between 25 and 35 cm and near the surface (0.49–0.53 µg mg^{-1} of TOC).

The Carbon preference index (CPI; Allan and Douglas 1977), which represents the predominance of odd (C_{23}–C_{33}) over even (C_{24}–C_{32}) *n*-alkanes was calculated and the values were marginally high (2–3) between 25 and 35 cm, but gradually decreased up-core. The Terrigenous Aquatic Ratio (TAR; Bourbonniere and Meyers 1996) takes into account the *n*-alkane signature of vascular plants (*n*-$C_{27,29,31}$) and phytoplankton (*n*-$C_{15,17,19}$); TAR ranged from 0.30 to 2.9 and showed a similar trend to CPI.

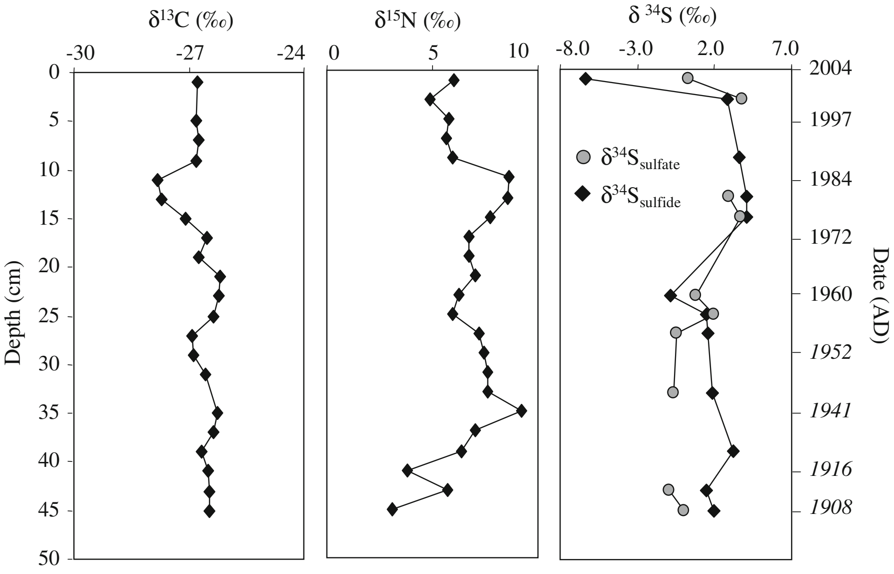


Fig. 5 $\delta^{13}C_{organic}$, $\delta^{15}N_{total}$, $\delta^{34}S_{red}$, and $\delta^{34}S_{oxi}$ versus depth in Lake Nainital sediments

The concentrations of most pigments increased upcore (Fig. 7). The only exception was zeaxanthin, which was high (0.39–2.3 mmol g^{-1}) in bottom sediments and decreased upwards. *β*,*β*-carotene was present in high concentrations throughout the core with concentrations varying between 0.24 and 5.8 mmol g^{-1}. Echinenone, myxoxanthophyll, and alloxanthin occurred in high concentrations, up to 5.1, 0.27, and 1.0 mmol g^{-1}, respectively, in surface sediments. Lutein was absent in most of the sediment layers. However, lutein was high (0.09 mmol g^{-1}) at a depth of 29 cm. Lutein was also found between 9 and 13 cm and varied from 0.02 to 0.03 mmol g^{-1}. Chlorophyll *a* and *b* concentrations varied from 0.28 to 0.76 mmol g^{-1} and 0.02 to 0.17 mmol g^{-1}, respectively. The maximum Chl *a* concentration (0.76 mmol g^{-1}) occurred between 31 and 33 cm. The CD:TC (chlorophyll derivative:total carotenoid) ratio in the core varied between 0.04 and 0.48; high (0.11–0.48) values occurred near the mid-section of the core. Similarly, the ratio between *β*,*β*-carotene/zeaxanthin varied between 0.11 and 3.4. The values were high, 2.0 and 3.4, at 39 cm and 41 cm, respectively.

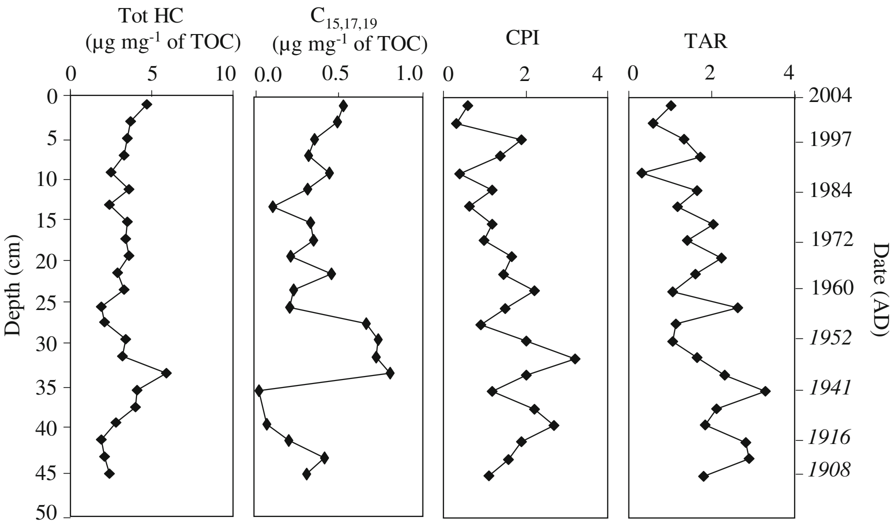


Fig. 6 Total hydrocarbon concentration (HC) and their ratios (CPI, TAR, and P_{aq}) in Lake Nainital sediments

Discussion

Sediment chronology

Porosity and loss-on-ignition measurements in sediments from both cores in Lake Nainital are comparable (Fig. 2). Hence, extrapolating ages from the dated core to the core in which the paleolimnological variables were measured, while not ideal, is acceptable. Moreover, these undisturbed parallel cores were collected within 1 m distance of one another, during the same sampling trip. The average sedimentation rate based on the ^{210}Pb dates is 4.7 mm year^{-1}, which is comparable to previous estimates (e.g. Kumar et al. 1999, 2007). They observed that sedimentation rate is lowest (4.8 ± 0.04 mm year^{-1}) in the deepest part of the lake, but increases progressively towards the shore (10.2 ± 0.04 mm year^{-1}). This is due to landslides, surface run-off, and external input from the catchment, the effects of which are most apparent near the periphery of the lake (Kumar et al. 2007).

Elemental concentrations

TOC flux in Nainital Lake varies with depth in the sediment (1.0 to 3.5 g m^{-2} year^{-1}), but is generally low compared to eutrophic lakes (Brenner et al. 1999; Punning and Tougu 2000; Vreča and Muri 2006; Jinglu et al. 2007). It is unlikely that variation in TOC can be due to differences in grain size since the sediments are characterized by silt-to-clay size fractions throughout the core (Fig. 3). The variation in TOC could result from early stage diagenetic alteration. Studies elsewhere suggest limited OM degradation in deeper anoxic sediments (Hodell and Schelske 1998; Harvey et al. 1995; Hedges et al. 1999; Meyers 2003). However, this is a contentious

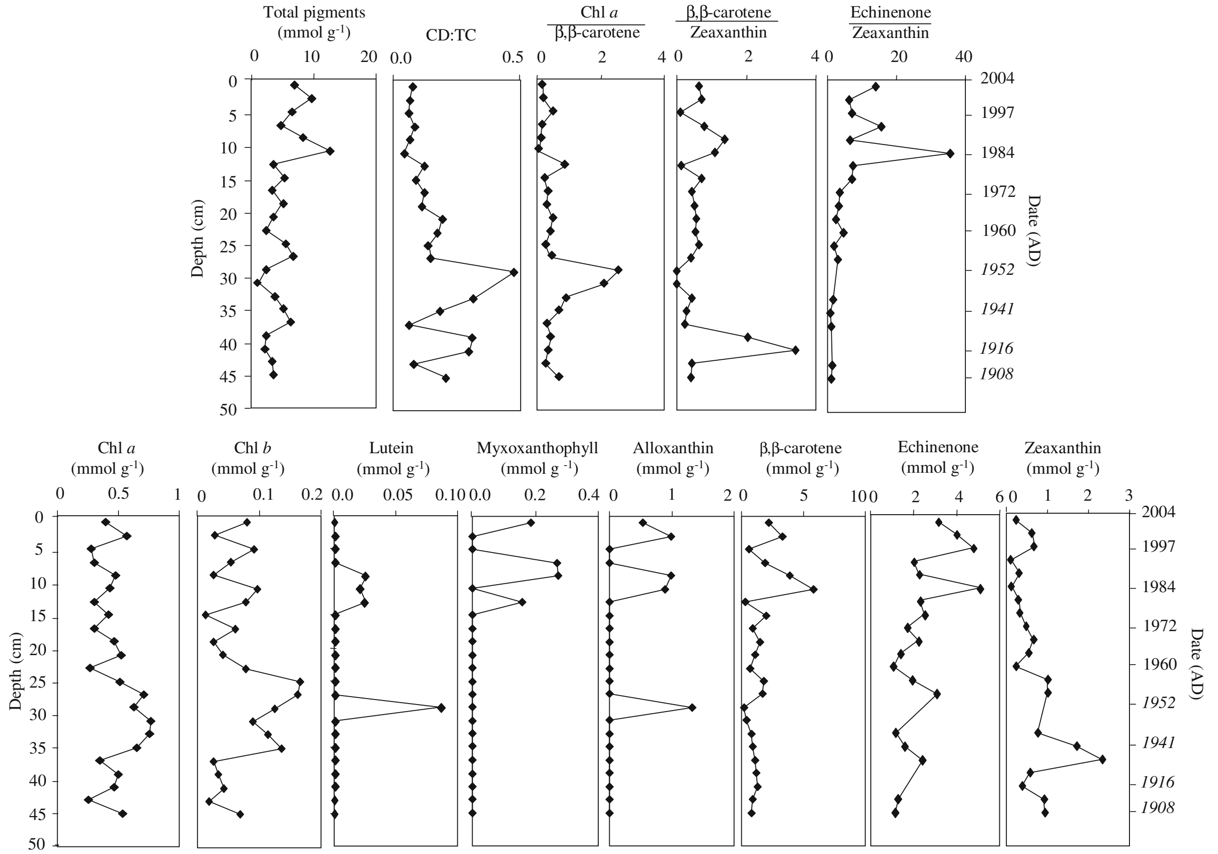


Fig. 7 Distribution of specific pigments (Chl *a*, Chl *b*, total carotene, *β*,*β*-carotene, zeaxanthin, echinenone, alloxanthin, and lutein) and ratios (CD/TC, Chl *a*/*β*,*β*-carotene, *β*,*β*-carotene/zeaxanthin, and echinenone/zeaxanthin) in Lake Nainital sediments

issue since recent studies indicate that OM degradation under anoxic conditions is equal to or sometimes even greater than degradation under oxic conditions (e.g. Pedersen and Calvert 1990; Hedges and Keil 1995; Bastviken 2004). In particular, the labile OM fraction, which is presumably accessible to most enzymes (regardless of the O_2 concentration), is depleted rapidly. Hence, OM type and changes in delivery rate largely affect the distribution of TOC.

Deposition of N in the lake indicates an up-core increase. Maximum N flux (0.30 g m^{-2} $year^{-1}$) occurs during the 1950s, coinciding with increase in TOC flux (up to 3.5 g m^{-2} $year^{-1}$). The increase in N flux is most likely related to rapid urbanization that started in the early 1950s (Pant et al. 1980). Urban development led to deforestation and higher inputs of nitrate-rich domestic waste into the lake, which triggered the change.

The external sources of S input into the lake include springs and ground water, which erode the gypsum-rich Krol and Tal formations before draining into the lake (Das 2005; Chakrapani 2002), as well as anthropogenic input from the catchment. The flux for total S in Nainital sediments does not show a specific trend (Fig. 4). Because of reducing conditions and sulfate reduction, the rate of sulfide accumulation in these sediments is high (0.30–0.80 g m^{-2} $year^{-1}$). Presence of sulfate (0.01–0.21 g m^{-2} $year^{-1}$) in such a reducing environment is, however, surprising, especially in the deeper sediments (Fig. 4). Most probably this is due to oxidation of sulfide minerals during sample handling and represents an artifact. The cores were sliced in the field and refrigerated. After returning to the laboratory, the samples were freeze-dried, which can affect the oxidation state of S (Hjorth 2004).

Elemental ratios

The atomic C/N ratio in Nainital sediments is 10–15 and suggests algal-derived material as the primary source of sediment OM. This is consistent with other studies, which indicate that atomic C/N ratios >20 imply input of vascular plants, whereas lower C/N ratios (5–8) indicate principally algal-derived OM (Meyers 1994, 2003). The presence of inorganic N in sediments can, however, alter C/N ratios and thereby confound the interpretation of OM sources (Talbot 2001). The regression line for the scatter plot between N_{total} and C in Nainital sediments suggests an absence of inorganic N because the intercept is low (0.009). Because there is no inorganic N in these sediments, and the C/N (atomic) of algal matter is ~8 and that of terrigenous OM is ~25 (Meyers 2003), we can estimate the percent of autochthonous, i.e. algal-derived OM (%C_{al}). The calculated %C_{al} values range from 52 to 80% (Fig. 4), and confirm that the OM source in Lake Nainital sediments is essentially autochthonous (algal-derived). Moreover, the C/N ratios indicate that run-off waters from the catchment do not increase the terrestrial OM component, even though the lake is surrounded by mountains and nearly 48% of the catchment is forested.

Sub-aquatic springs with high sulfate concentrations (2–4 mmol l^{-1}) derived from weathering of dolomites and limestones enriched in gypsum feed Lake Nainital (Das 2005; Chakrapani 2002). Hence, large inputs of S affect the C/S ratio in this lake, and the ratio deviates from values typically observed in freshwater sediments (typically >20; Berner and Raiswell 1984; Urban et al. 1999). Moreover, stratification by mid- to late-summer causes seasonal anoxia in the hypolimnion, and incorporates S as sulfide (pyrite) in bottom sediments. Thus, the atomic C/S ratio decreases with depth (Fig. 4), and the low (4.3–18) values represent a reducing environment associated with eutrophic conditions (Putschew et al. 1995; Urban et al. 1999). The increase in S accumulation with depth could also result from preferential mineralization of C relative to S. Consistent with this observation, there is a decrease in pore water DOC levels with depth (Fig. 4). Urban et al. (1999) reported a decrease in C/S ratios with depth in Swiss lakes, and correlated this to human-induced trophic state shifts. In particular, Lake Nainital has a striking similarity with the alpine Lake Cadango, which has C/S ratios between 5.9 and 11 (Putschew et al. 1995). The upper part of Lake Cadango mixes regularly, whereas the lower part remains stagnant and is anoxic.

Productivity changes

The *PP* equation proposed by Muller and Suess (1979) does not take into account variations in terrigenous input, but rather, provides information on the integrated preserved total carbon. Hence, it is important to compare the *PP* trend based on production of autochthonous OM, and then relate the *PP* values to the lake's trophic status. Because OM deposited in these sediments is primarily from in-lake production (low C/N ratio and high %C_{al} values), *PP* calculated based on the n-$\sum C_{15,17,19}$ values indicates a similar trend to the TOC-derived *PP* (Fig. 4).

Paleoproductivity estimates in Lake Nainital based on TOC do not vary much (average 675 g C m^{-2} $year^{-1}$), except for increases that occur around ~1950 and ~2000. The increase in *PP* around 1950 coincides with the beginning of increased urbanization in the catchment. Although human population and urbanization in the catchment increased steadily (Singh and Gopal 1999), the reason(s) for a decrease in *PP* in subsequent years (1960–1980) is unknown. Meyers (1997) indicated that primary production in mesotrophic freshwater bodies is from 100 to 310 g C m^{-2} $year^{-1}$, whereas in eutrophic systems it is from 370 to 640 g C m^{-2} $year^{-1}$. Based upon these rough estimates, the eutrophic status in Lake Nainital has remained mostly unchanged over the last ~95 years.

Stable isotope records

Carbon isotopes

The $\delta^{13}C$ values of sediment OM show little variation (−26.5‰ to −27.8‰) with depth. Based on these $\delta^{13}C$ values, it is impossible to determine whether C_3 vascular plants or phytoplankton are the primary sources of OM because they use isotopically identical sources of inorganic carbon, i.e. atmospheric CO_2 or dissolved CO_2 in lake water. The $\delta^{13}C$ values of OM in Nainital Lake are, however, similar to values in many eutrophic lakes affected by external input of nutrients (Schelske and Hodell 1995; Brenner et al. 1999; Routh et al. 2004; Vreča and Muri 2006; Choudhary et al. 2008). Under eutrophic conditions, elevated productivity in the lake is related to preferential removal of dissolved $^{12}CO_2$ by primary producers from water, which leaves the dissolved inorganic C enriched in ^{13}C. As the availability of $^{12}CO_2$ gradually diminishes in the lake, a progressively greater fraction of the $^{13}CO_2$ is incorporated into OM. Furthermore, additional in-lake processes could involve active uptake of bicarbonate (Law et al. 1998) and release of isotopically light biogenic CH_4 (Kendall et al. 2001). This phenomenon is common when lakes become eutrophic and anoxic conditions develop (Gu and Schelske 1996; Brenner et al. 1999; Vreča and Muri 2006). However, we have not measured methane in Nainital sediments or in the water column, and hence, the role of methanogenesis in affecting $\delta^{13}C$ of sedimentary OM is speculative.

There is a decrease in $\delta^{13}C$ values from 1972 to the early 1980s, after which they increase to higher values in surface sediments; this period in the 1970s and 1980s coincides with enrichment of $\delta^{15}N$ (Fig. 5). The variability in $\delta^{13}C$ values perhaps results from input of soil-derived or terrestrial OM with lighter isotopic composition that was incorporated due to major landslides in this region during 1982 and 1987 (Singh et al. 2001), assimilation of ^{13}C-depleted CO_2 formed during degradation of sinking OM (Hollander and Smith 2001), or contribution of isotopically-depleted CO_2 from use of fossil fuels (Schelske and Hodell 1995; Vreča and Muri 2006). The decrease in $\delta^{13}C$ and C/N values coupled with an increase in $\delta^{15}N$ values in this interval most likely indicates enhanced algal productivity. Consistent with this idea, algal-derived *PP* also increases during this period (Fig. 4). Likewise, other studies have also proposed a similar relationship between stable isotopes, elemental concentrations, and *PP* (e.g. Herczeg et al. 2001; Routh et al. 2004, 2008; Brenner et al. 2006; Choudhary et al. 2008).

Nitrogen isotopes

In Lake Nainital, the $\delta^{15}N$ values increase up-core from 3.1 to 5.1‰ (Fig. 5) with elevated values occurring at depths of 30–35 cm (1941–1952) and 10–15 cm (1972–1990). Higher $\delta^{15}N$ values in these intervals coincide with elevated N input (particularly at 30–35 cm), which affect in-lake productivity. The $\delta^{15}N$ value of sedimenting OM is typically related to the supply and utilization of the dissolved inorganic nitrogen (DIN) pool. When the DIN pool is small, the preferential uptake of ^{14}N by algae diminishes, and $\delta^{15}N$ values become larger. Elevated $\delta^{15}N$ values can result from anthropogenic inputs of sewage and soil-derived nitrate, yielding values as high as 10‰ in sedimenting OM (Teranes and Bernasconi 2000; Talbot 2001; Routh et al. 2007). Previous studies have reported an increase in inputs of sewage and nitrogenous wastes into Lake Nainital in recent years (Ali et al. 1999; Chakrapani 2002). Similarly, enrichment of $\delta^{15}N$ in the sediments due to loss of isotopically light ammonia by degassing can lead to isotopic enrichment of the DIN pool (Teranes and Bernasconi 2000). Consistent with this idea, Pant et al. (1980) reported an increase in ammonia concentration from 19 to 156 μg l^{-1} between the period 1954 and 1975. Likewise, NLRSADA (2002) indicated 0.10 mg l^{-1} of ammonia in the water column, implying ammonification as an important process in Lake Nainital.

Notably, the $\delta^{15}N$ values in Nainital Lake suggest algal material from primarily non-N_2-fixing phytoplankton ($\delta^{15}N$ is typically >2‰; Talbot and Laerdal 2000; Herczeg et al. 2001). Although cyanobacterial pigments echinenone and zeaxanthin are abundant (see below), their role in N_2 fixation is open to question. Typically, the $\delta^{15}N$ value of sedimented OM produced by N_2-fixing cyanobacteria is between −3 and 1‰ (Fogel and Cifuentes 1993), which is outside the range of $\delta^{15}N$ values observed in Nainital sediments. However, the core exhibits a trend towards lower $\delta^{15}N$ values in recent years; this coincides with an increase in abundance of N_2-fixing cyanobacteria since the 1980s.

Sulfur isotopes

Occurence of microbial sulfate reduction in Lake Nainital is based on indirect geochemical evidence (low Eh, decrease in DOC, H_2S emanation, and high sulfide flux in sediments; Fig. 4). As bacterial sulfate reduction progresses, the $\delta^{34}S$ of dissolved sulfate becomes unusually high, exceeding the $\delta^{34}S$ of evaporite (10–30‰) and sulfide (−40 to 10‰) minerals (Grossman and Desrocher 2001). Sulfate reduction in surface sediments in Nainital Lake results in decrease of sulfate (Fig. 4) and low (−6.4‰) $\delta^{34}S$ in the sulfide fraction (Fig. 5). In contrast, there is little difference between the $\delta^{34}S$ of sulfate and sulfide fractions in deeper anoxic sediments. This is consistent with other studies, which indicate that sediments from lakes with anoxic bottom waters display less overall isotopic fractionation (Fry et al. 1995; Urban et al. 1999). The authors suggest that most of the sulfate in deeper anoxic sediments is reduced, involving little fractionation, whereas in near-surface sediments, less rapid sulfate consumption allows larger isotopic fractionation. Lack of $\delta^{34}S$ fractionation in deeper sediment implies that sulfate that enters the lake is quickly reduced because the water above is reducing, and conditions are suitable for sustaining sulfate reduction (availability of OM and sulfate). The small $\delta^{34}S$ fractionation (~1.5–2‰; Fig. 5) in deeper sediments, is most likely due to oxidation from sample handling as discussed earlier. Consistent with this, Fry et al. (1995) also suggested that sulfide oxidation after the formation of reduced S exerts a relatively minor effect on the $\delta^{34}S$ composition of sulfide minerals.

Biomarker records

n-Alkanes

The total hydrocarbon content in Nainital sediments shows an up-core increase to a depth of 35 cm. Above this depth, there is little variation in total hydrocarbon content (Fig. 6). Total hydrocarbon concentration covaries with n-$\sum C_{15,17,19}$ and implies a gradual shift in algal productivity. The sediments indicate low CPI (average 1.5) and TAR (average 1.7) values, and represent OM produced by in-lake sources (i.e. algae, submerged and emergent freshwater plants). Consistent with this evidence, different species of algae (*Microcystis aeruginosa, Spirogyra adnata, Mougeotia scalaris*, and *Oedogonium* sp.), photosynthetic bacteria, and floating and submerged macrophytes (*Polygonum amphibium, Potamogeton pectinatus*, and *P. crispus*) thrive in the lake (Pant et al. 1980; Singh and Gopal 1999; Gupta et al. 1999).

Increased CPI values at specific intervals in the core imply higher input of terrestrial OM (particularly n-$C_{27,29,31}$ alkanes; Fig. 6). This interpretation is probably flawed based on the other lines of evidence (C/N, $\%C_{al}$, in-lake productivity, and pigments), which imply limited terrestrial input. Because diagenetic losses of the non-hydrocarbon components of total OM exaggerate the importance of different OM sources based on absolute amounts of specific hydrocarbons, interpretation of OM sources must be carefully verified. This exaggeration is especially true for land plants (Meyers 2003), which tend to produce proportionally more hydrocarbons (particularly n-$\sum C_{27,29,31}$ alkanes) than algae, and consequently, over-represent the fraction of land-derived OM, particularly in small lakes. Moreover, short-chained n-alkanes are likely to degrade faster during early diagenesis (Meyers and Ishiwatari 1993; Peters et al. 2005).

Pigments

The total concentration of pigments is relatively high (1.2–12.5 mmol g^{-1} of TOC), and is consistent with high primary productivity in the lake (Fig. 7). The CD:TC ratio suggests autochthonous sources of sediment OM and reducing conditions (Rybak et al. 1988). Moreover, the CD:TC ratio represents typical eutrophic conditions as indicated by Sanger and Crowl (1979).

The Chl trends demonstrate considerable variability. This is expected because Chl degrades rapidly to form pheophytin and pheophorbide, and is rarely well-preserved in sediment records (Leavitt 1993). Moreover, fluctuations in the zooplankton population, e.g. *Brachionus*, *Rotatoria*, *Phillodina*, *Cyclops*, *Bodo*, *Eutricha*, *Epistylis*, and *Vorticella* (Pant et al. 1980), which feed on green algae, can lead to significant alterations in the distribution of Chl (Drenner and Hambright 1999). The high concentrations of Chl *a*, Chl *b*, and β,β-carotene and their ratio (Chl *a*/β,β-carotene) around 27–33 cm and 5–13 cm suggests elevated productivity (Griffiths 1978; Kowalewska 2001; Bianchi et al. 2002). The concentration of β,β-carotene remains almost constant (0.98 mmol g^{-1}) until 13 cm, except for some variations between 29 and 31 cm; after this β,β-carotene indicates a steady increase in concentration. β,β-carotene is very stable and it can persist even under oxygenated conditions, unlike other pigments (Hodgson et al. 1998; Bianchi et al. 2000; Leavitt and Hodgson 2001). Low concentration of β,β-carotene in deeper sediments may be due to less phototrophic organisms in the water column.

The appearance of lutein, myxoxanthophyll, and alloxanthin in the upper half of the core suggests an increase in productivity, and a possible change in the phytoplankton community in response to high nutrient influx and sewage disposal (Ali et al. 1999; Chakrapani 2002; Fig. 7). The presence of these pigments suggests a change in phytoplankton species to a system dominated by green algae and *Cryptophytes* and cyanobacteria (Leavitt and Hodgson 2001). The absence of these carotenoids in deeper sediments is most likely due to their low stability (Leavitt and Hodgson 2001). Particularly, sugar-containing functional groups and polyene side-chains make these carotenoids susceptible to oxidative degradation (Leavitt et al. 1989; Leavitt and Hodgson 2001).

Echinenone and zeaxanthin are the more abundant carotenoids and they occur in variable concentrations throughout the core. Echinenone is considered a specific marker for filamentous N_2-fixing cyanobacteria (e.g. *Anabaena*, *Aphanizomenon*), whereas zeaxanthin is more characteristic of non-N_2-fixing, colonial species (e.g. *Microcystis*, *Oscillatoria*; Paerl 1988; Leavitt 1993; Bianchi et al. 2000, 2002. Nagdali and Gupta (2002) indicated that *Cyanophyceae* represents about 51% of the total phytoplankton population in this lake. The sediment depths above 25 cm, however, show a marked increase in echinenone, with a corresponding decrease in zeaxanthin concentrations, and thus an increase in the echinenone/zeaxanthin ratio (Fig. 7). This suggests a gradual shift in the phytoplankton community to filamentous, N_2-fixing cyanobacteria, which thrive in highly competitive environments relative to colonial species (e.g. *Microcystis*, *Synechococcus*) because of their symbiotic relationship with aquatic plants (Masepohl et al. 1997). The increase in cyanobacteria is probably related to elevated P inputs. Phosphate concentrations in wastewater discharged into the lake (mainly from sewage drains) have an average value of 210 μg l^{-1} (NIH 1999). Similarly, phosphate concentration measured by Nagdali and Gupta (2002) in the water column was >46 μg l^{-1}, which is higher than the critical P loading value for a lake of this mean depth (Vollenweider 1976). Finally, denitrification processes in the sediments favor cyanobacteria because during respiration, they use dissolved nitrate or nitrite instead of oxygen.

Human-induced effects?

Previous studies in Lake Nainital indicated heavy metal pollution, an increase in sewage discharge, and other problems associated with urban development in the catchment (Pant et al. 1980; Ali et al. 1999; Chakrapani 2002). The perceived impacts of these changes on the sediment and water quality, however, need to be reexamined. For example, although heavy metal concentrations in Nainital sediments are reportedly high (Das et al. 1995; Chakrapani 2002), metal fractionation experiments reveal that most of the heavy metals are present in the residual phase (Patra et al. 2006). The residual fraction is mostly immobile and therefore, less bioavailable. Moreover, since the surrounding lithology is prone to chemical weathering (Chakrapani 2002) and land slides, heavy metals will continue to accumulate in these fine-grained lake sediments.

Paleolimnological findings in this study yielded a few surprises. There has been little change in the input of terrestrial OM into the lake from external runoff; OM in the lake sediment consists primarily of algal-derived matter. Although there has been a change in the phytoplankton community (increase in cyanobacteria population), the trophic status of the lake has been eutrophic and remained largely unchanged over the last nine decades. Unlike other urban water bodies in the region (e.g. Lake Sattal, Choudhary et al. 2008), Lake Nainital does not seem to have been strongly impacted by human activities in the catchment. Instead most of the changes in the geochemical proxies are related to ongoing biogeochemical processes in the water-column and sediments. Nachiappan et al. (2002) completed detailed isotope mass balance studies on Lake Nainital, and came to the similar conclusion that Lake Nainital is not seriously impacted by anthropogenic activities.

Conclusions

The different geochemical variables investigated in this study provide a detailed record of biogeochemical changes in Lake Nainital spanning the last ~95 years. Geochemical proxies indicate anoxic conditions in bottom sediments influence in-lake processes. Deposition of organic C and N shows some variations, particularly in the deeper layers—these changes coincide with eutrophic conditions and higher productivity in the lake. Sulfur is added to the lake mainly from weathering processes.

Organic matter deposited on the lake bottom is primarily from in-lake algal material. Stable C and N isotopes indicate positive shifts in their values coinciding with microbial processes, productivity shifts, and OM degradation. In particular, agricultural and sewage input have increased the δ^{15}N values. The S isotopes indicate sulfate reduction associated with anoxic degradation of OM. Specific biomarkers such as hydrocarbons and pigments signify algal-derived material and elevated productivity towards the start of rapid urbanization in the lake's catchment (during the 1950s). The pigments signify a change in phytoplankton community to a cyanobacterial-dominated system in recent years. However, the trophic state of the lake has remained largely unchanged over the last several decades. Finally, we conclude that the overall impact of human-induced changes in the lake's catchment is most likely limited.

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