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EDITORIAL

The water dispute in the Cauvery river basin continue to receive daily attention in the newspapers in the country; we have not been able to address the issue related to water in different places at different times such that the problem is allowed to be kept bubbling all the time. Global issues related to water is assuming alarming proportions and overshadows other environmental issues such as global warming and climate change. The recently held (in Delhi) international meeting on follow up of Kyoto protocol attracted wide spread public interest suggesting to the general awareness of all related problems. Thus public perception of environment is slowly but surely changing and it is a good sign for the welfare of mankind.

With the setting up of separate ENVIS centre for Environmental Law at Bangalore, we will now focus exclusively on the Biogeochemical aspects of environment and the present newsletter is the first one without any “law” related information. In order to expand our services, we have now opened a commercial web based service (<http://envisjnu.net>) that has greater capacity so that we hope to place abstracts also in the web for easy reference by the readers.

The present newsletter contains report on three important international meetings related to Biogeochemistry held in different places. Usual lists of recent publications, daily news and conferences are also given.

We welcome suggestions from our readers for improving our services farther and comments on both of our web sites.

Prof. V. Subramanian

Editor

Using geochemical proxies for interpreting contemporary and paleolimnological records

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Introduction

Study of different lake systems across the world indicates that environmental conditions particularly those involving periods of high sedimentation rates and greater lacustrine primary productivity preserve evidence of short/long-term natural processes and cultural activities. These evidences e.g., variation in bulk organic carbon, biomarker accumulation, stable isotope signals, and trace metals have been widely used (see Bernasconi et al., 1997; Kaushal and Binford, 1999; Sternbeck and Hallberg, 2000; Meyers and Teranes, 2002; Routh et al., 2004). Particularly, lacustrine organic matter characteristics provide a lot of information relevant for understanding these complex and fragile ecosystems. Organic matter in lakes is produced by organisms that have lived in and around the lake, and includes a complex mixture of lipids, carbohydrates, proteins, etc. Accumulation of organic matter in lake sediments reflect not only the types and amounts of original materials, but also the extent of alteration and degradation of the starting material integrating the different origins of organic matter, delivery routes, depositional processes, and preservation. These complex organic molecules in lake sediments have been widely used to interpret paleoecological and paleoenvironmental histories (for review see Meyers and Lallier-Vergès, 1999; Meyers, 2003).

Here we have briefly reviewed the use of different paleolimnological proxies and how they can be used in lakes. We have also discussed a case study (Lake Brunnsviken in Stockholm, Sweden) where we applied some of these paleolimnological proxies to relate the historical changes in the watershed to the sediment characteristics.

Discussion

Paleolimnological proxies such as total organic carbon, biomarker molecules, trace element distributions, and stable isotopic compositions can be used to measure changes in watershed disturbance and aquatic primary productivity. Two types of information provided by these geochemical proxies are the origin of sedimentary organic matter and the kinds of biota that produced it. While some of these proxies are relatively conservative and vary little, others are strongly influenced by sediment-water interaction, biological processes, and anthropogenic activities. Despite the early diagenetic alterations in lacustrine sediments, sedimentary organic matter typically retains specific information about the different sources, their delivery, and the abundance of biota that produced it.

Total organic carbon represents the organic matter that escaped remineralization during sedimentation, and reflects the different origins of organic matter, delivery routes, depositional processes, and preservation (Meyers, 2003). TOC concentrations are expressed as weight/weight ratios and therefore are influenced by other sediment components. For example, variation in grain size affects TOC, and consequently, TOC concentrations can become higher in the deeper parts of the lake where fine-grained sediments predominate.

Biomarkers are organic compounds which can be directly related to a specific source because they retain the basic carbon skeleton during and after incorporation in the sedimentary environment. Straight chained n-alkanes are a common biomarker in lake sediments. These compounds are useful for discriminating the proportions of terrestrial and aquatic organic matter because of their low susceptibility to microbial degradation (Meyers 2003). The principal sources of these biotic hydrocarbons in lake sediments are: 1) algae and photosynthetic bacteria enriched in n -C_{15,17,19} alkanes, 2) vascular plants enriched in n -C_{27,29,31} cuticle waxes, and 3) submerged and floating macrophytes characterized by n -C_{21,23,25} alkanes (Meyers, 2003). Organic matter sources in sediments have been distinguished based on different hydrocarbon ratios such as the Carbon Preference Index (CPI, Allan and Douglas, 1977), Terrestrial-Aquatic Ratio (TAR, Bourbonniere and Meyers, 1996), and the aquatic macrophyte n -alkane proxy (P_{aq} , Ficken et al., 2000). Immature sediment extracts with significant input of terrestrial organic matter are dominated by the odd-carbon-numbered n -alkane preference (CPI values $\gg 1$), particularly n -C₂₇, C₂₉, and C₃₁ alkanes. In contrast, TAR ~ 1 characterizes aquatic hydrocarbons (Bourbonniere and Meyers 1996). $P_{aq} < 0.1$ corresponds to terrestrial plants, 0.1-0.4 to emergent macrophytes, and 0.4-1 to submerged/floating macrophytes (Ficken et al., 2000).

Carbon/nitrogen ratios help to identify the origins of sedimentary organic matter. Atomic C/N ratios >20 indicate vascular plant material, whereas lower C/N ratios indicate a mixture of algal and/or marine OM sources (Meyers and Ishiwatari, 1993). OM in algae, phytoplankton, and zooplankton is characterized by high protein content; hence low C/N ratios, whereas terrestrial plants are characterized by low protein content, hence high C/N ratios. This fundamental difference in organic matter serves as a reliable parameter for paleolimnologic reconstructions. Once organic rich sediments deposit, C/N values appear to experience little further change, and any variation in them supports the idea of change in organic matter input rather than representing a diagenetic artifact (Kaushal and Binford, 1999).

Carbon isotopes have been most commonly used to differentiate the different organic matter sources in lakes. The $\delta^{13}C$ values of algal and C₄-type materials are distinctively different, but there is little difference between algal versus terrestrial C₃-type material. Carbon isotopes have also been widely used as an indicator of enhanced aquatic productivity in lakes (e.g., Hodell and Schelske, 1998; Brenner et al., 1999). Primary producers preferentially remove dissolved ¹²C from water and leave the remaining dissolved inorganic carbon depleted in ¹²C (e.g., Bernasconi et al., 1997; Hodell and Schelske, 1998; Meyers and Teranes, 2001). When productivity is high, the availability of ¹²C gradually diminishes, and a progressively greater fraction of the ¹³C is incorporated into organic matter. The consequence is that the $\delta^{13}C$ of organic matter produced under conditions of high productivity becomes less

negative. Because many factors affect the carbon isotopic signal of sedimented organic matter, separating an organic matter source from in-lake processes based on $\delta^{13}\text{C}$ values can become complicated.

$\delta^{15}\text{N}$ values have been used to identify organic matter sources and to reconstruct paleoproductivity histories (e.g., Herczeg et al., 2001; Talbot et al., 2002). The $\delta^{15}\text{N}$ signature of organic matter from algae using dissolved inorganic nitrogen (DIN) is *ca.* 8.5‰ versus C_3 -type plants using atmospheric N_2 with values of *ca.* 0.5‰ (Peterson and Howarth, 1987). Drawdown of the DIN reservoir yields larger $\delta^{15}\text{N}$ values in algal organic matter. However, interpreting the $\delta^{15}\text{N}$ values is not always straightforward. For example, denitrification or anthropogenic input from farm runoff and sewage can result in larger $\delta^{15}\text{N}$ values (Teranes and Bernasconi, 2000), whereas an abundance of cyanobacteria, which directly fix atmospheric N_2 , leads to lower $\delta^{15}\text{N}$ values (Fogel and Cifuentes, 1993). Moreover, shifts in phytoplankton assemblages may influence the $\delta^{15}\text{N}$ values, adding to the complexity.

Case study

Lake Brunnsviken (LB): LB is a slightly brackish lake (2.8-4.6‰) with a maximum depth of 14 m, and is situated 3 km north of central Stockholm. The lake has a total surface area of 1.56 km² and a drainage area of 14 km². Brackish water from the Baltic Sea (salinity of 6-8‰) enters through a narrow passage between the lake and Ekshagen Bay. More than 40% of the lake's catchment area is urbanized. Phosphorus and nitrogen levels are both high, and promote intense annual spring and summer algal blooms.

Around the mid-1800s, the earliest algal blooms in the lake were reported (Norberg, 1997). Farming waned in the early 1900s, and the land was used to establish new university campuses. Construction of major roads and housing led the way to rapid population growth and development. Urbanization around the lake expanded rapidly, and direct disposal of sewage and industrial wastes into the lake started in the 1940s. Sewage disposal however, gradually diminished and was completely stopped in 1969. The water quality deteriorated and in an effort to improve it, oxygen was pumped into the hypolimnion. Water quality monitoring that started in 1974 indicates a trend towards greater water clarity and substantially diminished P, N, and chlorophyll levels. However, odors of H_2S and petroleum, and high trace element levels in sediments persist.

In LB greater accumulation of TOC after the mid-1800s resulted from enhanced primary productivity that reflects changes in the agriculture and associated soil disturbance that started in the catchment area around 1816 (Fig. 1). The high accumulation rates of TOC and N identify past episodes of increased productivity. The modest increases in all three parameters from 1863 to 1870 correspond to the historical reports of algal blooms in the mid-1800s (Norberg, 1997). Immediately above, the low TOC accumulation rate in zone 2 is however, unrelated to early diagenetic alteration. The amount of natural post-burial loss of organic carbon is likely to be less in LB because of its strong density stratification, and the presence of an oxygen-depleted hypolimnion. Archival records indicate that farming in this area waned around the early 1900s, and the land was left fallow. Algal productivity was low and forest litter was the major source of organic matter delivery into the lake. This is consistent with the high C/N values (~25). A later increase in primary productivity in the lake (in zone 3) can be related directly to the addition of sewage and industrial waste. In fact the 1950s recorded some of the highest TOC and N accumulation rates. After direct input of sewage and industrial waste into the lake stopped, and steps were taken to improve the water quality, a sharp fall in TOC accumulation rate occurred (in zone 4). The exceptionally high $\text{C}_{\text{organic}}/\text{N}_{\text{total}}$ ratios in sediments deposited from 1984 to 1989 indicate presence of woody land plant debris.

Black carbon is the highly condensed carbonaceous residue produced from incomplete combustion of biomass and fossil fuels. Accumulation rates of BC differ significantly from the TOC pattern. The highest BC levels in sediments were deposited from 1932-1954, and then they decrease starting in the early 1960s until stabilizing in the 1970s. Sweden's greater dependence on oil, hydro and nuclear energy over wood and coal since the mid-1960s (IEA, 2000) resulted in an overall decrease in BC accumulation.

General agreement between changes in trophic state and human-induced anthropogenic activities in the lake suggests that changes in $\delta^{13}\text{C}_{\text{organic}}$ values reflect shifts in paleoproductivity. Elevated lake productivity increases both TOC accumulation rates and $\delta^{13}\text{C}_{\text{organic}}$ values. The less negative Suess-corrected $\delta^{13}\text{C}_{\text{organic}}$ values in sediments deposited in 1847 and from 1932-1967 indicate that primary production was elevated at these times. ^{13}C enrichment in organic matter during periods of increased productivity can occur due to several reasons. First, algae preferentially use the lighter (^{12}C) isotope for photosynthesis, thereby depleting it, and forcing the cells to use ^{13}C for carbon fixation. Second, increased primary production may deplete the aqueous CO_2 levels forcing the usage of HCO_3^- as a carbon source (C in HCO_3^- is 8‰ heavier than C in aqueous CO_2). Lastly, as lakes become eutrophic, deeper waters and sediments experience longer periods of anoxia that leads to methanogenesis, and production of isotopically light CH_4 and heavy CO_2 (e.g., Gu and Schelske, 1996).

Changes in the corrected $\delta^{13}\text{C}_{\text{organic}}$ values in response to changes in organic matter delivery are subtle in comparison to those of C/N values. Given the fact that $\delta^{13}\text{C}_{\text{organic}}$ values of lacustrine algae and C_3 plants are mostly similar (Meyers and Ishiwatari, 1993), this is not surprising. Generally large increases in aquatic productivity are needed before the effects of selective removal of dissolved $^{12}\text{CO}_2$ become evident in sediment records. Moreover, changes in nutrient concentration and productivity may not always yield linear shifts in the $\delta^{13}\text{C}_{\text{organic}}$ values throughout the lake's trophic trajectory (Brenner et al. 1999).

When the dissolved inorganic nitrogen (DIN) pool is small, the preferential uptake of the lighter isotope by algae diminishes, and $\delta^{15}\text{N}$ values become larger. Such values appear where more negative $\delta^{13}\text{C}_{\text{organic}}$ values indicate the decreased paleoproductivity that would result from limited nitrate availability. In contrast, smaller $\delta^{15}\text{N}$ values can result from greater availability of DIN for biological utilization, and this condition stimulates primary productivity (Hodell and Schelske, 1998; Meyers and Teranes, 2001). Parts of the LB sediment record that exhibit smaller $\delta^{15}\text{N}$ values correspond to: 1) low C/N values diagnostic of algal organic matter, and 2) high TOC accumulation rates indicative of elevated productivity. Previous studies related similar concurrent shifts to lower $\delta^{15}\text{N}$ and C/N values with increased primary productivity and/or trophic state in Florida lakes (e.g., Gu et al., 1996; Brenner et al., 1999). The authors postulated that the isotopic shift might represent greater contributions of ^{15}N -depleted organic matter produced by N_2 -fixing cyanobacteria. Eutrophication in LB has indeed been related to intense cyanobacterial blooms in the mid-1900s, and even in recent years, cyanobacteria continue to overtake the siliceous algae during summer. However, the $\delta^{15}\text{N}$ values only reach 4.3‰, which

is outside the range of N_2 -fixation (-3 to 1‰; Fogel and Cifuentes, 1993). This questions the actual role of cyanobacteria in declining the $\delta^{15}N$ values. Additional factors may play a role in causing the excursions of up to ~4‰ in $\delta^{15}N$ signatures. For example, anthropogenic inputs and denitrification processes could increase the $\delta^{15}N$ values (Terranes and Bernasconi, 2000). While enhanced anthropogenic inputs from farming (late 1800s) and sewage disposal (1940-1969) have occurred in the past, the $\delta^{15}N$ values are surprisingly low (only 4 to 6‰) during these periods. Moreover, artificial aeration since 1973 should have effectively reduced water column denitrification.

Ongoing work

The same principles involving different paleolimnological proxies used in the above study in LB are also being applied in other lake systems where we are working actively e.g., Lake Marviken (Sweden), Lake Zeekoe (S. Africa), and Lakes Nainital and Sambhar (India). Our idea is to extract long cores and tie the recent historical records with long-term paleoclimate records in these lakes. Work is presently on way in this direction with drilling and extracting long cores from these geographically diverse lake systems.

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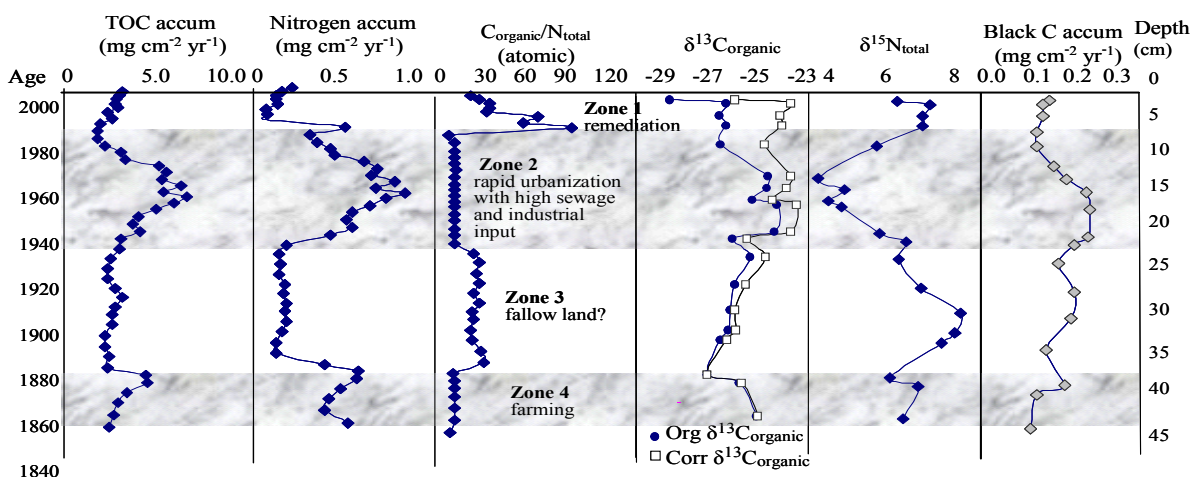


Fig. 1: Sediment geochemistry in Lake Brunnsviken, Sweden (data modified from Routh et al. 2004)

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Book Review:

Review of Volume of Abstracts and Souvenir of Second International Conference- Ground Water For Sustainable Development (IGC-2006)

The book of "Volume of Abstracts and Souvenir, IGC- 2006" has compilation of abstracts presented in "*Second International Conference Groundwater for Sustainable Development*", which was held from 1-4 February 2006 at India International Centre (IIC) in New Delhi. The book is edited by Ramanathan AL, Bhattacharya P, Chandrasekharam D, Keshari AK, Thangarajan M and Bundschuh and published by Allied Publishers Private Limited, New Delhi. This volume is divided into two categories of Oral Presentation and Poster Presentation of 246 and 74 abstracts respectively. This conference was organized jointly by School of Environmental Sciences, Jawaharlal Nehru University, New Delhi, KTH, Sweden and IIT Delhi.

The abstracts in Oral Presentation category has been distributed into seven sessions of topics having serious environmental concern like Sustainable Water Resources Assessment, Recharge process and Artificial Recharge, Groundwater Management, Water and Environment, Modelling and Its Application in Soft and hard Rock Aquifer Systems, Arsenic and Fluoride in Groundwater, and Coastal Groundwaters: Impact of Tsunami. It has large numbers of abstracts contributed by authors from India and abroad. Some of the authors are of International repute like Bundschuh J and Bhattacharya P. They have discussed on crucial issue of Arsenic and Groundwater. Their abstracts are entitled "Rural Latin America- A Forgotten Part of the Global Groundwater Arsenic Problem?" and "Mineralogy and Geochemistry of Groundwater Arsenic in the Central Gangetic Plain in Ballia District of UP, India", respectively. It is difficult to summaries each and every abstract contributed by authors in this review, few of them are like Environmental Isotopic Hydrogeochemical Investigation for Characteristics of Groundwater in Tiruvanmiyur Coastal Aquifer, Tamil Nadu, India by Shivanna et al.; Sustainable Lei-Drainage Groundwater of Rawalpindi-Islamabad (North Pakistan), and the Potentials of Recharge. Malik AH; Management of The Salalah plain aquifer, Oman by Shammass and Jacks; Local Groundwater Supply and Sanitation in Sunurban Dhaka, Bangladesh by Jacks et al. etc. All the topics mentioned above demonstrate that the organizers have worked hard to ensure a comprehensive coverage of all possible topics on Groundwater and its contamination. For this deserve full compliments, for they ably succeed in including such a wide variety of topics on ground water at one place.

Similarly, Poster presentations category also had topics of environmental concern in four main sessions, Sustainable Water Resources Assessment, Water and Environment, Modelling and Its Application in Soft and Hard Rock Aquifer Systems and Groundwater Management. Causes and Challenges of Surface Water Pollution in India, Macro and Micro Chemical Constitute in Ground Water in Sri Lanka- An Overview, Redesign of the Groundwater Level Monitoring Network in the Nyamandhlovu Aquifer, Zimbabwe etc.

This Volume of Abstracts and Souvenir, IGC- 2006 has important topics for the researchers, policy makers and planners. One may hope that book containing full papers of this important Conference would be published soon which would definitely serve the interests of the scientific community and other interested readers.

SOME RECENT PUBLICATION

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