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Biogeochemistry of shallow lake sediments: a case study from Verlorenvlei, South Africa

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Studying the biogeochemistry of shallow lake sediments, especially the source of sedimentary organic matter (OM), is challenging because of the low preservation of OM in shallow lake sediments. Here we report the source of sedimentary OM in a shallow freshwater lake, Verlorenvlei, in South Africa using a number of biogeochemical proxies. Elemental carbon and nitrogen ratio (C/N), and stable C and N isotopes ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) indicate algal source of the sedimentary OM. Total organic and inorganic C, different phosphorus fractions, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values indicate repetitive presence of non-N-fixing cyanobacteria under moderate N-limited conditions. Cyanobacterial population in Verlorenvlei is likely influenced by the availability of dissolved inorganic C. Cyanobacterial proliferation in the lake has ceased with accelerated N input as recorded at the top of the core.

Keywords: Carbon, cyanobacteria, nitrogen, organic phosphorus, shallow lakes, stable isotopes.

PRIMARY production is a major biotic process in the lakes. In-lake primary production responds quickly under stresses induced by anthropogenic activities such as external nutrients (nitrogen and phosphorus) input from

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catchments¹⁻³. Limitation of one nutrient over another can favour certain plankton species to dominate over the rest¹. Nitrogen limitation, for example, can create suitable conditions for cyanobacterial proliferation¹. To understand and predict the response of lake ecosystem to various catchment activities, and for effective management of a lake, a broader understanding of the lake primary productivity is necessary. This has made primary productivity studies using lake sediments a major research focus since the past several decades^{2,4,5}. However, such studies have mainly been conducted in deep and seasonally stratified lakes where prevailing anoxic conditions effectively preserve organic geochemical record⁴⁻⁶. Shallow lakes, in contrast, offer considerable challenges due to the rapid degradation of organic matter (OM) in the oxic water column and at the sediment–water interface⁷. The main objectives of the present study were to investigate the sources of sedimentary OM in a shallow lake, Verlorenvlei, South Africa with a focus on the variation in primary production using biogeochemical proxies such as total organic carbon (TOC), total inorganic carbon (TIC), N concentrations, different phosphorus (P) fractions, elemental ratios (C/N and N/P) and stable isotopes of C and N ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$).

The coastal lake Verlorenvlei is located near Eland's Bay approximately 180 km north of Cape Town, South Africa (Figure 1). It is one of the largest (13 km long and 1.5 km wide; catchment 1890 sq. km) shallow (mean depth 2.5 m, maximum depth 5 m), natural lakes and one of the few freshwater coastal lakes in South Africa that provides valuable freshwater resource in a marginal semi-arid coastal landscape⁸. The lake encompasses a mesotrophic freshwater system, a reed swamp and a small estuary that connects it to the sea under occasional extreme storm conditions. The lake is situated in the subtropical Mediterranean winter rainfall climate zone, although the catchment area is semi-arid to sub-arid in nature (annual average rainfall <300 mm per year)⁹. An unnamed river and its tributaries feed the lake during winter and early summer rainfall. The lake experiences free water circulation and water temperature varies from 11°C to 25°C (Table 1). The catchment comprises privately owned farmlands and natural grazing lands for sheep and cattle. Extensive ploughing occurs in the area, especially on the hills south of Verlorenvlei, and the lake is reportedly threatened by the over-exploitation of surface and groundwater by accelerated potato farming¹⁰.

Unconsolidated and low-lying sand (Tertiary to Recent), which overlies shales of Malmesbury Group, dominates the regional geology of Verlorenvlei. Sandstone outcrops of the Table Mountain Group, fine-grained rocks of the Malmesbury Group and shales of the Klipheuwel Formation are also present within the catchment^{11,12}.

Verlorenvlei is famous for its avian diversity, and has high botanical importance due to its unique position at

the transition between karroid and fynbos vegetation types^{8,11}. Marshlands are present along the main river and its tributaries. Extensive beds of emergent aquatic macrophyte and dense reed are present along the margins of the lake. Large masses of filamentous green algae (*Chaetomorpha* and *Cladophora*) and spring cyanobacterial (*Microcystis aeruginosa*) bloom have been reported to occur in the lake⁹.

For the present analysis, a 21.5 cm long sediment core from the deepest section of the lake was collected by pushing a plexiglass tube through the water column (<1 m) into the sediments (Figure 1). The tube was carefully pulled out without disturbing the upper layers. The core was transported on ice to the laboratory where it was sectioned at 2 cm intervals and the subsamples were freeze-dried. We did not find any visible evidence of bioturbation (e.g. burrows, chironomid mounds and/or epibenthic fauna) in the sediments.

Water was collected in austral winter (January) and summer (September) during a single year from the middle of the water column. All sampling bottles were rinsed at least three times with lake water before collection of the water sample. For dissolved inorganic carbon (DIC)

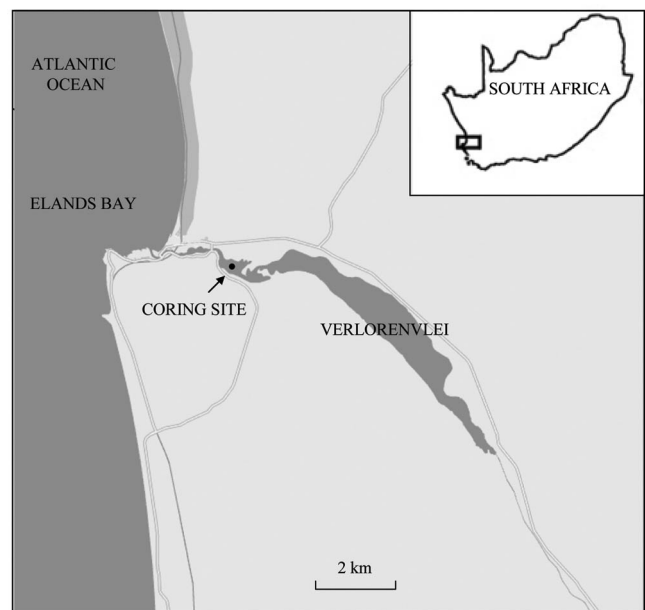


Figure 1. Location of Verlorenvlei in the Western Cape of South Africa and sampling site in the lake.

Table 1. Seasonal variations in physical and chemical characteristics in Verlorenvlei water column

	Temperature (°C)	Dissolved oxygen	pH	DIC (mg/l)
Summer	25.3	13	8.6	26
Winter	11.7	13	7.7	3

analysis, water samples were filtered using 0.45 µm Sarstedt nonpyrogenic sterile filters immediately after collection, and stored at 4°C until analysis. The filters were cleaned with deionized distilled water before use. The pH, dissolved oxygen and temperature were measured during sampling using a WTW® multi-parameter meter and associated electrodes. Each electrode was calibrated prior to the measurements.

All sample containers and laboratory glassware were pre-cleaned with P-free detergent, soaked for 24 h in HNO₃ (for P analysis) followed by rinsing with deionized distilled water. Acids, reagents and standard solutions used during the sampling, digestion and analyses were of suprapure grade.

DIC representing dissolved carbonate was analysed on a Shimadzu TOC-5000 analyser using the TOC-IC mode¹³. Sample reproducibility of duplicate runs was approx. ± 10%.

Total C (TC), TOC and N contents were measured using a LECO 932 CHNS elemental analyser (detection limit 100 µg C and precision ± 0.2%). Analyses of six replicates of internal standards provided coefficient of variation of 0.3 and 0.1 for C and N respectively. Sediments were treated with HCl to remove carbonates before analysing the TOC content. TIC represents the carbonate fraction in sediments and it was calculated by subtracting TOC from TC values¹⁴.

The $\delta^{13}\text{C}_{\text{organic}}$ in the acid-treated and freeze-dried sediments, and $\delta^{15}\text{N}_{\text{total}}$ compositions of the freeze-dried sediments were determined using a Carlo Erba 2500 elemental analyser coupled to a Finnigan MAT Delta Plus mass spectrometer. Results were expressed in the conventional delta (δ) per mille notation (‰), using the international Vienna PeeDee Belemnite limestone standard (V-PDB) for organic C and atmospheric nitrogen for total N. The results of the C and N isotope analysis are expressed according to the following formula

$$\delta (\text{‰}) = [(R_{\text{sample}}/R_{\text{standard}}) - 1] \times 1000 \quad (1)$$

where R_{sample} for C is the $^{13}\text{C}/^{12}\text{C}$ ratio of the sample and R_{standard} is the $^{13}\text{C}/^{12}\text{C}$ ratio of VPDB. For N, R_{sample} represents the $^{15}\text{N}/^{14}\text{N}$ ratio of the sample and R_{standard} is the $^{15}\text{N}/^{14}\text{N}$ ratio of atmospheric nitrogen. The precision for C and N isotope analyses was ± 0.18‰ and ± 0.06‰ respectively. Reproducibility of duplicate analyses was ± 0.1‰ and the standard deviation was <1‰.

The fractional composition of P in the freeze-dried sediments was determined by following a sequential extraction scheme that divided the sedimentary P fraction into two pools¹⁵: (i) HCl-P representing the chemical precipitate as well as adsorbed and detrital form of refractory P fraction bound to Ca (mainly apatite), and (ii) organic P (OP) representing the P fraction associated with OM. The process is described in detail by Ruban *et al.*¹⁵. The different P fractions were analysed colorimetrically on a

Hitachi U-1100 spectrophotometer using a mixed reagent (5 N sulphuric acid, ammonium molybdate, 0.1 M ascorbic acid and potassium antimonyl tartrate), and following the method of Murphy and Riley¹⁶ (absorbance measured at 880 nm). Typical precision of the duplicate run was <10%. The concentration (C in mg/g) of P (dry mass) was calculated using the following equation

$$C = \frac{SV}{1000 M} \quad (2)$$

where S is the concentration (mg/l) of P in the extract, V the volume of the reagent used for extraction (20 ml) and M is the mass of the test sample (200 mg dry mass).

Table 1 presents the water chemistry of Verlorenvlei. The lake water pH was relatively high and the lake remained oxic throughout the year⁹. DIC noticeably varied between the winter and summer seasons (Table 1).

TOC concentration (by dry weight) was 0.5–1.1% from the bottom of the core up to 8 cm (Figure 2). TOC was 0.3% between 8 and 4 cm, but the concentration increased above 4 cm and peaked to nearly 4% near the top of the core. TIC displayed (Figure 2) lower values (0.2–0.3%) at 16–18 cm and (0.3–0.4%) at 10–12 cm between peaks at 14 (0.8%) and 8 cm (1.1%). TIC was lowest at 6 cm (0.08%), but increased upwards to approx. 0.9% in surface sediments. Nitrogen concentration showed little variation and was approx. 0.1% from the bottom of the core up to 8 cm. Nitrogen was lowest (0.02%) at 6 cm and then increased upwards to reach the highest concentration (0.5%) in surface sediments (Figure 2). Atomic $\text{C}_{\text{organic}}/\text{N}_{\text{total}}$ ratio displayed alternate high (≥ 8) and low (~ 4) values from the bottom of the core up to 6 cm. The C/N ratio varied from 8 to 11 between 6 cm and top of the core (Figure 2). The mean TOC, TIC and N concentrations and C/N ratio in the sediment core were 1.27%, 0.47%, 0.17% and 7.75 respectively. The $\delta^{13}\text{C}$ value increased upwards from the bottom of the core (−21.6‰) up to 4 cm (−20.3‰), with lower value (−21.0‰) at 14 and 6 cm. The $\delta^{13}\text{C}$ decreased above 4 cm and fell to −21.4‰ at the top of the core. The $\delta^{15}\text{N}$ displayed relatively higher values (3.7‰) at 18, 14 and 2 cm and lowest value (3.3‰) in surface sediments. The mean $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values were 3.6‰ and −22.1‰ respectively.

Figure 2 depicts the results of sequential extraction of P (OP and HCl-P). The concentration of OP gently increased from the bottom of the core (1.4 µmol/kg) up to 8 cm (2.2 µmol/kg). It dropped to 0.6 µmol/kg at 6 cm followed by a sharp increase to reach the highest value (6.8 µmol/kg) near the top of the core. HCl-P concentrations were low (≤ 0.2 µmol/kg) between the bottom of the core and 16 cm; above this the HCl-P fraction was absent, except in surface sediments where the concentration was 1.1 µmol/kg. Total N/OP (N/P) ratio ranged from 27 to

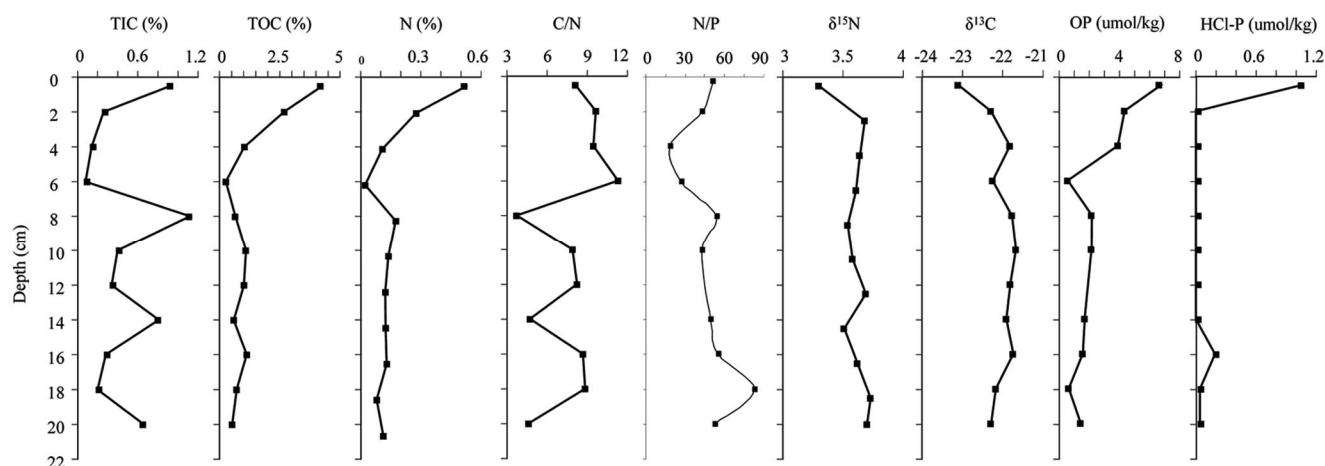


Figure 2. Depth variation of TIC, TOC, N, C/N and N/P ratios, $\delta^{15}\text{N}$, $\delta^{13}\text{C}$, OP and HCl-P fractions in Verlorenvlei sediments.

83, except at 4 cm depth where it fell to 19 (Figure 2). The mean OP, HCl-P concentrations and N/P ratio were $2.53 \mu\text{mol/kg}$, $0.12 \mu\text{mol/kg}$ and 48 respectively.

TOC represents the fraction of OM that escapes remineralization during sedimentation¹⁷. The changes in sedimentary TOC concentration are widely used as a proxy to describe the abundance and preservation of sedimentary OM, and changes in lacustrine palaeoproductivity^{2,5,18–20}. Similarly, atomic $C_{\text{organic}}/N_{\text{total}}$ ratio has been widely used to identify the sources of OM in lake sediments^{4,21}. Organic matter derived from algae shows low C/N ratios ($\sim 4\text{--}10$) due to their high protein content and absence of cellulose. In contrast, terrestrial plants are characterized by low protein and high cellulose content, and show high C/N ratios (≥ 20)^{22,23}.

In Verlorenvlei, the overall low TOC concentration from the bottom of the core up to 8 cm (Figure 2) indicates low supply of OM. This is followed by a sharp increase in TOC above 8 cm, showing an increase in OM supply. Typical $C_{\text{organic}}/N_{\text{total}}$ ratios (4–11; Figure 2) suggest algae as the dominant source of sedimentary OM. Syn- and post-depositional selective degradation of OM during early diagenesis could modify the C/N ratio of sedimentary OM²². However, a lack of systematic increase or decrease in the C/N ratio with depth implies that the ratio preserves the source signature of OM in Verlorenvlei. Our explanation is consistent with similar observations in sub-aqueous sediments²². The sedimentary OP fraction, which is higher than other P fractions (Figure 2), roughly follows the algal-derived TOC profile. This implies that the OP synthesis is controlled by in-lake primary production. Algal-derived OP is considered refractory because it consists of high-molecular-weight compounds²⁴. Hence, similar trend of TOC and OP indicates that productivity record has not been affected by early diagenesis of sedimentary OM²⁵. Moreover, the steep up-core increase in TOC and OP values above 5 cm depth suggests a progressively higher supply of in-lake

algal-derived OM. Interestingly, the C/N ratio at 16–18, 10–12 and 2–6 cm falls in the range of moderate N-limited conditions (8.3–14.6)²⁶.

Algae remove dissolved CO_2 during photosynthesis. This process increases the pH and mediates CaCO_3 precipitation²⁷. This makes the sedimentary record of TIC a useful proxy for palaeoproductivity in lakes^{18,19,28}. Lowenstam²⁹ has reported that while all types of algae are capable of precipitating CaCO_3 during photosynthesis, cyanobacteria are not efficient in this process³⁰. Therefore, the amount of CaCO_3 precipitated in sediments is not only a function of primary productivity, but also depends on the plankton species. Lowenstam's finding can be extended to Verlorenvlei, especially at depths (16–18, 10–12 and 2–6 cm), where the decline in TIC concentration (Figure 2) suggests a relative increase in cyanobacterial population over other algal species. Moderately low N/P ratios^{31,32} (Figure 2) throughout the core and previously reported cyanobacterial blooms of *M. aeruginosa*⁹ are consistent with our explanation³³. HCl-P is commonly associated with aggregation of PO_4^{3-} on algal (non-cyanobacterial) CaCO_3 cells¹⁸; their absence below surface sediments indicates low precipitation of the Ca-bound P fraction due to an insignificant non-cyanobacterial algal population. This further supports our argument of cyanobacterial proliferation under N-limited conditions^{30,34}. The dominance and repetition of non-N-fixing cyanobacteria can be explained in terms of gas vacuole synthesis and the availability of IC. Gas vacuoles in N-fixing cyanobacteria provide buoyancy and access to unlimited supply of atmospheric nitrogen^{35,36}. However, gas vacuole synthesis depends on the availability of IC (ref. 37). Overall low DIC concentration (Table 1) in Verlorenvlei should limit the formation of gas vacuoles^{36–38,39} and provide no advantage to N-fixing cyanobacteria. Our argument is supported by the reported blooms of non-N-fixing cyanobacteria, *M. aeruginosa*, in Verlorenvlei⁹. The increase in TIC and HCl-P concentrations in surface

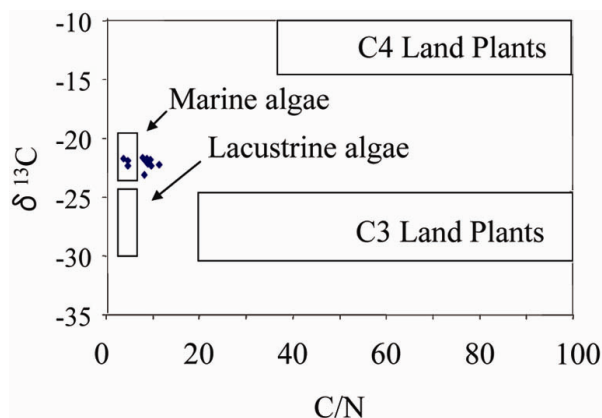


Figure 3. Relationship between C/N and $\delta^{13}\text{C}$ in Verlorenvlei sediments (after Meyers²²).

sediments (Figure 2) most likely indicates an end in the repetitive cyanobacterial dominance in the lake.

Freshwater phytoplankton has typical $\delta^{13}\text{C}$ values between -20‰ and -30‰ (ref. 40). In contrast, OM produced by C_4 plants, growing either on land or at the lake bottom, has $\delta^{13}\text{C}$ values between -10‰ and -15‰ (refs 4 and 17). Moreover, $\delta^{13}\text{C}$ is relatively unaffected by post-photosynthetic processes^{18,19}. These make $\delta^{13}\text{C}$ a popular proxy to trace OM sources and changes in the lake^{18,19,41}.

The $\delta^{13}\text{C}$ values (-22 to -21‰) in Verlorenvlei sediments (Figure 2) are consistent with the algal source character of OM as suggested by the C/N ratios, and indicate typical algal-dominated system. The relationship between C/N and $\delta^{13}\text{C}$ (Figure 3) suggesting marine algal-derived OM is justified due to the close proximity of the lake to the coast, and its occasional connection to the sea. The gradual upward increase of $\delta^{13}\text{C}$ from the bottom of the core implies a slow increase in primary production. Although reeds and emergent aquatic macrophytes (C_3 vascular plants) are abundant in the lake, we cannot determine their significance in the $\delta^{13}\text{C}$ budget of sedimentary OM because both macrophytes (-30‰ to -12‰)⁴² and lacustrine algae use isotopically identical CO_2 , present either in the atmosphere or dissolved in water^{22,42,43}.

Nitrate is the most common form of dissolved inorganic nitrogen (DIN) used by non-N-fixing species, whereas N-fixing cyanobacteria utilize N from atmospheric nitrogen. The typical (7–10%) higher $\delta^{15}\text{N}$ value of dissolved NO_3^- , in comparison to atmospheric nitrogen, helps to distinguish the N-fixing cyanobacterial source of sedimentary OM⁴. The observed $\delta^{15}\text{N}$ values (3.3–3.7‰; Figure 2) that lie outside the range of atmospheric N-fixation ($\delta^{15}\text{N}$ typically = $0 \pm 2\text{‰}$)^{44,45} represents non-N-fixing species ($\delta^{15}\text{N}$ typically $>2\text{‰}$)^{2,43,45,46} as a source of OM in Verlorenvlei. This finding is consistent with our earlier interpretation. The fall in $\delta^{15}\text{N}$ values above 18 cm most likely indicates the initiation of non-N-fixing

cyanobacterial proliferation. This change might have been triggered by the decrease in N/P ratio at these depths (Figure 2). However, the sudden drop of $\delta^{15}\text{N}$ in surface sediments is caused by the supply of $\delta^{15}\text{N}$ -depleted fertilizers from agricultural run-off⁴⁷.

Primary producers are the main source of sedimentary OM in Verlorenvlei. The lake suffers from a moderate N-limited condition where non-N-fixing cyanobacteria show a repetitive proliferation depending on the relative availability of DIC. Diminished cyanobacterial dominance recorded in surface sediments is caused by increased N input from the catchment.

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