Anthropocene

Assessing human impact on Rostherne Mere, UK, using the geochemistry of organic matter

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ABSTRACT

This study investigates recent changes in the geochemistry of organic material from a hypereutrophic lake (Rostherne Mere, United Kingdom) using the geochemical and molecular composition of radiometrically dated sediment cores. Modern samples suggest that recent sedimentation is dominated by algal production; however, a minor component of allochthonous organic material is present. Sediment cores reveal that absolute proxy values and the magnitude of observed changes are broadly homogenous across the lake basin. A transition to environmental conditions favouring enhanced algal productivity in recent sediments is suggested by higher total organic carbon (TOC) and lower carbon to nitrogen ratio (C/N), carbon isotope composition of organic matter ($\delta^{13}C_{org}$), and average *n*-alkane chain length. A strong covariance between TOC and Rock-Eval Hydrogen Index implies this transition is driven by an increasing algal contribution rather than being a response to variations in the source of organic matter. Decadal trends and abrupt shifts in organic geochemical proxies are suggested to be directly related to changes in external anthropogenic nutrient loading following the construction and decommissioning of sewage treatment plants. The development of hypereutrophic conditions likely occurred in stages, where rapid transitions are associated with the commencement of sewage effluent input in the 1930s, population increases in the 1980s, and a dramatic reduction in external nutrient loads in the 1990s. Recovery of the lake ecosystem is limited by internal nutrient recycling, and organic proxies indicate that the geochemistry of sediments has remained relatively constant since effluent diversion. This study highlights the utility of organic geochemical parameters in tracing recent eutrophication processes in lakes to provide evidence for the timing and scale of anthropogenic environmental change.

1. Introduction

Organic matter is a key biogeochemical component of lake sediment, and comprises a complex mixture of material that originates from organisms living within the lake and in its surrounding catchment. In many productive lakes, the autochthonous detritus of phytoplankton is the dominant source of organic material to sediments (Cohen, 2003), although the contribution from macrophytes and allochthonous organic matter pools, such as terrestrial plant materials and soils, can also be important (Meyers, 1997). The geochemical composition of lacustrine organic matter can be used to distinguish the source of material preserved in lake sediments and to identify alteration pathways, therefore providing information on environmental change over the history of a lake (Meyers and Ishiwatari, 1993). Many studies use established bulk geochemical proxies, including the carbon isotope composition of organic matter ($\delta^{13}C_{org}$) and carbon to nitrogen ratio (C/N), for palaeoenvironmental reconstructions (Meyers and Teranes, 2001), but these proxies cannot fully discriminate between different organic pools (Holtvoeth et al., 2016). Therefore, a combination of other techniques is needed.

Rock-Eval pyrolysis is a screening technique typically associated with determining the hydrocarbon potential of petroleum source rocks (Espitalie et al., 1977); however, the technique has more

recently been applied in palaeoenvironmental investigations to examine the organic composition of sediments from soils, wetlands, and lakes (Zocatelli et al., 2012; Khan et al., 2013; Sebag et al., 2013; Lacey et al., 2015; Newell et al., 2016). These studies highlight how Rock-Eval parameters can be used to assess the relative contributions from different sources of organic matter in sediments, and they provide evidence on the geochemical quality and degradation history of organic material. In addition, biomarkers can trace specific compounds to an individual organism, group, or process (Peters et al., 2005), enabling the recovery of detailed palaeoenvironmental information (Castañeda and Schouten, 2011). While the geochemical analysis of bulk sediment is useful for detailing general trends, biomarkers provide specific information on production, delivery, and preservation of organic sediment components (Meyers, 1997). For example, homologues of saturated, long, straight-chained hydrocarbons, the normal alkanes (*n*-alkanes), can differentiate sources of organic matter. Short-chain *n*-alkanes are typical of aquatic algae (nC_{15-21}), a large component of which are dominated by the nC_{17} alkane (Clark and Blumer, 1971; Cranwell et al., 1987). Mid-length chains (nC_{23-25}) are associated with submerged aquatic macrophytes, and longer chains (nC_{27-35}) are a dominant component of higher plants and emergent macrophytes (Eglinton and Hamilton, 1967; Ficken et al., 2000).

Organic matter from both aquatic and terrestrial sources may also be subject to mineralisation and degradation, and consequently, it is important for palaeoenvironmental reconstructions to identify the extent of alteration (Meyers and Teranes, 2001). The concentration of hydrogen in hydrocarbons is influenced by the redox conditions of the depositional environment because hydrocarbons are commonly volatile in the presence of oxygen (Cohen, 2003). Therefore, Rock-Eval proxies can provide evidence on the geochemical quality and degradation history of organic matter.

Recent eutrophication of lakes is common due to the increased input of phosphorus (P) and nitrogen (N) from effluent, agricultural runoff, and other anthropogenic nutrient sources. Eutrophication can lead to a loss of biodiversity and also directly affects the health of humans and animals through declining water quality (Krivtsov et al., 2001; Moss et al., 2005). One such eutrophic lake is Rostherne Mere in the United Kingdom (UK). Over much of the 20th century (1935–1991), the lake received effluent from a local sewage treatment works in addition to nutrient-rich runoff from surrounding farmland (Carvalho et al., 1995). The site is of international importance (designated as a National Nature Reserve, Ramsar site, and Site of Special Scientific Interest) and has a long-standing history of scientific monitoring since 1912 (Pearsall, 1923; Reynolds and Bellinger, 1992). In addition, Rostherne Mere has a well-documented history of anthropogenic catchment disturbance, making it a unique site to investigate human impact on the lacustrine environment through the organic geochemistry of lake sediments. Previous geochemical work on surface sediments and a 30 cm core collected from the deepest part of the lake suggested a high contribution of algal material to the most recent sediments (Brooks et al., 1976; Gaskell and Eglinton, 1976; Cardoso et al., 1983), although no chronological work was carried out on the core. Analysis of molecular and isotope composition of a 35-cm sediment core taken from the lake in 1993 (Prartono and Wolff, 1998) also indicated a strong allochthonous contribution in surficial sediments. Similar to previous work, no dating was carried out on the core, and end-member materials were not defined.

We present a new multi-proxy organic geochemical record from Rostherne Mere that combines total organic carbon (TOC) and total nitrogen (TN) concentrations (from which we calculate C/N), $\delta^{13}C_{org}$, Rock-Eval parameters, and biomarkers (*n*-alkanes) on radiometrically dated sediment cores. This study also uses trap

sediments, fresh vegetation, and soil samples to identify the main constituents of modern sedimentary organic matter and improve end-member characterisation, as well as evaluate the role of degradation in both anoxic and oxic environments through litter bag experiments. Our main aim was to assess quantitatively the geochemistry of recent sedimentary organic matter to provide a calibration of modern materials and to identify the primary drivers and timing of environmental change at Rostherne Mere. This assessment supports characterisation of the transition to hypereutrophic conditions and the effectiveness of remedial actions at the lake. We hypothesise that major shifts in the geochemical composition of sediments will occur contemporaneously with the introduction and cessation of sewage effluent input as a result of organic matter productivity changes due to variations in external nutrient loading. Overall, this work seeks to demonstrate the efficacy of using organic geochemistry to investigate the impact of human activity on lacustrine environments.

2. Study site

Rostherne Mere (53°20′N, 2°24′W) is the most northerly of a sequence of three meres, together with Mere and Little Mere, located 17 km southwest of Manchester in the Shropshire-Cheshire plain, UK (Fig. 1). The elongate lake basin most likely formed as a kettle hole, which deepened due to gradual subsidence caused by the dissolution of underlying salt-bearing strata following ice sheet retreat at the end of the last glacial period (Banks, 1970; Reynolds, 1979). The lake has a maximum depth of 31 m and an average depth of 14 m and covers an area of approximately 0.5 km², making it one of the largest and deepest of the Shropshire-Cheshire meres (Reynolds, 1979). The large lake volume of 6.6×10^6 m³ (Woof and Wall, 1984) produces a long water residence time of 1.5–2.7 years (Carvalho, 1993; Moss et al., 2005), although recent high resolution monitoring suggests a residence time of closer to ca. 0.8 years (Radbourne, 2018). The majority of water inflow to Rostherne Mere is from Rostherne Brook (~75%), which enters at the southwest margin of the lake and drains 7 km² of the 9-km² catchment (Carvalho et al., 1995). The remaining water input is divided between contributions from small springs and transitory drainage ditches, groundwater, and direct rainfall (Carvalho, 1993; Carvalho et al., 1995). Water output comprises evaporation from the lake surface during the summer months and river outflow through Blackburn's Brook at the southeast margin. The lake is monomictic, and thermal stratification typically arises between April and November, causing anoxia in the hypolimnion. Dissolved oxygen stratification takes place from early Summer, and peak deoxygenation occurs during late September to early October and can extend to the base of the thermocline around 12-m water depth (Davison and Woof, 1984; Scott, 2014). The stratification regime is enhanced by eutrophication, which has increased over the 20th century due to anthropogenic nutrient enrichment sourced from increased agricultural runoff and upstream sewage effluent input (Carvalho et al., 1995; Krivtsov et al., 2001). Two sewage treatment plants have discharged effluent into the lake since their construction in 1935, dominating the external nutrient load sourced from Rostherne Brook. After the sewage flow was diverted from the catchment in 1991, external nutrient loads decreased by up to 75% (Moss et al., 1997). Conversely, internal nutrient variation was relatively consistent between years, steadily decreasing until ~2002 (Moss et al., 2005), and has since stabilised, showing only minor oscillations (Radbourne, 2018). High concentrations of P and N accumulate in the hypolimnion during the spring-autumn period of stratification and anoxia and are then released and transferred to the epilimnion following overturn in late November (Carvalho et al., 1995; Scott, 2014). The substantial degree of internal nutrient loading within the basin results in high levels of primary