EUTROPHICATION AND TOXIC CYANOBACTERIA – STABLE ISOTOPES OF SEDIMENTARY CHLORINS REVEAL HISTORICAL CHANGES IN LAKE ZURICH

S. Naeher[1,2,*], H. Suga[3] , N.O. Ogawa[3], Y. Takano[3], C.J. Schubert[4], K. Grice[1], N. Ohkouchi[3]

[1] Curtin University, Australia
[2] Now at GNS Science, New Zealand
[3] Japan Agency for Marine-Earth Science and Technology (JAMSTEC), Japan
[4] Swiss Federal Institute of Aquatic Science and Technology (Eawag), Switzerland
[*] *Corresponding author: s.naeher@gns.cri.nz*

Chlorophylls are the essential pigments for photosynthesis and represent the most abundant and most important pigments on Earth (e.g., Keely, 2006). Specifically, chlorophyll *a* (Chl *a*; Fig. 1) is widespread in aquatic and terrestrial environments and represents the main pigment in algae, cyanobacteria, aquatic macrophytes and vascular plants. In the water column and the underlying sediments, the chlorophylls are subject to a large array of structural transformation and decomposition processes leading to a large variety of chlorins, such as pheophytins, pheophorbides and pyropheophytins (e.g., Keely, 2006). Despite various structural alterations, the carbon and nitrogen isotopic compositions of pigments are hardly altered during early diagenesis due to the preservation of the tetrapyrrole macrocycle, and this provides unique opportunities for the reconstruction of surface water environments and the biogeochemical cycling of both carbon and nitrogen (e.g., Ohkouchi and Takano, 2014).

In this study, we investigated the distributions and carbon and nitrogen isotopic compositions ($\delta^{13}C$ and $\delta^{15}N$ values) of chlorins in the sediments of Lake Zurich in Switzerland to reconstruct the impact of eutrophication on phototrophic communities and the biogeochemical cycles in the surface water for more than the last 100 years (Fig. 1; Naeher et al., 2016a,b). The combination of our datasets with historical information and high resolution monitoring data (since 1936) provides a unique framework to evaluate the response of compound-specific $\delta^{13}C$ and $\delta^{15}N$ signatures of pigments to environmental and climatic changes.

Despite rapid degradation of the pigments in the water column and sediments, the $\delta^{13}C$ values of the chlorins mainly followed the historical trends of eutrophication and reoligotrophication. However, $\delta^{13}C$ offsets between Chl *a* and its derivatives pheophytin *a* (Phe *a*) and pyropheophytin *a* (PPhe *a*) were due to relatively higher contributions of older, redeposited organic matter (OM), likely resulting from a high degree of sediment focusing and a lower productivity. Further, $\delta^{13}C$ values of the pigments together with bulk sediment $\delta^{13}C$ values and C/N ratios indicated that the phototrophic communities in the lake use a ^{13}C-depleted carbon source, which is mainly of aquatic origin.

The $\delta^{15}N$ values of chlorins (-4 to 4‰; Fig. 1) reflect the predominance of nitrate assimilating phototrophs, especially the toxic, non-N_2-fixing cyanobacterium *Planktothrix rubescens* prevalent during sediment deposition (Fig. 1). Historical shifts in $\delta^{15}N$ values of Chl *a* followed mostly the trends in eutrophication and reoligotrophication, but were also affected by community assemblage shifts to diatoms and/or other cyanobacteria during the eutrophication maximum in the 1970s. The low $\delta^{15}N$ values of Chl *a* since the 1990s reflect the recent oligotrophication trend, characterised by decreasing phosphate to nitrate ratios of the lake water and reduced water column mixing, which appears to be responsible for the higher persistency and predominance of *P. rubescens* in the lake. The ^{14}C age of TOC in the surface sediments revealed significant contributions of older, redistributed OM, which also explains the offsets between $\delta^{15}N$ values of Chl *a* and its diagenetic derivatives (i.e. pheopigments).

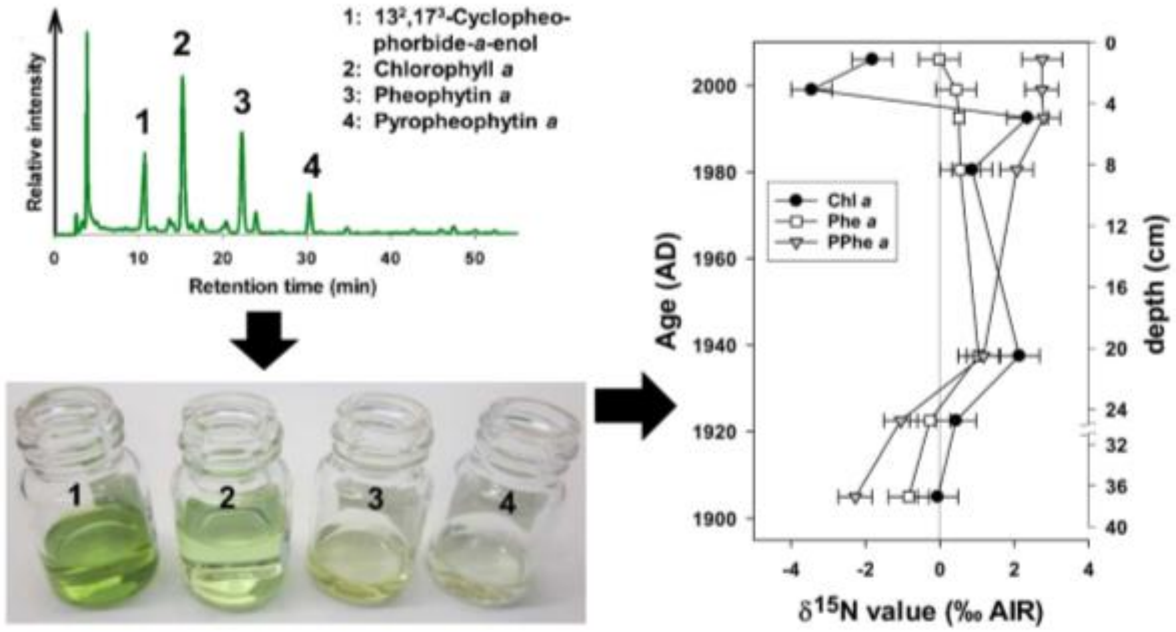

Figure 1 *Pigments were isolated by HPLC for compound-specific $\delta^{15}N$ analysis. Profiles of $\delta^{15}N$ values of pigments (chlorophyll* a*, pheophytin* a *and pyropheophytin* a*) were obtained from sediments of Lake Zurich, Switzerland (adapted from Naeher et al., 2016b)*

References

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