doi:10.2533/chimia.2014.333

Highlights of Analytical Sciences in Switzerland

Division of Analytical Sciences

A Division of the Swiss Chemical Society

Lake Sediments Tell the Story of Climate Change

Sebastian Naeher[ab], Ryan P. North[bc], Adrian Gilli[d], David M. Livingstone[c], and Carsten J. Schubert*[a]

*Correspondence: Dr. C. J. Schubert[a], Tel.: +41 58 765 21 95, E-mail: carsten.schubert@eawag.ch

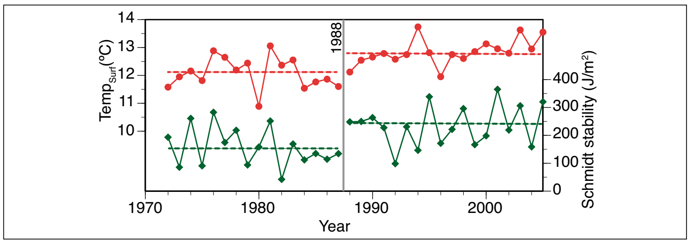
[a]Eawag – Swiss Federal Institute of Aquatic Science and Technology, Seestrasse 79, CH-6047 Kastanienbaum. [b]ETH Zurich, Institute for Biogeochemistry and Pollution Dynamics, Universitätsstrasse 16, CH-8092 Zurich. [c]Eawag, Ueberlandstrasse 133, CH-8600 Dübendorf. [d]ETH Zurich, Geological Institute, Sonneggstrasse 5, CH-8092 Zurich

Keywords: Lake Zurich · Mn/Fe ratio · Oxygen · Redox-sensitive elements · Time series

Climate change and eutrophication may both contribute to a dramatic decline in oxygen (O_2) concentrations in lakes and oceans. An analysis of Lake Zurich's 70-year dataset of monthly water column measurements revealed a clear impact of rising air temperature on the lake's water temperature and O_2 concentration. A pronounced shift to higher air temperature in the late 1980s corresponded with an increase in water temperature. Warming was greater in the lake's surface water than in the deep water, leading to an increase in water column stratification, which resulted in a general decline in bottom water O_2 concentrations.

In an attempt to extend Lake Zurich's O_2 record further back in time, a sediment core from the lake's deepest region (137 m) was analysed with non-destructive X-ray fluorescence (XRF) core scanning to obtain high-resolution manganese (Mn) and iron (Fe) element profiles. As the sediment core contains semi-annual laminations (*i.e.* similar to tree rings) dating back to 1895, the XRF data, which have a sampling resolution of 0.3 mm, provide high-resolution trace metal records. Because Mn and Fe differ with respect to their redox behaviour, the Mn/Fe ratio in sediment cores has been considered a proxy for anoxic conditions for decades, but this has never before been validated with monitoring data. Using the Lake Zurich core, we could show that the Mn/Fe ratio is moderately correlated with the measured maximum annual bottom-water O_2 concentration ($R^2 = 0.6$; $n = 66$; $p < 0.01$; 1936–2010). Sedimentary processes like the deposition of turbidites ('underwater mass movements') or diatom blooms reduce the consistency of this relationship. Although the elemental profiles are relative, normalising the Mn signal with Fe corrected for differences in porosity, water content, terrestrial inputs and calcite dilution. Based on this correlation,

Lake Zurich (copyright Zürichsee Tourismus).



The effects on Lake Zurich of a sudden climate shift in the late 1980s included increases in the mean annual surface temperature (upper curve) and in the thermal stability of the water column (Schmidt stability, lower curve).

bottom-water O_2 concentrations from 1895 to the present were reconstructed to gain insight into the impact of high external phosphorus loading on bottom-water O_2. Applying this method to cores from shallower water depths revealed a breakdown of the Mn/Fe ratio that most likely resulted from the lateral transport of redox-sensitive elements and their subsequent enrichment in the deepest part of the lake.

The Mn/Fe ratio was shown to be useful as a semi-quantitative proxy for past bottom-water oxygen concentration in Lake Zurich. Combined with monthly monitoring data, the method shows the long-term impact of eutrophication and climate on bottom-water oxygen concentrations.

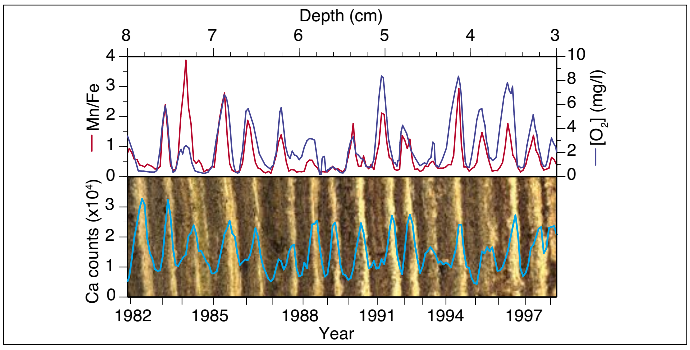
Acknowledgements

The lake data used in this study were kindly provided by the City of Zurich Water Supply (WVZ). This research forms part of project 'HYPOX', funded under the European Commission's Seventh Framework Programme (contract no. 226213).

Received: March 12, 2014

References

S. Naeher, A. Gilli, R. P. North, Y. Hamann, C. J. Schubert, *Chem. Geol.* **2013**, *352*, 125.
R. P. North, D. M. Livingstone, R. E. Hari, O. Köster, P. Niederhauser, R. Kipfer, *Inland Waters* **2013**, *3*, 341.
R. P. North, R. L. North, D. M. Livingstone, O. Köster, R. Kipfer, *Global Change Biol.* **2014**, *20*, 811.



XRF profiles of Ca (lower panel, light blue curve) and of the Mn/Fe ratio (upper panel, red) for sediments deposited in Lake Zurich from 1982 to 1998. The light sediment layers consist of $CaCO_3$ precipitated during summer. This seasonal deposition allows the Mn/Fe ratio to be aligned with the bottom-water O_2 concentration (upper panel, dark blue), which is highest during water-column turnover in spring. The Mn/Fe record captures semi-quantitatively the oxygenation of the deeper lake basin. Note that the Mn/Fe peak (in spring) precedes the Ca peak (in summer).

Can you show us your analytical highlight?
Please contact: Dr. Veronika R. Meyer, EMPA St.Gallen, Lerchenfeldstrasse 5, 9014 St.Gallen
Phone: +41 58 765 77 87, Fax: +41 58 765 77 62, Mail to: veronika.meyer@empa.ch