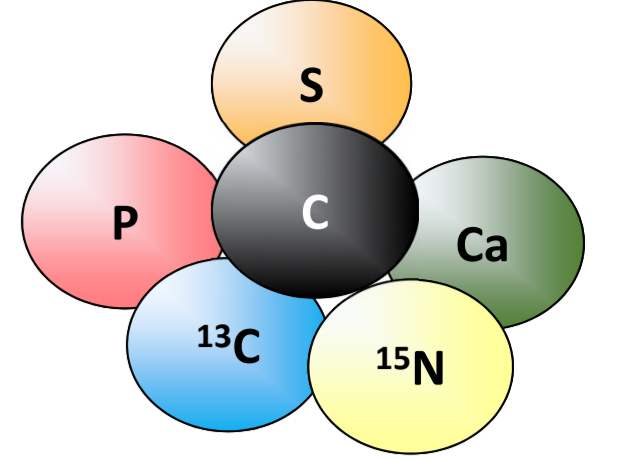


Isotope analyses to assess sediment cores from freshwater lakes in Jiangsu Region

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Introduction

The lakes in the Jiangsu province of China provide water to 30 million residents, including more than 2 million living in Wuxi. Pollution of the lakes has been ongoing for decades in spite of efforts to reduce pollution. Industrial activities in the lake region tripled, and the population increased significantly during 1980s and 1990s. In 1993 alone, one billion tons of wastewater, 450000 tons of garbage, and 880000 tons of animal waste were dumped into the shallow lake Taihu. Because of pollution the lakes in the region suffered a major algae bloom, containing also cyanobacteria, in May 2007.

Sampling and Methods

Sampling campaigns were conducted at three representative sites near the intake areas of Lake Yangcheng (Y-I) and Lake Taihu (T-I and T-CF) during March 2019. The sampling location T-I was dredged approximately 20 cm before sampling. Twelve sediment samples were collected from different vertical layers at each site. For analysis the samples were lyophilized.

Sampling location	Sampling date	Sampling depth [cm]					
SIP Yangcheng (Y-I)	29.03.2019	0-5	5-10	10-15	-	-	-
Wujiang Crab Farm (T-CF)	21.03.2019	0-6	6-12	12-18	18-24	24-30	30-31.5
Wujiang Intake area (T-I)	21.03.2019	0-6	6-12	12-18	-	-	-

Total carbon/nitrogen-Analysis (TC/TN): EA-IRMS consisting of a "Thermo Scientific Flash 2000 EA" coupled to an IRMS "Thermo Scient Delta V plus" by a "Conflow IV".

Total inorganic carbon (TIC) (only carbonates): The $\delta^{13}\text{C}$ -TIC values of the sediment were measured by HS-EA-IRMS*. The amount of TIC is calculated as the difference between TC and NDOC as well as by the isotope ratios of $\delta^{13}\text{C}$ -TIC, $\delta^{13}\text{C}$ -TC and $\delta^{13}\text{C}$ -NDOC by the following equation: $c(\text{TIC}) = (\delta^{13}\text{C}(\text{TC}) * c(\text{TC})) - (\delta^{13}\text{C}(\text{NDOC}) * c(\text{NDOC})) / \delta^{13}\text{C}(\text{TIC})$.

*The carbon isotopic composition was determined by Head-Space-Elemental analyzer - isotope ratio mass spectrometry (HS-EA-IRMS) consisting of a "HS DANI HSS 86.50" coupled with an EA "Thermo Fisher Scientific Flash 2000" and coupled to an IRMS "Thermo Fisher Scientific Delta V" by a "Conflow IV". A test tube was filled with 1.0 g Phosphoric acid (100 %) and put into the Head-Space vial. The vial was flushed with Helium, capped with a crimper and heated to 50°C until the phosphoric acid turned liquid. Before measurement, the vial was stored for 24 hours to permit all carbonates to convert to CO_2 after acid and sediment were well mixed by shaking.

Not dissolvable organic carbon/nitrogen (NDOC/NDON): The sample from the TIC analyses was diluted with 5 mL TIC-free water and then washed with 50 mL TIC-free water into a filter (LabSolute Sorte 2015, Geyer, Renningen, Germany). The sediment was dried at 50°C overnight. Samples of 5 mg were analyzed as described above (TC/TN-analysis). All samples were prepared and measured at least two times.

Non-Target-Analysis: A gas chromatograph "Agilent 6890" equipped with a qMS Agilent 5973N and parallel an IRMS "Finnigan Delta S" were used. The injection system was a thermal desorption unit "Gerstel-TDU 2" and a cold injection system "Gerstel-KAS 6". Sample separation was performed with a "MEGA-PAH" (60 m x 0.32 mm ID x 0.5 µm FD) serial to a "MEGA 5" (60 m x 0.32 mm ID x 0.32 µm FD) column.

Element-Analysis: Sediment samples were homogenized by stirring before freeze-drying (FreeZone 2.5, Labconco, Kansas, USA), sieving (<2 mm) and then milling in a vibratory disc mill (Scheibenschwingermühle TS, SIEBTECHNIK, Mülheim an der Ruhr, Germany). Finally, samples were analyzed by Wavelength Dispersive X-ray Fluorescence (WDX; S4 Explorer, Bruker, Billerica, USA) for Si, Na, Ca, K, Mg, Fe, Mn, Al, and P as well as Energy Dispersive X-ray Fluorescence (EDX; Epsilon 5, Malvern Panalytical, Malvern, UK) for S, As, Cr, Cu, Zn, Ni, and Pb.

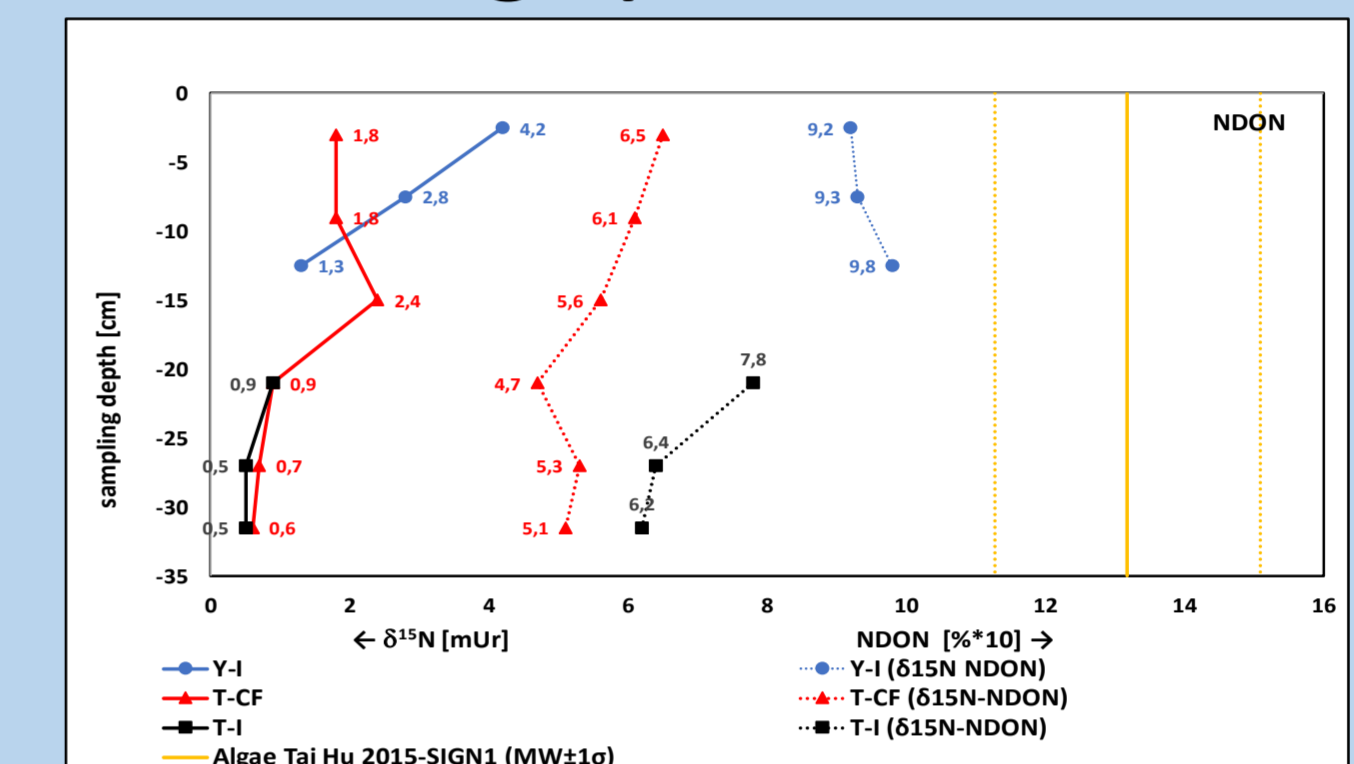
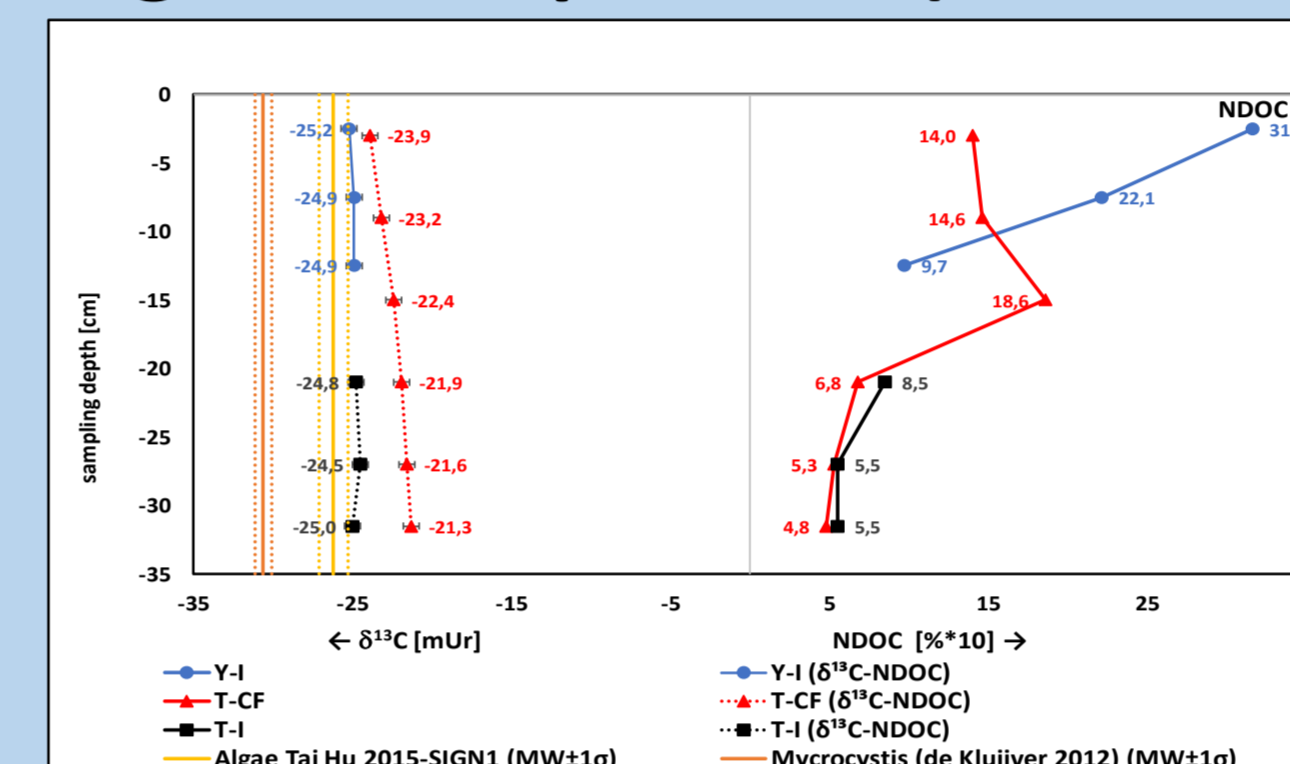
Location, geological and hydrological situation



Lake Taihu is a lake in the Yangtze Delta and one of the largest freshwater lakes in China. The lake is in Jiangsu province and a significant part of its southern shore forms its border with Zhejiang. With an area of 2338 km² and an average depth of 1.9 m it is the third-largest freshwater lake entirely in China. Lake Taihu is linked to the Grand Canal and is the origin of a number of rivers, including Suzhou Creek (Qin, 2008).

Lake Taihu is located in the South China Domain which occupies most of the South China Plate. The area is characterized by a variety of stratigraphic sequences, although two influences tend to be dominating the geology. The first one is the extensive deposition of sedimentary rocks and the second is the coastal influence induced through the proximity to the East China Sea.

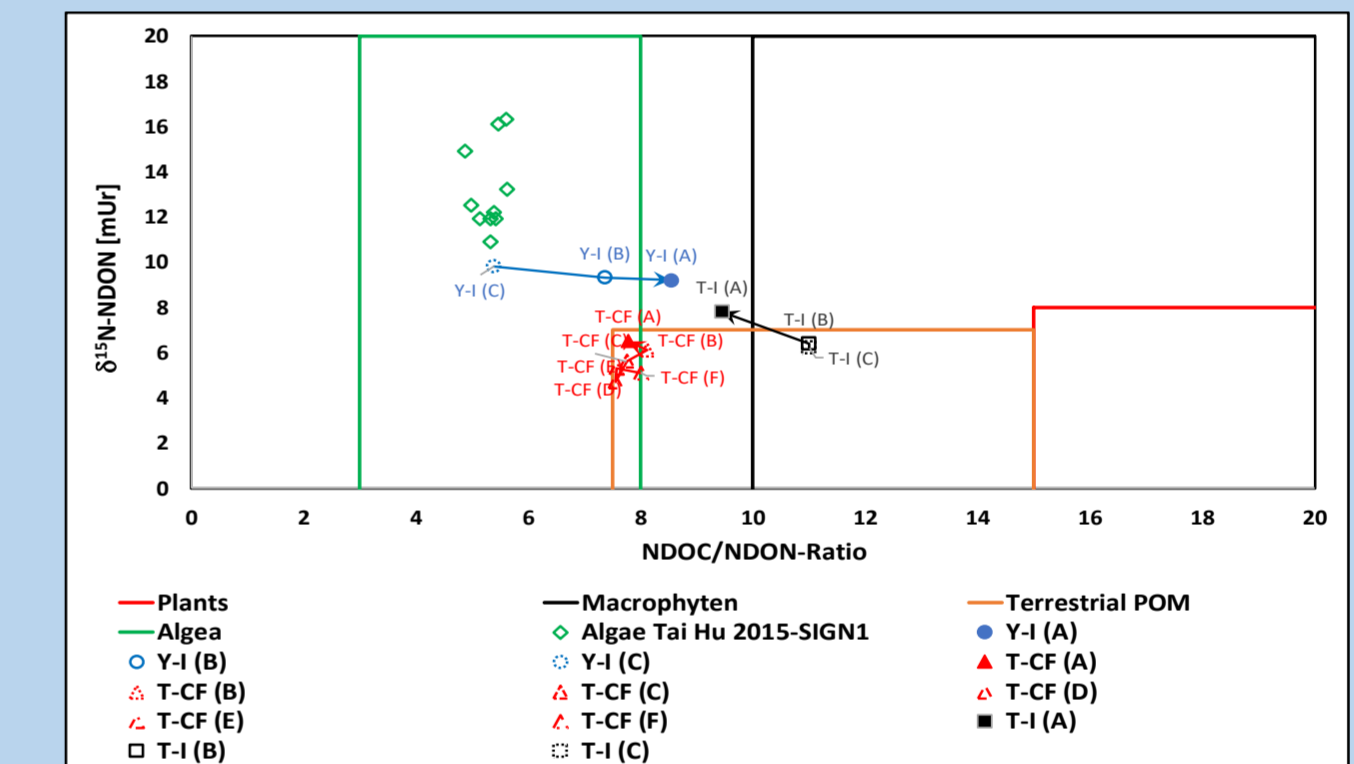
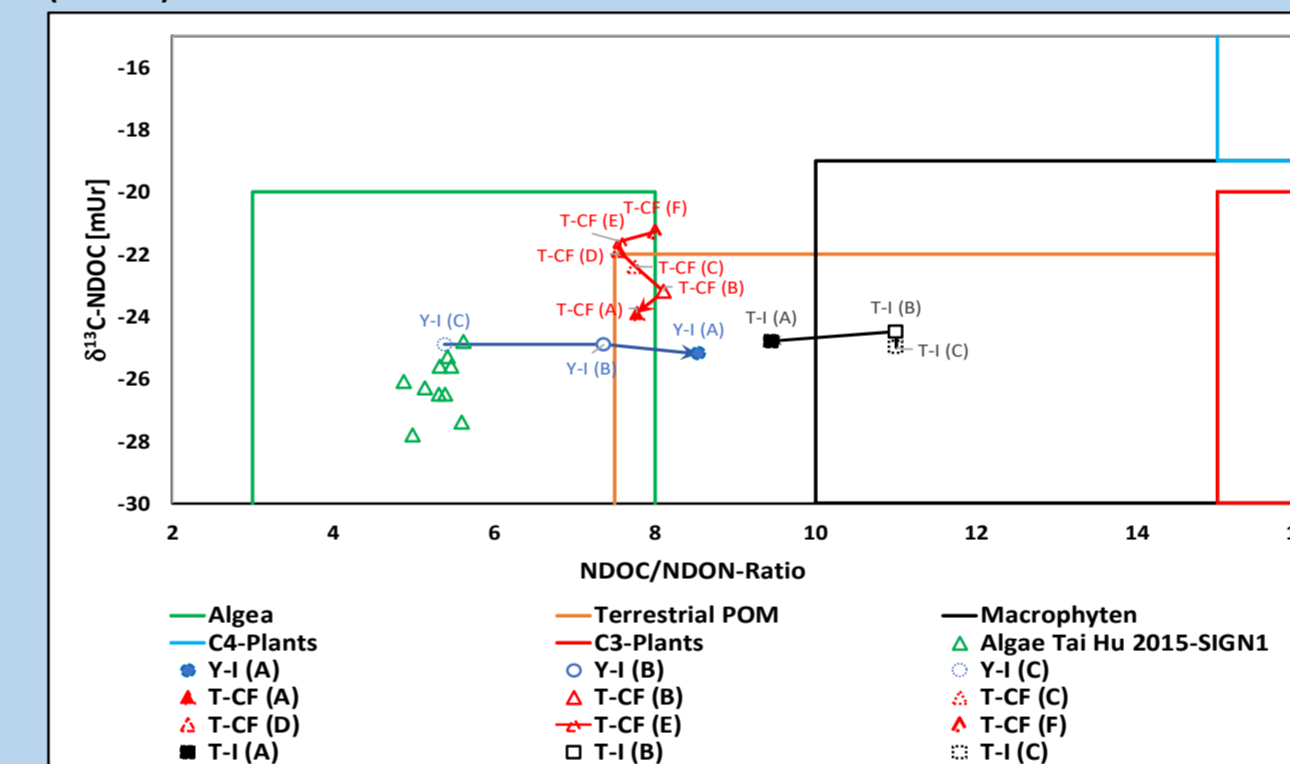
Organic composition (NDOC-NDON - Non-Target)



The NDOC-content shows a maximum for the sampling location T-CF. This maximum is in the same layer as the Ca-Maximum. Therefore, it is possible that the Ca is organically bound in extracellular polymer substances (EPS). This EPS could be produced by cyanobacteria (Liu, 2018). The NDOC-content at T-I is nearly identical to the NDOC-content at T-CF for the lower layers, in contrast the NDOC-contents at Y-I, which increases in the top layers.

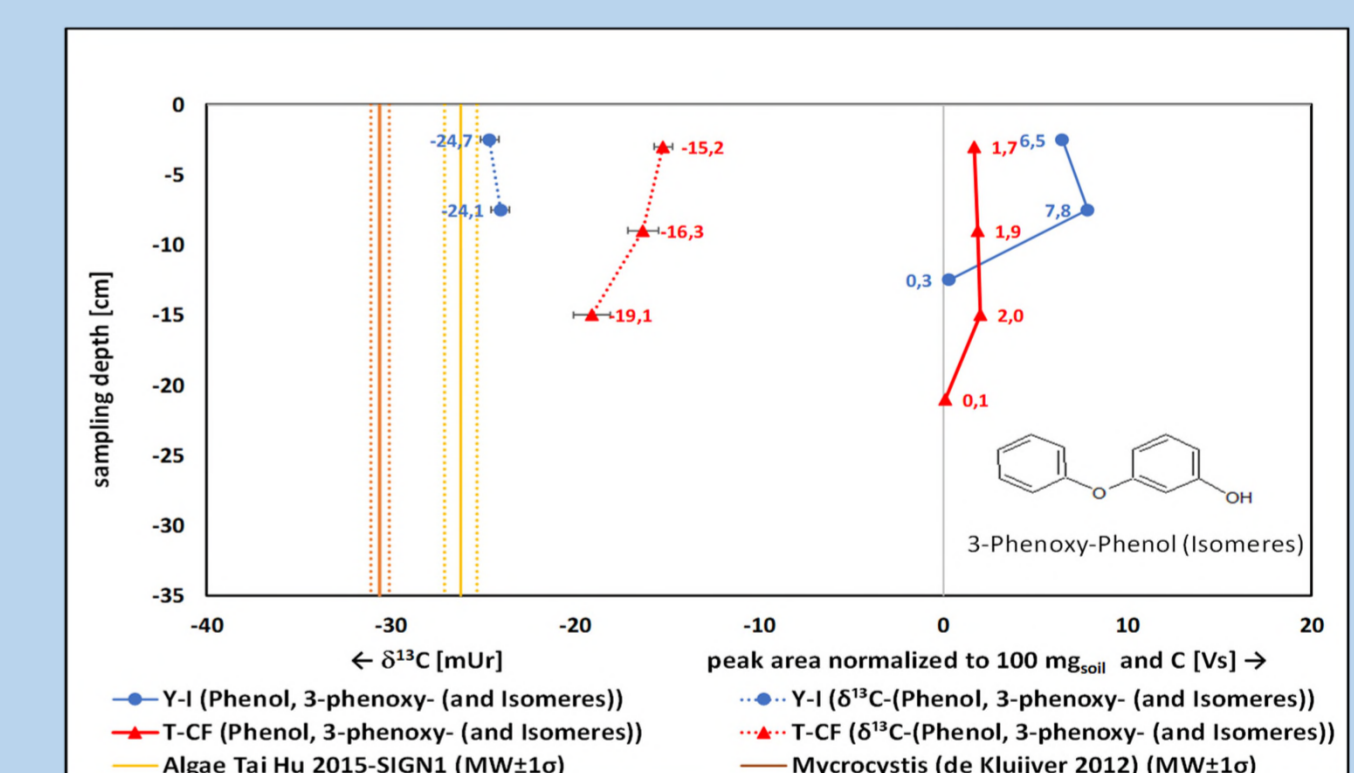
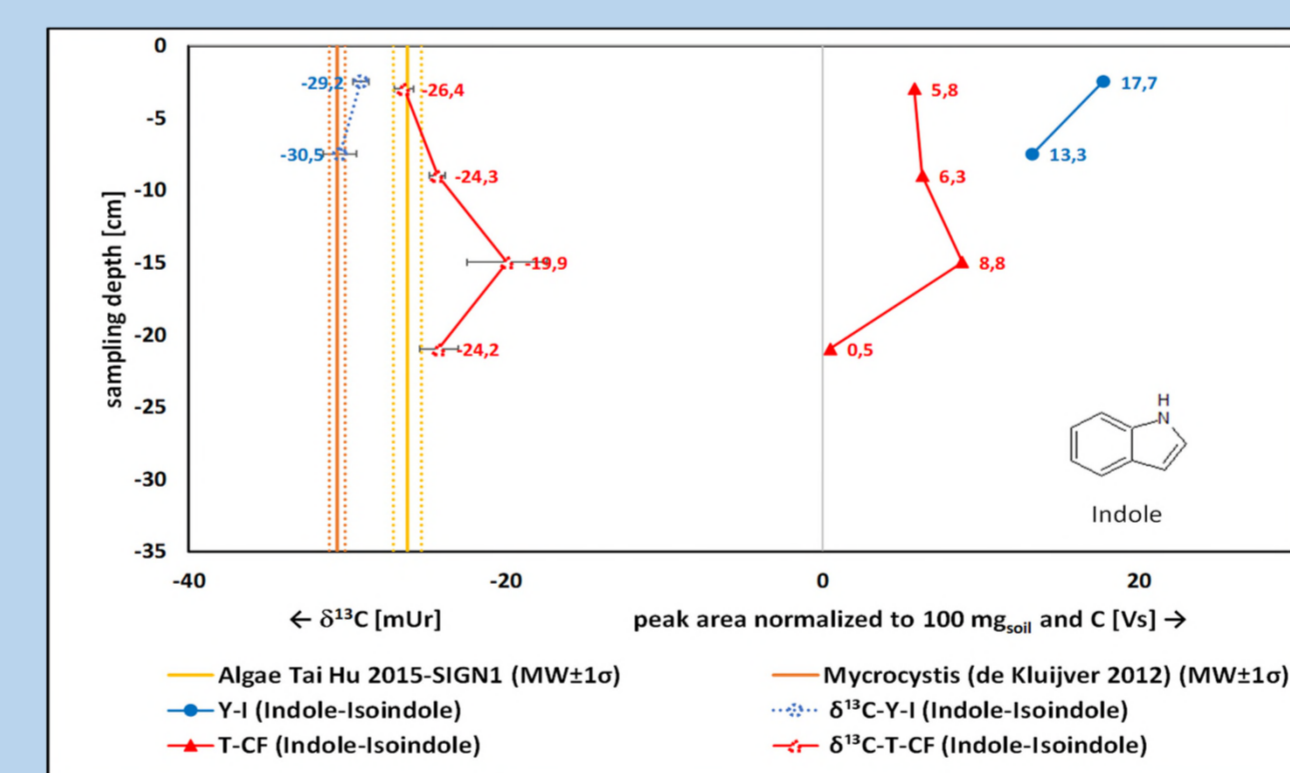
The $\delta^{13}\text{C}$ -NDOC values for T-CF show a decrease from the bottom to the top layer. This indicates a decreasing fraction of TIC to NDOC with depth (possibly caused by submerged macrophyte (Xu, 2019)). The $\delta^{13}\text{C}$ -NDOC values at T-I and Y-I show no significant change with depth and are in the range of $\delta^{13}\text{C}$ -OC values for algae or normal organic matter.

The NDON- and NDOC-content show the same functional behaviour. The sample locations T-CF and T-I show decreasing $\delta^{15}\text{N}$ -NDON values with depth. Contrary, Y-I shows increasing $\delta^{15}\text{N}$ -NDON values with depth. This indicates a change of the organic material in the sediment by depth (time).



The correlation between $\delta^{13}\text{C}$ -NDOC or $\delta^{15}\text{N}$ -NDON and NDOC/NDON-ratio provides for a better understanding of the origin of the organic matter in the sediments. The organic matter seems to be a mixture of organic matter from algae and terrestrial POM for all depths at the sampling location T-CF. The sampling location T-I is dominated by organic matter of macrophytes and terrestrial POM. The top layer seems to be dominated by terrestrial POM. This shows especially for the sampling locations T-I and T-CF a big difference between the composition of the organic matter although the spatial separation is small.

Completely different is the sampling location Y-I. The organic matter of the bottom layer is dominated by organic matter of algae while the top layer is dominated by terrestrial POM. The middle layer is a mixture of the both endmembers.

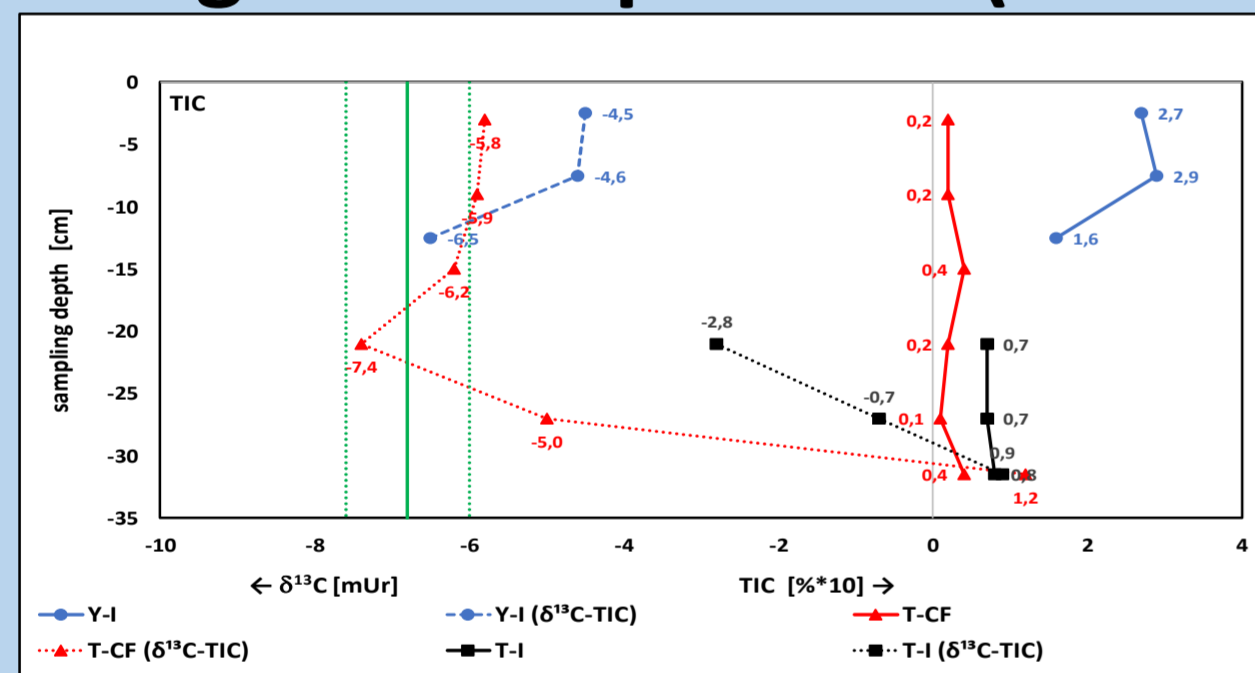


The sediments were investigated by thermal desorption. Two typical compounds of the thermal desorption are presented here. One is Indole, a compound produced from N-containing organic matter and the other is the isomer Phenoxy phenol (PhPh), a compound which is a pyrolysis product of lignin (Kaal, 2017). Only for the sampling locations T-CF and Y-I $\delta^{13}\text{C}$ values of the compounds were measurable.

Indole: The $\delta^{13}\text{C}$ values of Indole and PhPh for Y-I are in the range of $\delta^{13}\text{C}$ values of normal organic matter (C3-plant, algae, terrestrial POM or macrophytes). The $\delta^{13}\text{C}$ values at T-CF are different. The relative amount of Indole correlates with the Ca-anomaly for T-CF. The enrichment of the $\delta^{13}\text{C}$ values shows a similar functional behaviour like the Ca content. The $\delta^{13}\text{C}$ value is in the range for algae and macrophytes.

PhPh: The relative concentration of PhPh shows no correlation to the Ca-anomaly. In addition, the $\delta^{13}\text{C}$ values are highly enriched compared to PhPh for Y-I. In the top layer it seems that Lignin is dominated by C4-plants. The role of Lignin from C4-plants in T-CF decreases with depth. The results show that the sediments at T-CF have a very different history than the sediments at Y-I, indicating that the vegetation at T-CF has changed from C3-plants to C4-plants.

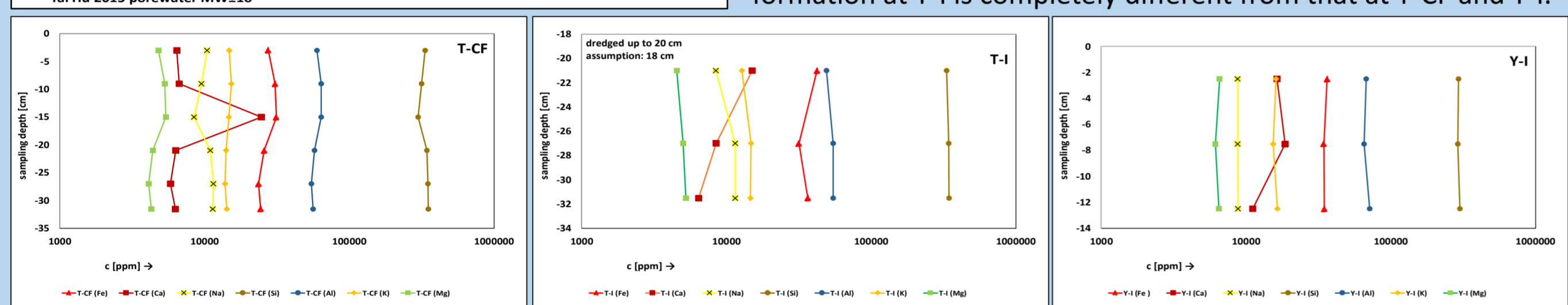
Inorganic composition (TIC - Elements)



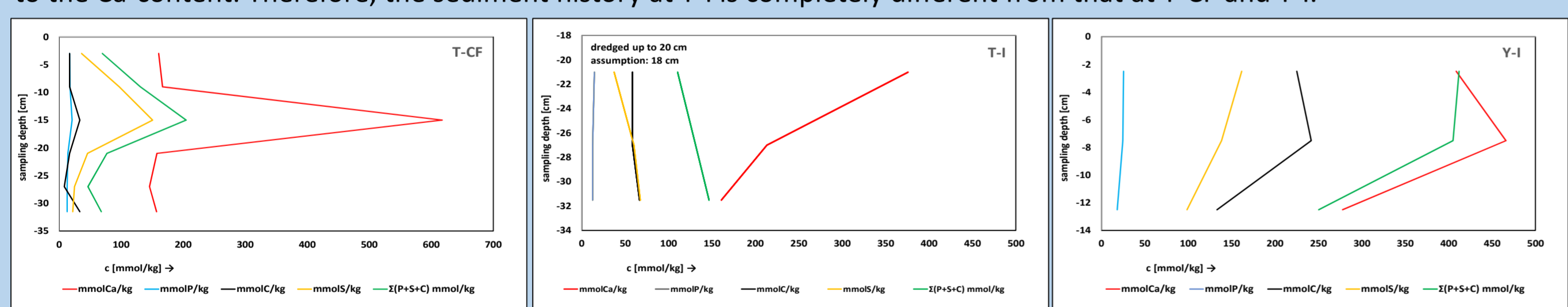
The TIC-content for the sampling locations T-CF and T-I is low as compared to Y-I.

The bottom layer at Y-I has a lower TIC-concentration as compared to the layers above. The TIC-concentrations at T-CF and T-I are nearly constant with depth.

The bottom layers at T-CF and T-I show $\delta^{13}\text{C}$ -TIC values of marine carbonates. The layers above show a larger influence of fresh water carbonates. This effect is stronger at T-CF than at T-I. On the contrary, the $\delta^{13}\text{C}$ -TIC values at Y-I show an inverse trend, with enriched $\delta^{13}\text{C}$ -TIC values in the upper layers. The TIC-formation at Y-I is completely different from that at T-CF and T-I.



For all layers at T-CF and T-I the Ca-content shows a correlation with the NDOC-content of the same functional behaviour. Only at Y-I the correlation of Ca-content with TIC is observable. Possible Ca-containing Al-silicates show no direct correlation to the Ca-content. Therefore, the sediment history at Y-I is completely different from that at T-CF and T-I.



All layers at T-CF and T-I show very low TIC-contents. For the layers at T-CF and T-I the amount of Ca^{2+} in mmol/kg should be comparable to the possible anions for precipitation (CaCO_3 , CaSO_4 and $\text{Ca}_3(\text{PO}_4)_2$). Therefore, the sum of P, S and TIC in mmol/kg should be approximately equal to the amount of Ca. In all layers at T-CF and T-I, excluding the bottom layer of T-I, the discrepancy is high. At Y-I this discrepancy is much smaller. Therefore, Ca is not precipitated as CaCO_3 , CaSO_4 and $\text{Ca}_3(\text{PO}_4)_2$. This Ca anomaly was also found by Rose (2004) and explained by the precipitation of Calcite. In this work, the low TIC-content cannot be the reason for the anomalous Ca maximum, as shown by the diagrams.

Results and Conclusions

The inorganic parameters show for most of the investigated layers a discrepancy between the possible precipitated Ca-species and the available required anions (especially carbonate). This effect is significant particularly for the T-CF core. The Ca must be complexed by organic molecules (EPS), if algae blooms are the reason for this discrepancy. In $\delta^{13}\text{C}$ -TIC analysis only the bottom layer shows marine $\delta^{13}\text{C}$ -TIC values. The other layers seem to be influenced by CO_2 produced by organic matter.

The organic parameters indicate that every core of both lakes has a completely different history of the organic matter. This is shown by the $\delta^{13}\text{C}$ -NDOC, $\delta^{15}\text{N}$ -NDON, as well as by the compound specific isotope analyses of the thermo desorption.

This investigation provides a better interpretation of the interaction between sediments and the lake water and traces the fate of organic matter in the sediment vs. time.

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