

Modeling Porewater DIC Concentrations and Stable Isotope Ratios in Freshwater Lakes

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Abstract

Pore waters extracted from lake sediments provide valuable information about environmental conditions, nutrient flow, climate history, and biogeochemical processes occurring in the sediment, as well as the overlying water column. While the chemistry of marine sediments has been studied extensively, there have been decidedly fewer studies examining early diagenesis of lake sediments, despite the important role it plays in ecosystem health and the significant impact it can have on global methane emissions. Pore water samples have been collected for Lake Wononscopomuc in Connecticut and Lough Carra, a marl lake in Ireland. Profiles have been determined for pH, alkalinity, and dissolved inorganic carbon (DIC), as well as the concentration of various dissolved species (Ca²⁺, sulfate, methane, etc.). In addition, profiles of stable carbon isotope (¹³C/¹²C) ratios have been generated for DIC and methane.

This summer, our work centered on developing explanatory models to understand the geochemical processes that produce observed DIC concentration profiles. We used the software PROFILE, developed for Berg et al. (1998), to model distinct zones of DIC and Ca²⁺ production and consumption. The program uses Fick's First Law to calculate diffusive flux and produces a very close fit with a generally small number of zones. Using our measured ¹³C-DIC values, we calculated ¹³C concentrations at measured depths and ran that data through PROFILE, which generated production rates and concentrations for ¹³C which then could be compared to our ¹³C data. For some cores, only one zone of relatively high ¹³C/DIC DIC production was required to produce a close fit to our measured values. However, it is possible that there multiple sources of DIC occurring at different depths and with different ¹³C values that produce a similar fit.

In most cores measured, ¹³C-DIC increases with depth to levels above what would be expected from decomposition of bulk organic matter, which has ¹³C values of -26 to -34‰. In Lough Carra, dissolution of calcium carbonate (CaCO₃), which produces ¹³C-DIC values between -5 and +1‰, may account for some of this isotopic enrichment, even though the porewaters are consistently supersaturated with respect to CaCO₃. Even there, the ¹³C-DIC values are too high to be explained by carbonate dissolution alone. As such, some other factor is likely at play, such as methanogenesis, which produces CH₄ with low ¹³C values (-60 to -70‰) and CO₂ with much higher values (approximately +10 to +20‰). Further study is required to determine the exact causes of the observed isotope profile.

Methods

We explored a variety of methods for modeling both the concentration and isotopic composition of DIC in the sampled sediment porewater. We assumed that the observed concentration profiles are in steady state, and not subject to significant seasonal or interannual changes. This allowed for us to calculate diffusive flux using Fick's First Law, a numerically simpler process than Fick's Second Law, which is used to solve for the change in concentration over time at a given depth in non-steady state concentration profiles.

For modeling DIC concentration, we explored the possibility of setting up a diagenetic model in Excel that incorporated production and flux, and for modeling ¹³C-DIC, we looked at using a visual programming environment such as STELLA or a mathematical modeling software such as MATLAB. In the end, however, the PROFILE software developed over 20 years ago proved effective in both cases. The software takes measured concentration of any solute as input, as well as the porosity of the sediment column and the diffusivity of that solute and produces two output files, one containing a statistical analysis of how many equally spaced zones of production and/or consumption yields the best fit, and one containing the modeled concentration given those zones of production. The software also allows for the user to incorporate bioturbation and bioirrigation, but considering that Lough Carra and Lake Wononscopomuc are both freshwater lakes, we made the assumption that any irrigation or bioturbation would have negligible effect on the profile as a whole.

$$J = -D \frac{\partial C}{\partial z} + vC + B$$

The general diagenetic equation, z represents depth below sediment-water interface, D the diffusivity (specific to a given solute), v the sediment burial velocity, C the concentration, J the diffusive flux, and B a constant for bioturbation/bioirrigation, which can be neglected for freshwater lacustrine environments.

We ran the software initially using two sets of boundary conditions: top and bottom concentration values, and values for concentration and flux at the top. We found that using top and bottom concentration values as our boundary conditions produced better fits, so we used that when running data from the rest of our cores. One other problem was finding a proper value for diffusivity for DIC, since DIC is composed of three inorganic carbon species with different diffusivity values and different relative proportions depending on the pH of pore water. We used the spreadsheet program CO2SYS to calculate the relative concentrations of CO₃²⁻, HCO₃⁻, and CO₂ at each depth interval based on our measured pH values, and then, following the approach of Clayer et al. (2018), used that data to calculate a composite diffusion coefficient for DIC in each depth interval.

We then ran our measured Ca²⁺ concentration data through PROFILE as well to see if we could model where calcium carbonate dissolution was occurring. In addition, we used The Geochemist's Workbench to calculate the saturation states of CaCO₃ for each core so we could see if zones of calcium production or consumption corresponded to zones of respective oversaturation or undersaturation. More work still needs to be done to determine the degree of correlation between saturation and production. Once we had modeled data for DIC and Ca²⁺ with PROFILE, we used DataGraph to plot that alongside our measured values.

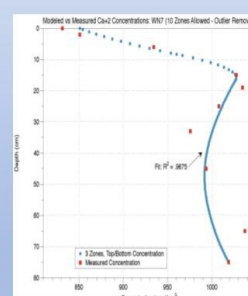
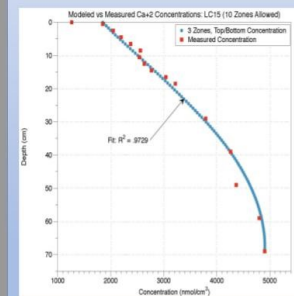
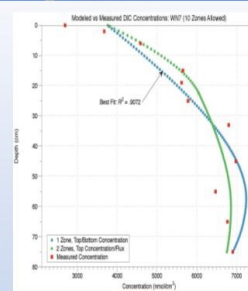
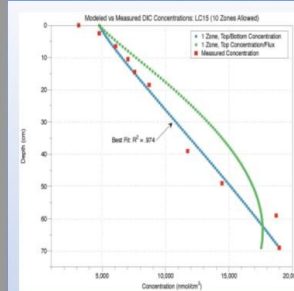


Lake Wononscopomuc



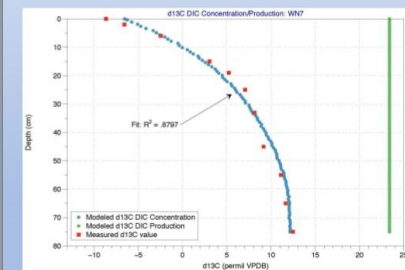
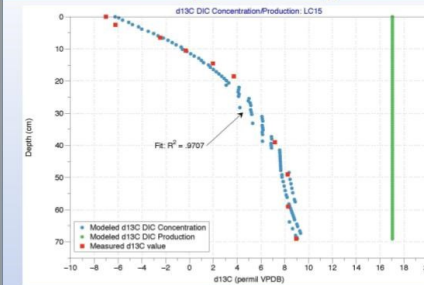
Lough Carra

Concentration Modeling Results



We modeled both DIC and calcium production and concentration using our measured pore water concentrations as inputs. Attached are the results of those model runs for cores LC15 and WN7. On several cores, we used both top/bottom concentration and top concentration/top flux as boundary conditions, but using top/bottom concentration consistently produced a closer fit, likely because it did not require the calculated flux parameter as input.

Isotope Modeling Results



Concentrations of ¹³C in each core were calculated from measured ¹³C values, run through PROFILE, and then the modeled results for production and concentration were converted back to ¹³C values using the same formula.

Calcite Saturation

The majority of the LC cores are oversaturated with respect to calcite, while the majority of WN cores are undersaturated. However, for some cores, sediment punch-in pH values were not available, potentially impeding accurate calculation of calcium carbonate saturation states.

Future Work

Many questions remain about the measured and modeled DIC profiles. It is an open question whether there is a correlation between production of DIC and calcite saturation at a given depth profile, for instance, and more accurate pH values than the ones currently available, which were calculated using titration alkalinity, are required. Additionally, more research must be conducted on the sources of ¹³C-enriched DIC, which will likely require more accurate methane concentration readings for some cores. An in-depth study on the specific chemical pathways that produce DIC in these lakes, and their corresponding isotope fractionations, is likely in order.

References

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