

This manuscript by Havas et al. presents and discusses a comprehensive dataset of DOC concentrations and $\delta^{13}\text{C}$ values from four redox-stratified Mexican lakes. They hypothesize peaks in DOC concentration are due to direct release by photosynthetic organisms, and that DOC $\delta^{13}\text{C}$ values uniquely record specific metabolic processes in phytoplankton. They then use these results to evaluate the possibility that a large DOC reservoir could explain past C isotope excursions. The manuscript is well written, thorough, and provides novel contributions to use of DOC and $\delta^{13}\text{C}$ to understand past environmental conditions. However, there are some changes which could improve the manuscript.

Notably, this manuscript appears to be a companion article to an additional study completed at the same time and on the same samples, Havas et al. (Submitted). While it is reasonable for the two manuscripts to be submitted separately, I feel that in some places the authors rely too heavily on the reader having already read Havas et al. (Submitted). I think it would be helpful if the authors were to explain early in the manuscript that these are two separate studies completed on the same samples and what data and major conclusions from the other paper are important for understanding this manuscript.

We thank the reviewer for reviewing our manuscript, and providing this positive appreciation. We agree that this manuscript relies on a previous companion paper on multiple occasions. Following the above general recommendations and specific reviewer's comment below (e.g. lines 75-82), we explicitly state in the introduction (line 87-90) that the new DOC data were measured from the same water samples and are thus comparable with previous data from Havas et al. (submitted). We indicate where necessary the data from the companion paper used for comparison.

Specific comments:

Line 72: It is mentioned how few studies have measured DOC $\delta^{13}\text{C}$ values, but does not give any context here or earlier as to why $\delta^{13}\text{C}$ values are informative and should be measured.

We agree that this aspect was lacking in the introduction. We have added a thorough description of existing literature about DOC $\delta^{13}\text{C}$ values (line 58-67).

Lines 75-82: This could be a good place to be more specific regarding new data in this manuscript vs. what is published elsewhere. The authors state what data they are reporting as new (concentrations and isotopic compositions of DOC) and list many other publications with background data on those sites. However, I think it would be helpful if they specifically note here that these are the same water samples used in Havas et al. (Submitted) and what data is used as context from Havas et al. (Submitted) (they noted DIC and POC measurements, but based on figure 2, it appears much more than that).

Additionally, it is unclear what analyses are referred to by "physico-chemical characteristics" without looking up the referenced manuscripts. Are Vilclará et al. (1993) and Zeyen et al. (2021) examples of the types of analyses referred to by "physico-chemical characteristics", or is data from those papers compared to as well as Havas et al. (Submitted)?

We thank the reviewer for this suggestion and we have indicated that DOC and DIC/POC as well as the water physico-chemical characteristics were measured from the same lakes and water samples. To clarify that the new DOC dataset is compared to specific pre-existing data from Havas et al. (submitted), we have removed the two other citations from that sentence. We also specify which "physico-chemical" parameters we rely on.

Line 185: $\delta^{13}\text{C}$ DOC was “mostly around”- could the authors be more specific? Ex: $\delta^{13}\text{C}$ DOC was $\pm 0.5\text{‰}$ from -26‰ ...

We have modified the text accordingly: “ $\delta^{13}\text{C}_{\text{DOC}}$ was $-25.9 \pm 0.4\text{‰}$ throughout the water column except...” (Line 195).

Line 245-246: The figure reference implies there is DIC And POC data in Fig. 3, which there is not.

The reviewer is correct. We have moved the reference to Fig. 3 to the end of the sentence about DOC. The reference to Havas et al (submitted) is only for DIC/POC data.

Line 248: Please provide a statistic and/or reference to where data can be found for the lack of correlation between [DOC] and salinity.

We have added R^2 and p values for the correlation between average salinity and DIC ($R^2=0.93$, $p=5.8*10^{-5}$) and DOC ($R^2=0.47$, $p=0.2$) values.

Line 277: In which lakes was the peak in oxic vs. anoxic waters? In section 5.2 it is mentioned it is possible there is an OM increase in anoxic waters due to better preservation, is this the only lake where the peak occurred in anoxic waters?

In Lake La Preciosa, a DOC peak is found only in the oxic waters. In Lake La Alberca, one peak is found in oxic and another in anoxic waters. In lakes Atexcac and Alchichica the DOC peaks are only present in anoxic waters (the increase starts in the oxycline for Atexcac).

We mention the preservation and accumulation of DOC in the anoxic waters of Alchichica in section 5.1.2. Alchichica is not the only lake where DOC increases in anoxic waters, but it is the only one where the increase could not be directly related to autotrophic production (as opposed to Atexcac and La Alberca). Therefore, the origin of this hypolimnetic DOC was interpreted as reflecting partial degradation (notably of POC) and accumulation in anoxic waters, preserving more recalcitrant DOM.

Line 312: Unclear what "different origins" refers to. DOC and POC have different origins? Or the origin of the offset is something other than a switch from CO₂ to HCO₃?

We agree that the phrasing was unclear. The “different origins” refer to what follows in the text, that is, the different possible explanations for the offset between $\delta^{13}\text{C}_{\text{DOC}}$ and $\delta^{13}\text{C}_{\text{POC}}$. We have modified the text to make it clearer (Lines 331-358).

Line 376: This paragraph (and much of the discussion above) seems to assume the reader already knows that the studied lakes have low CO₂ vs HCO₃ and local competition for CO₂. This seems important for the discussion regarding C isotope fractionation during photosynthesis, but this is the first time it's mentioned. Please elaborate on this data either in the site description (which has a brief mention of alkalinity, but no specifics) or earlier in the discussion.

We agree that this information is lacking prior to this part of the discussion. Following the reviewer's suggestion, we have added a brief notice of this important factor in the site description section: “Under these conditions, DIC is composed of HCO₃⁻/CO₃²⁻ ions with minor amounts of CO_{2(aq)} ($< 0.5\text{‰}$).” Line 112.

Line 394: A few summary/concluding sentences would be helpful for the reader.

We agree that the preceding discussion is quite dense and a summary would help the reader identify the take-home message. We have added a short summary, lines 379-384.

Section 5.1.1: nowhere in this section do the authors discuss the possibility of degradation of the hypothesized freshly produced OM by heterotrophic bacteria. At line 271, they note that oligotrophic conditions tend to inhibit heterotrophic bacterial activity and suggest this could account for the trend in DOC concentrations (lower concentrations in less oligotrophic lakes due to heterotrophic bacterial degradation), implying heterotrophic degradation should be considered. At the same time, in line 423, they note that negative $\Delta^{13}\text{C}_{\text{DOC-POC}}$ values would be expected from heterotrophic degradation of DOC, while all lakes discussed in section 5.1.1 had positive offsets. These two ideas seem to contradict each other. Please address the possibility of heterotrophic bacterial degradation in section 5.1.1 and any implications it may have for the conclusions in this section.

We have edited and clarified section 5.1.1. Because $\Delta^{13}\text{C}_{\text{DOC-POC}}$ shows (strongly) positive values for the first 3 lakes but negative ones for Alchichica, we propose different mechanisms as the origin of their respective DOC reservoirs. In section 5.1.1, we discuss how autotrophic DOC release could generate such positive $\Delta^{13}\text{C}_{\text{DOC-POC}}$ values. We have also addressed bacterial heterotrophy and photo-degradation, reaffirming why the very positive $\Delta^{13}\text{C}_{\text{DOC-POC}}$ are not consistent with these processes (326-329).

Line 426: It is unclear what this is referring to in Havas et al. (Submitted), but based on other references to this paper, it appears Havas et al. (Submitted) does not include $\delta^{13}\text{C}$ values of more labile vs refractory DOC molecules. Please reference more relevant papers which support heavier isotopic values for labile biomolecules.

We have replaced Havas et al. (submitted) with more relevant references (line 451-453).

Line 427: Please be more specific regarding what in the DIC and POM data was consistent with heterotrophic activity for readers who have not read the other paper.

The $\delta^{13}\text{C}_{\text{DIC}}$ of Alchichica decreased toward the bottom waters while $\delta^{13}\text{C}_{\text{POC}}$ increased, as expected from bacterial heterotrophic activity, which transfers light C to the DIC reservoir, while the bacterial biomass (POM) would become ^{13}C -enriched by consuming ^{13}C -rich labile organic molecules. The decreasing C:N_{POM} ratio is also consistent with that process.

We have added the DIC and POM data from Havas et al. (submitted) as requested (line 454-456).

Line 433: Unclear what this means. Was there a shift to cyanobacterial DOC found predominantly in the hypolimnion vs. other parts of the water column? Or did DOC in the hypolimnion shift to predominantly cyanobacterial origin vs. other sources?

We have now edited this sentence to clarify: "A shift of the cyanobacterial DOC from the epilimnion toward the hypolimnion of Lake Alchichica was described at the end of the spring (Alcocer et al., 2014a; 2022)". (Lines 461-462).

Lines 444-450: It's unclear exactly what the point of the paragraph is and how it relates to the section below. Perhaps it is more relevant to the start of section 5.3, explaining the large size of the DOC pool in these lakes vs. today's open ocean?

We thank the reviewer for this remark. We have moved this paragraph to the start of section 5.3.

Line 474: would be helpful to reader if this section ended with one summary sentence regarding the information potential of DOC $\delta^{13}\text{C}$ values vs. POC or DIC.

We have added a summary sentence as suggested.

Figures:

Fig. 2 caption: It is noted that the epi, meta, and hypolimnion layers are visually represented, but not described how. Please be specific that these are represented as grey shading in background (as noted in the main text)

We specified, as written in the text, that “epi, meta, and hypolimnion layers are represented for each lake by the white, gray, and dark gray areas, based on temperature profiles with the metalimnion corresponding to the thermocline”.

Fig. 3: Do these grey boxes correspond with the same depths as in Fig. 2? It is noted in Fig. 2 the grey boxes usually (but not always?) correspond with oxygen rich vs poor conditions. If these are the same, please note this. If not, it is somewhat confusing.

The shaded layers in Fig. 3 (and 4) indicate the same depths as in Fig. 2. They were drawn according to the thermal stratification in each lake (i.e. following the temperature vertical profiles) as indicated in the text. The confusion arises from the fact that the resulting epi-, meta- and hypolimnion layers correspond well to oxygen-rich, intermediate, and oxygen-poor conditions in three of the lakes, but not as closely for La Preciosa, where the oxycline layer is thinner than the thermocline (~5 vs 8 m).

To clarify this, we have added a sentence in the text: “... and correspond to the oxygen-rich, intermediate, and oxygen-poor layers in the four lakes, although the oxycline in La Preciosa is slightly thinner than the thermocline (~5 vs. 8 m).” lines 180-181. Additionally, we also clarified this point in the caption of Fig. 2 (see comment above) and refer to that figure in subsequent figure captions.

Fig. 3 & Fig. 4: it might be easier for the reader to visualize down water column trends if there were a line through the points from surface to deep.

Since these data are discrete analyses and not continuous or with a very tight sampling step, we think that the trend line is not pertinent here and will neither help the visualization of the data nor their interpretation.

Fig. 4 caption: should mention POC and DIC data for this calculation is from Havas et al. (submitted). I think it would be clearer if it read “Vertical profiles of the difference in $\delta^{13}\text{C}$ values of DOC and DIC (top)...”

We have added the reference to Havas et al. (submitted) and we changed the phrasing as recommended.

Technical corrections:

Line 151: Please be consistent with the number of decimal places and/or significant figures throughout the manuscript (here and in results).

We thank the reviewer for this remark. We have homogenized the significant figures throughout the manuscript.

Line 286: "nature of" not "nature pf" We have corrected the typo.

Lines 588-590: "Depending on the lake" is redundant considering the sentence begins with "Depending on environmental factors..." We have modified the text.