Review to "Nitrate dual isotopes and nitrification rates in central Chile"

General comments:

Recommendation: Return to author for major revisions

Scientific significance: (2): Yes, the paper is of a significant contribution and fits perfectly into the scopes of Biogeosciences, but needs improvements in the presentation.

Scientific quality: (3): Mostly yes. The authors use appropriate methods to target their scientific questions. The authors could improve their manuscript by considering more existing studies to compare with their main findings.

Presentation quality: (3): The structure of the paper needs improvement and many clarifications. In addition, the English should be improved throughout the manuscript.

General comments:

The manuscript by Choisnard et al. presents concentrations of various nitrogen compounds and related nitrate and nitrite dual isotopes to investigate the nitrogen cycling in the upwelling region off Concepción in central Chile. Based on 4 stations on the shelf plateau, their manuscript reveals a significant influence of upwelled waters on the variability between the sites. This provides valuable insights into the interaction and occurrence of the different nitrogen processes. The authors compare their results with those of other cruises conducted during different seasons, highlighting the effect of upwelling events in this region. However, the authors should consider to compare their data to other available transects in the southeastern Pacific to relate their findings to the OMZ in the Pacific Ocean or to other upwelling regions.

The manuscript describes assimilation in surface waters and denitrification in deeper waters as the main processes shaping the isotopic composition, but is only mentioned in passing. The text and title focus mostly on the process of nitrification, including the calculation of nitrification rates, which distracts the reader from the main findings.

Specific comments:

- 1) Building on the explanation in the general comments above, the title of the manuscript is too vague and too unspecific. It should at least include "upwelling" to better represent the finding of the study. The authors should think about their main message to the reader.
- 2) The use of the English language can be improved throughout the manuscript. I have indicated multiple cases in the technical corrections.
- 3) As a good scientific practice, the figure captions should include main findings of the text.
- 4) The results section can be shortened and are partly confusing to read (see more detailed comments below).
- 5) The discussion section needs a lot of clarification and can be shortened a lot. It contains many repetitions of the results and leaves the reader with many unanswered questions,

- which I will go into detail in the technical corrections. Additionally, the discussion would benefit from rephrasing to properly understand the interpretation. I would also suggest to restructure the discussion as multiple aspects are mentioned in the different sections which could be easily combined. This would allow the reader to follow the streamline more clearly.
- 6) For me, the data shows, and also how I understand the authors' interpretation is, that surface waters indicate N assimilation in surface waters and water column denitrification in the low oxygen zone. If this is the case, the manuscript describes this in a very complicated and confusing way. It should be more streamlined and concise. Related to this, it is not fully clear why it is important to calculate the nitrification rates in this region, as the authors highlight assimilation and denitrification as the main drivers of the N cycle in this region.
- 7) As primary productivity relies on both nitrogen and phosphorus, it would be interesting and important to see how the N:P ratios or N* behave along the transect.

Technical corrections:

Line 13: If enough space, I would recommend introducing the dual isotopes in the abstract: $\delta^{15}N$, $\delta^{18}O$.

Line 16: δ^{15} N-: What does the dash mean?

Line 25-26: If I understand the sentence right, it should be production, instead of productivity. To improve English: Coastal upwelling of nutrient-rich waters <u>fuels</u> high primary production and subsequent organic matter remineralization. This can result in low-O₂ waters in subsurface waters.

Line 40: I recommend to rephrase this sentence. It is not clear to me.

Line 45: The authors talk about expanding OMZs due to warming. I would suggest to include the following papers introducing a contraction and expansion of OMZs; one on deep timescales and one in the modern ocean. (Auderset *et al.*, 2022, Enhanced ocean oxygenation during Cenozoic warm periods, Nature. Duprey *et al.*, 2024, Decadel oscillations in the ocean's largest oxygen-deficient zone, Science.)

- Line 50: This is the case for the seasonal upwelling off central Chile.
- Line 52: Remove "months".
- Line 53: What is the unit of salinity? PSU? Should be provided throughout the text.
- Line 54: Please provide O₂ concentrations and nitrate concentrations as well. This helps the reader to compare the properties with the SAAW properties.
- Line 56: Related to the previous comment, could you please add the temperature and O₂ and nitrate concentrations here?

Line 58: Be more specific with the meaning of "N transformation pathways across the O₂ gradient".

Line 58-59: It feels like the sentence about NH₄⁺ and NO₃⁻ assimilation does not match with the previous statement about a decrease in PP during non-upwelling seasons. Please clarify.

Line 62: Here and also later in the paper, the authors talk about the importance of remineralization in this region. I am surprised that they only talk about NH₄⁺ accumulation and not about nitrate accumulation here as Figure 2f shows a high nitrate concentration at depth. The authors could consider to calculate the fraction of regeneration.

Line 64: It is not clear why high NH₄⁺ concentrations and nitrate assimilation fuel hotspots for fixed N removal. Please clarify.

Line 76-77: The authors use the word "depend" quite often. Please improve the English.

Line 78: Typo in "expected"; The word "vary" is not clear here, maybe rephrase as follows: its δ^{15} N is expected to be similar to the nitrogen source.

Line 80-81: Please improve the English: The difference between the N and O isotopes of NO3- along with the known isotope effects associated with specific processes allows <u>us</u> to infer which pathways...

Line 81: Typo in "influential"; "are most influential in shaping" is a vague phrasing and the meaning is not fully clear.

Lines 80-82: This sentence seems to hint towards $\Delta(15-18)$. It would be better to introduce it in the introduction than in the methods section.

Line 92: The authors refer to Table 1. Where is Table 1? Do they mean Figure 1?

Line 97/102: The authors should be more consistent with their phrasing: "onboard" vs "on board" is confusing; Improve the English: coupled to a continuous flow autoanalyzer

Line 98: What is the range of the "normal range sensor"?

Line 99: STOX sensor?; Improve the English: ", for estimating low concentrations"

Line 100: The meaning of 1to 12 cm is not clear. Do the authors mean every 1-12 cm?

Line 101-102: Improve the English: nutrient analysis <u>because</u> the pumpCTD was not deployed?

Line 104: Please add the units to the precision.

Figure 1: This Figure is not very meaningful; it could be improved in multiple directions. 1) Please increase the symbol size and the color legend. 2) Surface O₂ concentrations do not help the reader to identify the OMZ. Please choose a representative depth. 3) Authors could improve the figure by including contour lines at relevant depth for OMZ and/or bathymetry and/or indications for the upwelling (e.g., sea surface height, winds etc).

Line 118: Please put a line break after GasBench II. Additionally, it is weird to start a sentence with a number: E.g.: NO₂⁻ concentrations of 0.05 to 6.36 µmol L⁻¹ were present...

Line 123: Cite Kemeny et al., 2016.

Line 128: It is not clear how the concentrations of the international standards were chosen. "Emulating" suggests that the authors have only used one concentration of IAEA and USGS,

while 2 standards bracketing the sample concentration is typically used to better account for the $\delta^{18}O$ mass dependence.

Line 129: The standard deviation of the international standards is quite high. Therefore, I was wondering if the authors also run a reference standard in each batch. If yes, the uncertainty should also be provided for this one. The same holds true for replicate measurements of the samples themselves.

Section 2.4: I am not that much familiar with the method of nitrification rate measurements, but based on the method described here and also the referenced provided, it is not clear where the detection limit of nitrification rates come from. It seems that the nitrification rates are only calculated based on the tracer. I would suggest to provide more information about this method.

Figure 2: c): Nanomolar O₂ concentrations are not visible in the plot, an axis-break may help to identify this. Some stations show a "shading", such as station 18 in (e): Why is that? Did you conduct multiple measurements and this is the average with uncertainty?

Line 166: 1) Improve the sentence: "several hundred of nanomoles if O_2 -> per liter? 2) How deep is the bottom? This would be more visual from figure 1 if you would include the bathymetry.

Line 166-168: To help the reader, it would be good to include a threshold of O₂ concentrations to allow water column denitrification.

Line 167/Figure 2c: The authors say in the methods that the pumpCTD was not deployed at station 22. If I understood correctly, this is the reason why they do not discuss station 22 in the context of O_2 here. However, it is somewhat confusing to see O_2 concentration in Figure 2c of station 22. Please clarify.

Line 172 and throughout this section. The authors have used "dip" multiple times in the section. Please clarify meaning or use another word.

Line 175-193: These two paragraphs are confusing to read and need some clarification, and could be shortened as well.

Line 187: remove "at" offshore.

Figure 3: 1) There are no errors given for the isotope measurement. These should at least be mentioned in the methods section and ideally indicated in the figure. 2) Please be consistent with the type of legend and apply it to each figure.

Line 203/208: Please do not start a sentence with a δ .

Line 205: Improve the English: "...increase above the seabed ?to? ..."

Line 218: The evolution of nitrate $\delta^{18}O$ described here seems not fully obvious from Figure 3. Based on the figure, it seems that $\delta^{18}O$ even decreases at station 18 and are constant for station 26 relative to nitrate + nitrite. Please check.

Figure 4: 1) At first sight, the $\delta^{15}N$ and $\delta^{18}O$ appear to fall on a 1:1 line after removing the nitrite. However, when looking at the individual stations, for example station 26, the data differ from a 1:1 line. I think this deviation needs more attention and should also be

highlighted in the figure by connecting the data points of each station. 2) Please indicate the $\Delta(15-18)$ values at the grey lines. Otherwise, it is not clear what these lines represent.

Line 225: "Aside from surface samples" -> Which ones are the surface samples in Figure 4?

Section 3.3: I cannot identify the reason why $\Delta(15\text{-}18)$ and $\delta^{15}N$ of nitrite are discussed in the section of nitrification rates.

Figure 5: 1) It would be helpful to include the error bars in Figure 5a. Did the authors calculate the propagated error for this? The extreme jump to negative values in surface waters is only based on one or two data points per station and may have higher errors due to low lower nitrate concentrations. 2) Please change the axis break in Figure 5b to make the maximum nitrification rates at station 14 and 22 visible.

Line 239: This sentence is confusing and misleading. Please clarify.

Figure 6: 1) It would improve the understanding if the authors would add the error bars to this figure. The same question raises if the authors have calculated the propagated error for this?

2) Station 26 shows a 100‰ change from about 70 m to the surface and do not give an explanation for this. The most negative values occur where almost no nitrite is available, which could cause a huge uncertainty.

Line 255: Instead of "exhibited lower values", please use "negative"

Line 259: The comma between deeper and values is confusing, please rephrase.

Line 261: 1) Improve the English: "<u>The</u> most offshore station". 2) Please rephrase the sentence starting with: At this station,…

Line 266: Please extend why the understanding of the productivity in this region is important.

Line 273/Figure A1: In Figure A1, the defined temperature and salinity range of ESSW does not match with the description given here. Additionally, it is not obvious where surface water plot in Figure A1.

Line 275f: I am not specifically familiar with the OMZ in front of Chile, but by saying that the OMZ covers about ³/₄ of the water column, it is not clear if such an extent of the OMZ is only seasonal, especially during the upwelling season or if this is a permanent characteristic.

Line 277ff: This paragraph is confusing and difficult to understand. The text is not clear about how shallow the upwelled water is recorded. Does the ESSW reach the surface waters throughout the transect and it is consumed at the offshore stations or does ESSW only reach the surface in the coastal stations?

Line 283-284: 1) I would reverse this sentence: ... can be explained by higher phytoplankton uptake, as indicated by fluorescence (typo as well). 2) What is the reason for higher phytoplankton activity at that specific station?

Line 286ff: 1) This paragraph is also difficult to understand, as it contains multiple phrases that do not constitute complete sentences. 2) The authors should link their idea of changing nitrite accumulation to the abundance of nitrite- or ammonia-oxidizers. Is there any indication for this?

Line 291: It would be important to link the interpretation to the nitrate isotopes instead of discussing everything separately: the denitrification signal is clearly visible in the isotopes, which are not mentioned here, but are mentioned in a separate paragraph.

Line 298: Remove "measurements".

Line 303: It is not clear relative to what the $\delta^{18}O$ are more variable.

Line 305: Which source do the authors refer to?

Lines 305ff: Paragraph is again difficult to understand.

Line 327: There should be more discussion about the $\Delta(15-18)$.

Lines 333ff: This paragraph is confusing to understand and feels like a repetition to what have been said before.

Line 338: As the authors introduce anammox in the introduction, they should extend their discussion about it.

Line 351: Do the authors talk about isotopes here?

Line 386: Why do the authors refer to Figure A1 here? What about Figure 2a?

Line 404: Please extend the conclusions to highlight your main findings.