Peer Review Report

Manuscript ID: egusphere-2026-4372

Title: *Nitrogen fixation and atmospheric deposition influences on Mediterranean surface and intermediate water nutrient dynamics*

General Comments

This manuscript examines how atmospheric deposition and nitrogen fixation influence nutrient biogeochemistry and nitrogen isotopes in Modified Atlantic Water (MAW) and Levantine Intermediate Water (LIW). Combining dissolved organic nutrient data with nitrogen isotope measurements across the Mediterranean is valuable, particularly for a region where the sources of excess nitrogen remain actively debated. This study is interesting at least in my perspective.

My main concern, however, is that the proposed mechanisms are not yet fully clear or convincing. In particular, the chosen isotope endmembers cannot distinguish nitrogen fixation from atmospheric deposition, and the subsequent nitrogen–phosphorus budget contains several numerical inconsistencies. Furthermore, comparing summer station data against winter water-mass formation requires more careful framing. Fortunately, these issues appear addressable without new measurements—through revised calculations, sensitivity tests, and a clearer separation between direct observations and interpretations.

Major Comments

1. Isotope mass balance issues (Section 4.2; Eq. 1)

The estimated 31% contribution from newly fixed nitrogen (NFN) relies on pairing $\delta^{15}N_{new} = -1‰$ with bulk incoming MAW DON (2.85‰) to explain the isotopic signature of LIW nitrate (1.66‰). While Lines 634–637 briefly acknowledge that this signal may overlap with atmospheric deposition, Eq. (1) attributes the entire low-$\delta^{15}N$ input to nitrogen fixation, and atmospheric nitrogen is then added as a separate term in the subsequent budget (Lines 626–632). Because atmospheric DIN deposition in the eastern basin is also strongly depleted in ^{15}N (using the $-3.1‰$ value cited in the manuscript yields a 20% contribution in the same two-endmember calculation), Eq. (1) constrains a *combined low-$\delta^{15}N$ input* rather than fixation specifically. Treating atmospheric nitrogen as an independent addition on top of the isotope-derived "NFN" term therefore risks double-counting part of the same low-$\delta^{15}N$ input.

The choice of bulk DON as the background endmember also warrants further discussion. As noted in Lines 579–581, bulk DON is largely refractory, so its isotopic composition need not reflect the labile substrate actually remineralised into nitrate. Conversely, a nearly constant bulk DON concentration (Fig. 4b) does not rule out substantial gross turnover, nor does a small particulate nitrogen (PN) standing stock preclude a large cumulative flux through the particulate pool. A brief sensitivity analysis exploring plausible endmember ranges for remineralised organic matter, atmospheric deposition, and fixation would be very helpful here.

Wald et al. (2025) have demonstrated that either nitrogen fixation or atmospheric nitrogen deposition, individually or in combination, can explain the depleted nitrate isotope in the Mediterranean Sea, while partial degradation of Atlantic-derived DON may also contribute. In light of these findings, the isotope mass balance in Eq. (1) does not uniquely constrain nitrogen fixation, and the resulting 31% estimate should be presented as a scenario-dependent contribution rather than a definitive fixation fraction.

2. Reconcile the nitrogen–phosphorus budget before interpreting source magnitudes (Lines 608–641)

Several numerical steps in the nutrient budget appear to contain arithmetic or unit-conversion inconsistencies:

- In Lines 622–624, pairing the newly added N (3.92 Gmol N, derived from 0.72 μM in Line 607) with the DIP increase (0.35 Gmol P, derived from 65 nM) yields an N:P ratio of 11.2, whereas the text reports 15.4. The value of 15.4 appears to result from dividing the rounded 1 μM NFN concentration assumed in Line 618 (1000 nM/65 nM = 15.38) rather than the actual 0.72 μM estimate.
- In Line 624, the difference between the measured LIW N^* (1.1 μM) and the calculated N^* (-0.21 μM) is 1.31 μM. In the text, this concentration difference is written directly as "1.31 Gmol N (18.34 Gg N)"

without multiplying by the LIW formation volume (5.44×10^{12} m^3), which would instead correspond to roughly 7.1 Gmol N (100 Gg N).

- In Lines 627–631, applying the stated deposition range of 0.02–0.20 g N m^{-2} across 370,000 km^2 yields 7.4–74 Gg N, rather than 7.4–37.2 Gg N (unless a lower upper bound was used for the broader inflow region, which should be specified).

More broadly, comparing newly added N against the observed DIP increment alone does not determine the final N^* of LIW without accounting for pre-existing nutrient pools and physical mixing.

3. Clarify the seasonal and hydrographic basis of the LIW formation comparison (Sections 2.2 and 3.3)

While Lines 181–183 and 653–656 rightly note that the cruise took place during late spring and summer stratification whereas LIW forms during winter convection, the implications of this seasonal mismatch for the quantitative scaling in Section 4.2 need clearer framing. Because the pre- and post-formation groups combine different stations sampled on different cruise legs (May/June vs. July/August), and no isotope samples were collected directly within the Rhodes Gyre formation zone, Figure 4 represents a spatial comparison along an inferred circulation pathway rather than a direct observation of winter water-mass transformation. Scaling summer-derived concentration differences to a winter formation transport of 0.7 Sv over 90 days (Lines 608–610) is particularly sensitive to this assumption.

Please specify the exact hydrographic criteria (e.g., density or salinity bounds), sampling dates, and depth intervals used to define each group in Fig. 4, and discuss lateral mixing or seasonal evolution between legs as potential contributors to the observed contrasts.

4. Clarify sample matching and nutrient-pool calculations (Figure 2; Section 3.1)

At the western end of the MAW transect, Lines 201–205 report nitrate concentrations of 2–4 μM and DON of 5.3 ± 1 μM, while stating that DON accounts for 87% of TDN. Because 5.3 μM combined with 2–4 μM of nitrate would correspond to 57–73% DON, this apparent discrepancy likely arises from comparing broad inorganic nutrient ranges across multiple stations/depths against a smaller subset of paired DON samples (Fig. 1a). Please clarify how the means and percentages in Fig. 2b–c were calculated (e.g., whether percentages were computed only at stations and depths with paired DON measurements), as this underpins the later approximation that $\delta^{15}N_{TDN} \simeq \delta^{15}N_{DON}$.

In addition, please state the analytical detection limits for nitrate and phosphate and explain how below-detection values were treated when computing means and N^* (Lines 327–329). Finally, while the nitrate recovery check after long-term frozen storage (Lines 156–160) is reassuring, it does not directly verify the stability of DON or DOP over 10 years of storage; this caveat is worth noting briefly in Section 2.1.

5. Use gridded deposition data where feasible (Section 3.2; Table 1, Lines 318–323)

The basin-scale model statistics in Table 1 were estimated by reading six or seven points per basin off the colour bars of published maps in Kanakidou et al. (2020). While Line 307 notes that this is a rough approximation, visually sampling a small number of points from a coarse-resolution model grid makes the reported Mann–Whitney p-values difficult to interpret. Publicly available gridded TM4-ECPL deposition fields already provide monthly and annual DIN and DIP fluxes for 2010 (Myriokefalitakis, 2020; doi:10.5281/zenodo.4017209). Although remapped for an ocean model and representing 2010 rather than the 2008 simulation shown in Kanakidou et al. (2020), they derive from the same modelling framework.

I suggest either requesting the original 2008 gridded fields from the authors of Kanakidou et al. (2020) or computing basin medians directly from the publicly available 2010 gridded dataset (after checking consistency in chemical species and units). If visual estimates from the published maps are retained, I recommend removing the formal Mann–Whitney p-values for the modelled columns in Table 1 and simply reporting the approximate ranges read from the maps.

Minor Comments

1. **Lines 16–17 and 25:** N^* is a stoichiometric concentration anomaly (in μM), not an alternative expression for the molar N:P ratio. Please keep the terminology distinct.

2. **Lines 176, 178, and 185:** In-text references to Figure 2 for station locations and circulation pathways appear to refer to Figure 1 (or Figure 4a). Please check the figure numbering.
3. **Line 138 and Fig. 1 caption:** Please define "DOCN concentrations" (dissolved organic carbon and nitrogen?) or refer specifically to DON/TDN.
4. **Figure A3 caption (Line 694):** "chapter 3" –> "Section 3.2"?
5. **Figures 1, 2, and 6:** Several station numbers and circulation labels in Fig. 1 are difficult to read at print scale. In Fig. 2b–c and 2g–h, adding markers for the actual sampling locations along the distance axis would help readers see where organic and isotope measurements are sparse relative to inorganic nutrients. In Fig. 6, please annotate the fitted equations on the panels or in the caption.

References Relevant to the Comments

Kanakidou, M., Myriokefalitakis, S., and Tsagkaraki, M. (2020). Atmospheric inputs of nutrients to the Mediterranean Sea. *Deep-Sea Research Part II*, 171, 104606. doi:10.1016/j.dsr2.2019.06.014.

Myriokefalitakis, S. (2020). Atmospheric deposition fields of nutrients (N, Fe, and P) [Dataset]. Zenodo. doi:10.5281/zenodo.4017209.

Wald, T., et al. (2025). Origins of the Nitrate ^{15}N Depletion in the Mediterranean Sea. *Global Biogeochemical Cycles*, 39, e2023GB008035. doi:10.1029/2023GB008035.