Manuscript "*Neodymium budget in the Mediterranean Sea: Evaluating the role of atmospheric dusts using a high-resolution dynamical-biogeochemical model***"**

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Dear Pr. A. Mazumdar

We would like to thank you for providing us the opportunity to revise our manuscript, and we would like to thank Reviewer 1 for taking the time and effort necessary to review the manuscript. We sincerely appreciate all valuable comments and suggestions, which helped us to improve the quality of the manuscript (ms hereafter).

Color code
Editor/Reviewer
Authors response
Change in the manuscript (ms)

Anonymous Referee #1

Ayache et al. present a revised implementation of the marine neodymium cycle in the high-resolution regional ocean model NEMO-PISCES for the Mediterranean Sea that forms the natural extension of previous work with less complex implementations. The authors now consider sediments, rivers, and dust as sources of Nd, and they assess their respective contribution and impacts via a number of sensitivity experiments. Similar to other recent studies, Ayache et al. come to the conclusion that sediments are the major source of Nd to the oceans also in the Mediterranean Sea. They further find that despite contributing only ~5% to the total Nd flux, dust plays a critical role for surface and intermediate Nd concentrations and isotopic compositions substantially improving the mismatch to observations.

Overall, the manuscript is well-written, but the figures require some improvements. The findings are in agreement with previous studies, and the new implementation in such a high-resolution regional ocean model will surely be a good test-bed for future investigations further elucidating the marine Nd cycle. However, some aspects remain unclear and require clarification as I outline below.

We thank the Reviewer for his/her interest in the manuscript and for highlighting the main points that should be considered for the revision. We have now significantly revised our manuscript, and we have restructured and rewritten it to give a clear general overview of the model and our modelling approach.

Main points

I think it would be helpful to give a brief description of the modern/simulated circulation in the Mediterranean Sea in the introduction, as not everyone may be familiar with the details of it. This would further allow for a more robust assessment of the applicability of Nd isotopes as faithful water mass tracer in the Mediterranean Sea later on that is currently missing.

We agree with this suggestion that not everyone may be familiar with the modern circulation in the Mediterranean Sea. Hence, we have added a brief description of Mediterranean Sea circulation in the revised ms (see below).

"The Mediterranean is a concentration basin in which evaporation exceeds precipitation and river runoff. Warmer, fresher water enters at the surface from the Atlantic (Atlantic water – AW) through Gibraltar and colder saline water leaves below. The Levantine Intermediate Water (LIW) represents one of the main water masses of the Mediterranean Sea. It spreads throughout the entire Mediterranean basin at intermediate depths (between ∼ 150 and 700 m) (Pinardi and Masetti, 2000). The LIW participates in the deep convection processes of the western Mediterranean deep water (WMDW) occurring in the Gulf of Lion and in the Adriatic sub-basin for the eastern Mediterranean deep water (EMDW) (Millot and TaupierLetage, 2005)."

Why was no tuning of the Nd cycle parameters performed for this study, not even of unconstrained parameters of internal cycling? If this is too computationally expensive, this should be mentioned in the text also highlighting the downsides of an "un-tuned" Nd module with partly only poorly constrained parameters.

We agree with the referee that tuning the parameters of internal cycling of Nd cycle would give interesting information on the simulation and Nd oceanic cycle. However, internal Nd cycle depends on multiple quantities: particle fields (POCs, POCb, CaCO3 and BSi), partition coefficients (Kd) and settling velocities (w). Consequently, this issue requires to run many simulations which is not possible with our high-resolution model because it is too computationally expensive.

Moreover, there is currently not enough data to constrain the partition coefficients for all kinds of particles (POCs, POCb, CaCO3 and BSi). We have then carried out selected sensitivity tests to assess the impact of the processes on the Nd distribution and reach a better agreement with the observations. The best compromise was found by increasing only the partition coefficient for the small particles (*cf.* Figure A1).

We have tried to clarify and better justify the motivation of this choice in the revised manuscript.

"*We carried out sensitivity tests to assess the impact of this process on the Nd distribution and try to reach a better agreement with the observations. The best compromise was found by increasing only the partition coefficient for the small particles (cf. Figure A1). Internal Nd cycle depends on several parameters, particle fields* (POCs, POCb, CaCO3 and BSi), partition coefficients (Kds) and settling velocities (w). *Running many simulations for tuning these parameters is out of reach with the high computational cost of our high-resolution model."*

There appears to be no impact of riverine Nd to the Nd concentrations even at the surface. Even though in the text it is mentioned that there are small differences in the catchment areas, they are not visible in Fig. 3. I would have expected at least a visible difference close to the estuary of the Nile river. Since previous studies described the Nile as an important Nd source, I think the lack of a clear imprint thereof warrants a more detailed discussion of this.

The referee is right, the Nile has a very important impact on the Nd concentrations and the Mediterranean Sea circulation (e.g. during the Sapropel events for example). However, the construction of the Aswan High Dam had a major impact on the water discharge of Nile river (drastically reduced after 1964). River and runoff discharge forcing for the historical period are derived from the model of Ludwig et al. (2009) and the inter-annual data set of Vörösmarty et al. (1996). The detectable impacts of river discharge on modelled Nd concentration were limited to the areas near the catchment of the main rivers. This is clearly visible for the surface waters in the vicinity of the Rhone river mouth (see the difference between the red and green line in the surface water, Fig. R1). Finely, it is worth noting that the influence of river sediments is implicitly integrated in the BE term.

Changes were made in the text to clarify this point and we will introduce a new figure in appendix Fig. A6 (see below).

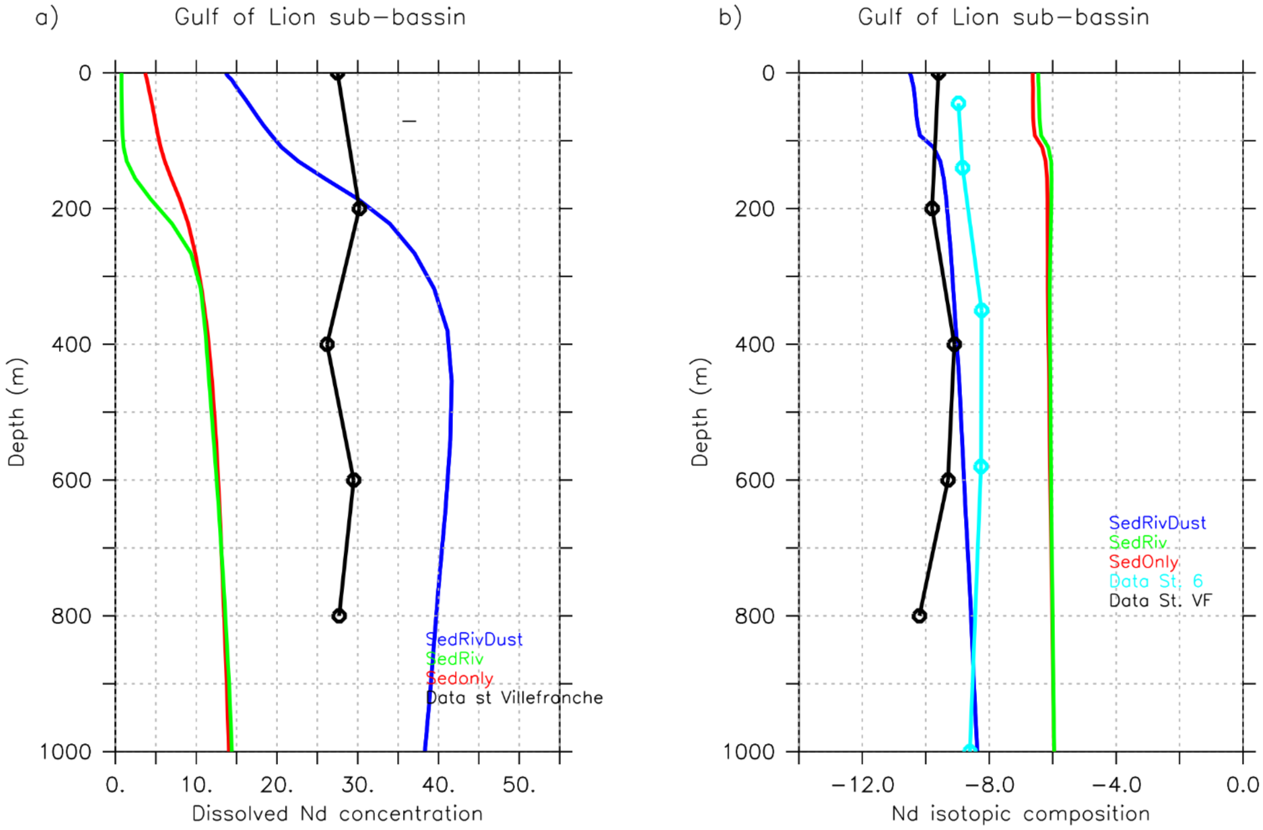

Figure R1: Comparison of the vertical profiles between in-situ data (from Henry et al. (1994)) and model output for: a) [Nd] (in pmol/kg), εNd in b).

“*The impact of river discharge on Nd concentration are limited to the areas near the catchment of the main rivers, i.e. the Rhone river. Almost all the main rivers presented* *a significant discharge decreases (Ludwig et al., 2009) as a consequence of massive dam constructions (e.g. Aswan High Dam for Nile river). The detectable impacts of river discharge on modeled Nd concentration are limited to the areas near the catchment of the main rivers, i.e. the Rhone river where the impact is clear in the surface water (see Fig. A6). Finely, it is worth noting that the influence of river sediments is implicitly integrated in the BE term"*

Why does the dust flux generate a subsurface Nd maximum? If it is related to the subsurface production than this subsurface maximum should also emerge for the other simulations. Further, in line 283 it is mentioned that this subsurface maximum of experiment SedRivDust is also found in the observations, however, the depth profiles of Fig. 5 show a rather constant vertical profile with no pronounced maximum in the subsurface. In addition, as mentioned in line 359, it is paradoxical that such a small Nd flux by dust can increase the Nd concentration by so much. This paradox is not resolved in the text, and requires more in-depth investigation due to its great impact on the Nd cycle. In particular, it is very surprising to me that the riverine flux has virtually no impact on the surface and intermediate Nd concentrations, while the dust flux has a very large impact, while both sources are similar in magnitude (3.7% versus 5.3%).

We agree with this remark. It seems paradoxical, to see a such impact of atmospheric dusts while it represents only 5.3 % of the total Nd and that the riverine flux has virtually no impact on the Nd concentration in the surface and intermediate water of the Mediterranean Sea (as mentioned in the text line 358-366). We performed sensitivity test simulations to better understand the influence of these inputs on the Nd oceanic cycle, *i.e.* on the dissolution rates of particulate Nd from atmospheric dusts, and on the spatial distribution of [Nd] and εNd in atmospheric dust (cf. Section 2.5).

Effectively, considering atmospheric dust inputs largely improved our simulation of the Nd oceanic cycle, with more realistic simulations of εNd and [Nd] in the main water masses of the Mediterranean Sea, due to its almost landlocked situation highly affected by dust deposition from the Sahara and Middle East. It also generates a maximum in subsurface water, also detected in some in-situ data, as shown in Fig. R2, especially in the Ionian and Algerian sub-basins.

The high impact of atmospheric dust is explained by its injection that covers a large area over the Mediterranean Sea, where the deep chlorophyll maximum (DCM) is present, and constitutes a well-documented structure (Cullen, 1982) with high particle concentration (Annexed figure A5) where Nd can be adsorbed and maintained in the water column; while river flow and BE only affect coastal regions where DCM is not present.

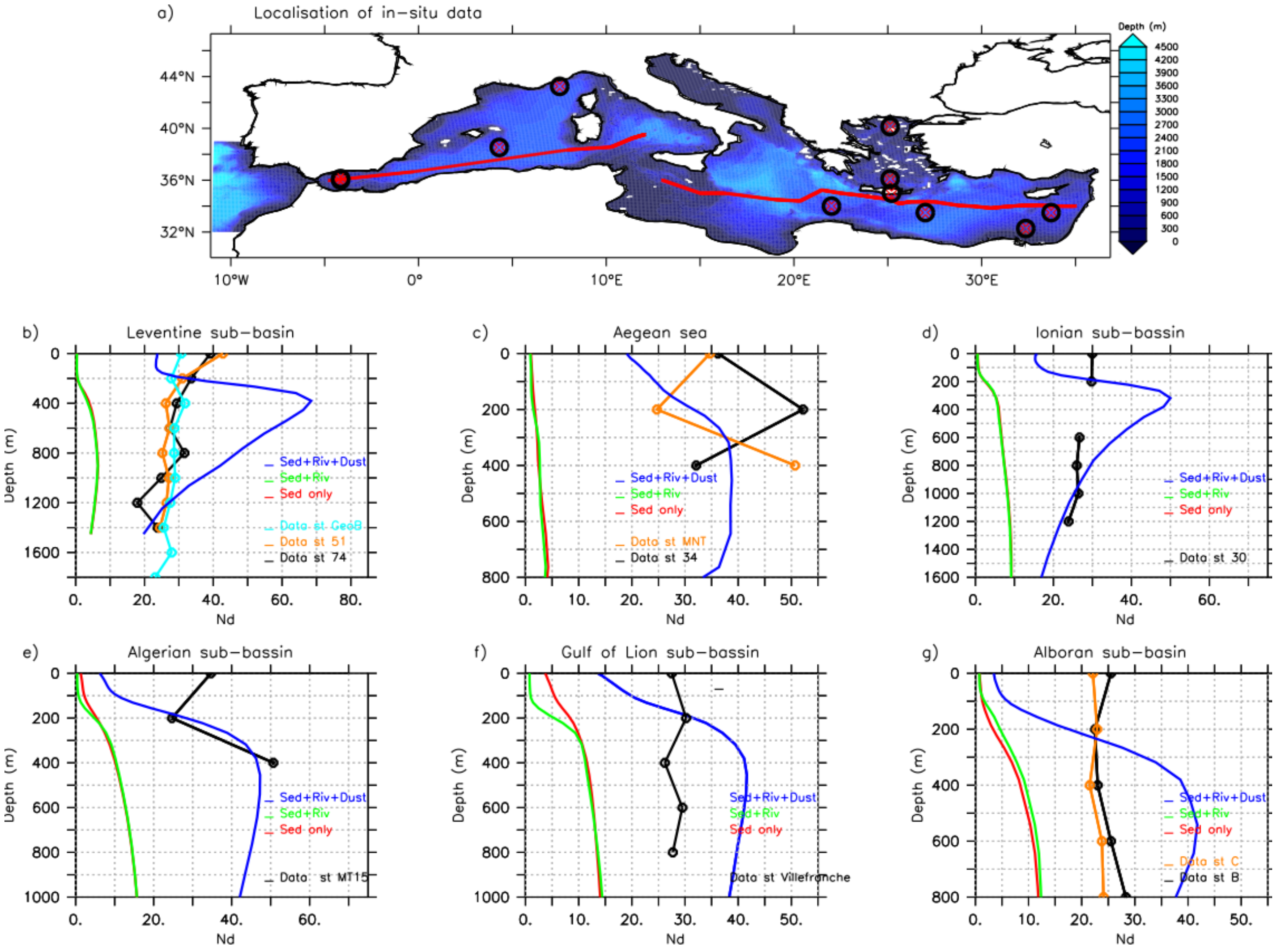

Fig. R2: **(a)** Map of the NEMO-MED12 model domain and bathymetry with location of the main Mediterranean sub-basins and in-situ observation. The solid lines (in red) represent the trans-Mediterranean vertical section. Comparison of the vertical profiles of [Nd] (in pmol/kg) between in-situ data and model output for Levantine **b)**, Aegean **c)**, Ionian **d)**, Algerian **e)**, Gulf of Lion **f)**, and Alboran sub-basins.

On the other hand, the detectable impacts of river discharge on the modelled Nd concentration were limited to the areas near the catchments of the main rivers. This is clearly visible for the surface waters in the vicinity of the Rhone river mouth (as demonstrated in Fig. R1 and explained in the previous answer). The impact of river is relatively lower due to the reduction of river discharge.

It is difficult to assess the agreement between simulations and observations based on the figures alone. It would therefore be helpful to also provide a more objective measure, such as the root mean squared error, mean absolute error or another appropriate metric.

We would like to thank the referee for this suggestion. We performed several sensitivity tests to better understand how the internal cycle and the various external sources affect the Nd cycle in the Mediterranean Sea. Nevertheless, it is important to mention that the magnitudes and variations of Nd fluxes related to the partial dissolution of river particles and atmospheric dust bear a significant uncertainty. Hence, we didn't provide a more quantitative measure because the model outputs are largely impacted by theses uncertainty in [Nd] from the different external sources. For instance, it would be useful to conduct similar analyses using other tracers (e.g. Sr, Si, etc.), or to use a more statistical analysis (e.g. TMM method) based on a multi-tracer approach.

Specific points

L26: I think it would be good to also cite more recent modeling work in this context (e.g., Gu et al., 2019; Pöppelmeier et al., 2022; Pasquier et al., 2022).

We would like to thank you for the mentioned references; we will introduce the references in the revised ms.

L64: I believe you are referring to Pöppelmeier et al. (2020), not Pöppelmeier et al. (2019).

Corrected

L75: Rempfer et al. (2011) and Gu et al. (2019) both also subtracted 70% of the total riverine Nd source not 30%.

We would like to thank the reviewer for this information, corrected in the revised ms

L152: ‘adsorption onto particles’ not ‘into particles’.

Corrected

L161: Following not Flowing.

Corrected

L162: Do you mean that [Nd] and εNd are calculated offline?

We simulate the two ^{144}Nd and ^{143}Nd isotopes independently (simulates as two tracers) then we calculate total Nd concentration and εNd as a diagnostic parameter in the model.

Clarified in the revised ms.

“*Flowing Arsouze et al. (2009) we simulate the two ^{144}Nd and ^{143}Nd isotopes independently (simulates as two tracers) then we calculate total Nd concentration and εNd as a diagnostic parameter in the model.*”

L163: Mass-dependent fractionation is corrected for during measurement anyway.

Indeed.

L185: Typo – ‘the the’.

Corrected

L200: The calculation of the sedimentary Nd flux remains unclear to me. How do you calculate the Nd flux from a bulk detrital concentration? Do you assume a constant and uniform dissolution rate? Since this source flux is so important for the Nd cycle, a more thorough explanation is required.

We agree with the referee that the sedimentary Nd flux is so important for the Nd oceanic flux. To date, there is no estimation of the Nd flux from the sediment (*i.e.* the Boundary Source) in the Mediterranean Sea. Based on our modeling approach, we estimate the BE flux at 89.43 ×10^6 g(Nd)/yr for the whole Mediterranean basin (as presented in the ms). The only available estimation of the Nd Boundary Source flux was the global "missing flux" calculated by Tachikawa et al. (2003) and by Arsouze et al., (2003) using a coupled dynamical-biogeochemical model. We therefore use their value as a reference for our simulations, taking into account the percentage of the Mediterranean Sea as compared to the total surface of the global ocean.

Previous studies in the North Atlantic Ocean (Arsouze et al., 2007) and Mediterranean Sea (Ayache et al., 2016) taking into account the variability of the lithology of the margin sediments did not improve the simulations (Arsouze et al., 2007; Ayache et al., 2016). This requires more laboratory experiments, targeted on the issue of the nature of the sediments, Hence, we assume the sediment flux as geographically constant with a uniform dissolution rate as first approximation after many sensitivity simulations on the representation of this flux, the same assumptions were used in other modelling study (*e.g.* Arsouze et al., 2009). Then we computed the flux for both ^{144}Nd and ^{143}Nd by multiplying this sediment flux to the Nd concentration along the margin, based on the observed spatial distribution (Fig. 2a and 2b, in the submitted ms). We used a mask-margin which represent the percentage of continental margin in the grid box which, *i.e.* the proportion of the surface in the grid where the boundary exchange process occurs. The oceanic margin extension of the Mediterranean Sea has been chosen to be between 0 and ~540 m following the margin definition used to model the iron cycle in the Mediterranean Sea by Palmiéri (2014).

A sentence has been added to the text to make this perfectly clear in the revised manuscript.

"*To date, there is no estimation of the Nd flux from the sediment (i.e. the Boundary Source) in the Mediterranean Sea. Based on our modeling approach, we estimate the BE flux at 89.43 ×10^6 g(Nd)/yr for the whole Mediterranean basin (as presented above, see Table. 2). Previous study taking into account the variability of the lithology of the margin sediments in the North Atlantic Ocean (Arsouze et al., 2007) and the Mediterranean Sea (Ayache et al., 2016) did not improve the Nd simulations. This requires more laboratory experiments, targeted on the nature and reactivity of the sediments. Hence, we assume the sediment flux as geographically constant with a uniform dissolution rate as first approximation after many sensitivity simulations on the representation of this flux, the same assumptions were used in other modelling study (e.g. Arsouze et al., 2009).*"

L228: Typos in references.

Corrected

L240: Experiment not experience, here and elsewhere.

Donne

L 273: From Fig. 3 it appears that simulated Nd concentrations fit rather well to the observations in the deep layer and the factor of two difference mentioned in the text appears to be only present at intermediate depths.

We agree with the referee on this remarque, the factor of two is manly present in the layer of intermediate water as shown in Fig.3 and Fig. 5.

Text was changed in the revised ms for clarification.

"Nd concentration is increasing with depth in these two experiments, however, simulated concentrations only amount to roughly half the observed concentrations in intermediate ~~and deep~~ waters."

L290/291: Remove 'globally' here and elsewhere, since you only consider the Mediterranean.

Done

L 300: The deep layer looks pretty much the same for all three experiments in Figs. 5f and 6

Yes, it's true if we look only to the average vertical profile in the whole basin, there is an important difference in the western basin between the two first experiences (SedOnly and SedRiv) and the experiment with the atmospheric dusts (SedRivDust).

Clarified in the text.

"*Overall, the average vertical profile of εNd simulated in the SedRivDust experiments is more consistent with the observed vertical profile (Fig. 5f), especially in the western basin where SedOnly and SedRiv largely overestimate the observations (Fig. 5d) in the surface and intermediate water.*"

L313/338: Experiment not experience.

Changed.

L320. A brief comparison also to other global studies would be helpful to set these results into a better context.

We agree with the referee on the suggestion, we have introduced (*state*-of-the-*art*) the main modeling approach in section 1 (L 50-67) with the estimations of the Nd flux based on different molding approaches. We have discussed our estimations against the global study of Arsouze et al. (2009) because we have used a similar modeling approach giving a better comparability of our results.

L332: Strike 'compared o in-situ observations'.

Corrected

L335-336: Maybe give river Nd concentrations also in pmol/kg for better comparability to dissolved ocean concentrations.

Done

L360-363: I don't understand how a dust dissolution of 10% can lead to lower surface Nd concentration when the input Nd flux is five times higher. As mentioned in the text higher concentrations lead to more efficient scavenging, but since particle concentrations should remain the same between both experiments, the net effect on the dissolved Nd concentration should remain an increase not a decrease (albeit less that the factor of five).

As shown in Fig. A3 the experiment with a dissolution rate of 10 % give a relatively similar Nd concentration and less radiogenic water in the surface water (Fig. A4). The main difference is shown in the intermediate water as a consequence of a more efficient scavenging, *i.e.* a more efficient transfer of tracer to the intermediate and deep waters. This rapid transfer gives a lower concentration in subsurface waters (figure A3).

Figs. 2, 5: Please use the Greek epsilon character in the figures.

Done

Fig. 3: Please note whether these are averages over the mentioned depth intervals. Further, in the caption it is noted that the intermediate layer is from 250 to 600 m while in the text it is 200 to 600 m.

Clarified, Fig. 3 display horizontal maps of Nd concentration averaged over the depth ranges surface (0- 200 m), intermediate (200-600 m) an deep water (600-3500 m).

Figs. 3, 4: Please use the same colorbar for both figures to allow for better comparability.

Changed

Fig. 6: The tick-labels of the colorbar appear to be rounded thus missing the digit after the comma.

Done

References

Gu, S. et al. Modeling Neodymium Isotopes in the Ocean Component of the Community Earth System Model (CESM1). J. Adv. Model. Earth Syst. 11, 624–640 (2019).

Pasquier, B. et al. GNOM v1.0: an optimized steady-state model of the modern marine neodymium cycle. Geosci. Model Dev. 15, 4625–4656 (2022).

Pöppelmeier, F. et al. Influence of elevated Nd fluxes on the northern Nd isotope end member of the Atlantic during the early Holocene. Paleoceanogr. Paleoclimatology 35, e2020PA003973 (2020).

Pöppelmeier, F. et al. Neodymium isotopes as a paleo-water mass tracer: A model-data reassessment. Quat. Sci. Rev. 279, 107404 (2022).

Rempfer, J., Stocker, T. F., Joos, F., Dutay, J. C. & Siddall, M. Modelling Nd-isotopes with a coarse resolution ocean circulation model: Sensitivities to model parameters and source/sink distributions. Geochim. Cosmochim. Acta 75, 5927–5950 (2011).

We would like to thank Referee #1 for the mentioned references; we will introduce the references in the revised ms.

References

Arsouze, T., Dutay, J. C., Lacan, F., and Jeandel, C.: Modeling the neodymium isotopic composition with a global ocean circulation model, Chemical Geology, 239, 165–177, https://doi.org/10.1016/j.chemgeo.2006.12.006, 2007.

Arsouze, T., Dutay, J.-C., Lacan, F., and Jeandel, C.: Reconstructing the Nd oceanic cycle using a coupled dynamical – biogeochemical model, https://doi.org/10.5194/bgd-6-5549-2009, 2009

Ayache, M., Dutay, J.-C., Arsouze, T., Révillon, S., Beuvier, J., and Jeandel, C.: High-resolution neodymium characterization along the Mediterranean margins and modelling of Nd distribution in the Mediterranean basins, Biogeosciences, 13, https://doi.org/10.5194/bg-13- 5259-2016, 2016.

Cullen, J. J.: The Deep Chlorophyll Maximum: Comparing Vertical Profiles of Chlorophyll a, Canadian Journal of Fisheries and Aquatic Sciences, 39, 791–803, https://doi.org/10.1139/F82-108, 1982.

Henry, F., Jeandel, C., Dupré, B., and Minster, J.-F.: Particulate and dissolved Nd in the western Mediterranean Sea: Sources, fate and budget, Marine Chemistry, 45, 283–305, https://doi.org/10.1016/0304-4203(94)90075-2, 1994.

Pinardi, N. and Masetti, E.: Variability of the large-scale general circulation of the Mediterranean Sea from observations and modelling: a review, Palaeogeography, Palaeoclimatology, Palaeoecology, 158, 153–173, 2000.

Millot, C. and Taupier-Letage, I.: Circulation in the Mediterranean Sea, The Handbook of Environmental Chemistry, 5, 29–66, doi:10.1007/b107143, 2005

Ludwig, W., Dumont, E., Meybeck, M., and Heussner, S.: River discharges of water and nutrients to the Mediterranean and Black Sea: Major drivers for ecosystem changes during past and future decades?, Prog. Oceanogr., 80, 199–217, doi:10.1016/j.pocean.2009.02.001, 2009.

Palmiéri, J.: Modélisation biogéochimique de la mer Méditerranée avec le modèle régional couplé NEMO-MED12/PISCES, http://www. 590 theses.fr/2014VERS0061, 2014.

Vörösmarty, C. J., Fekete, B. M., and Tucker, B. A.: Global River Discharge Database (RivDIS V1.0), International Hydrological Program, Global Hydrological Archive and Analysis Systems, UNESCO, Paris, 1996.

Tachikawa, K., Athias, V., and Jeandel, C.: Neodymium budget in the modern ocean and paleo-oceanographic implications, Journal of Geophysical Research, 108, 3254, https://doi.org/10.1029/1999JC000285, 2003.