Response to comments from referee #1: Dr. Tanhua

On behalf of all authors, we would like to thank the reviewer for their thorough reading of the manuscript and their constructive remarks and suggestions. Your comments provided valuable insights to refine and clarify the manuscript. We have taken into consideration all suggestions.

In the following, we try to address all issues raised as best as possible.

Below, the reviewers' comments are given in *italic blue* and responses in normal black font.

It seems to be a two-step procedure with data flagged as questionable (i.e. flag "3") removed from the adjusted product. For cruises where the whole cruise was considered as of "poor quality" (as assessed from excessive scatter etc.) are still included in the product but flagged as questionable.
Why include questionable cruises in the product at all?
In the adjusted product, flags were based on the results of the 2nd QC, so "flag 3: Adjusted and recommended questionable", is a flag based on 2nd QC recommendation in section 4.4. i.e. It is a layer of flags in the final product for "flag 2: adjusted and acceptable" and "flag 3: adjusted and recommended questionable". We did clarifyy better it in Table 3 and in the supplementary Materials (Supplementary material – Part 2 (A2)). As mentioned in section 4.4, we have done the evaluation of the cruise overall quality but leave it up to the users how to appropriately use these data.

I appreciate having access to the original data (i.e. prior to adjustment), but that does not preclude the need to link to the individual cruise files. These can be in a common format on a dedicated place, or it could be links to the original data file in a repository (NODC, SeaDataNet, or similar). That has value since for instance some of these cruises probably have associated "other" data, such as oxygen etc. that might be of use for the user. I recommend to establish links to the original data files.
This last comment does also go for the meta-data of the cruises. I guess in most cases this would include reference to a cruise report. I could not find any such references, please add links to cruise reports.
We agree that it is important to have easy access to the original, individual data files and metadata. Some of the cruise metadata such as cruise reports are available on http://www.seaforecast.cnr.it/reports/, but not all. We will add cruise reports for the missing cruises and submit all the individual cruise files to the SeaDataNet repository.

For the secondary QC, the authors choose to adjust all data to 5 reference cruises that was considered to have particularly high quality. One of the reasons was the well-known issue with bias in nutrient measurements being introduced by freezing of samples and analyzing them on land post-cruise.
We have modified the text to state that this is one of the criteria, but not a requirement for being a reference cruise.

However, not all reference cruises had nutrient measured on-board. Why then include them as reference cruises?
As reference cruises, we use only cruises that are known to have followed best practice standards, where nutrient analysis followed the recommendation of the World Ocean circulation experiment (WOCE) and the GO-SHIP protocols, and have undergone rigorous quality control following GLODAP routines or in the framework of the MedSHIP programme. We believe that observations of these cruises are of high degree of reliability, independently if the analysis was made on-board or on-land.

Although it seems that the low-nutrient water of the Mediterranean might be less prone to bias due to freezing, the result from this study seem to suggest something different with all three variables being adjusted preferentially upward or downward. That might be an interesting result. Or maybe this is a function of bias in the measurements??

We agree it could be due to bias in the measurement, we did not generalize it to all cruises. We tried to understand and find out what was the source of bias in the observations and the storage time was one of them. Freezing is not the main cause of the bias if samples were well preserved and unfrozen. One of the main reasons for the upward and downward biases would be the lack of use of Reference Material for Nutrients in those cruises as also noted in CARINA (Tanhua, T., Brown, P. J., and Key, R. M.: CARINA: nutrient data in the Atlantic Ocean, Earth Syst. Sci. Data, 1, 7–24, https://doi.org/10.5194/essd-1-7-2009, 2009.) or the most recent global comparability exercise (Aoyama, M.: Global certified-reference-material-or reference-material-scaled nutrient gridded dataset GND13, Earth Syst. Sci. Data, 12, 487–499, https://doi.org/10.5194/essd-12-487-2020, 2020)

It would be useful to have a directory of crossover plots for all cruises. The method of GLODAP and CARINA could be taken as an example, but a repository on the web where the crossoverplots can be downloaded would go a long way. This would allow users to judge the validity of the adjustments.

Yes, we want to make available the crossover plots following the crossover and adjustment Data Repository for CARINA or GLODAP, however it cannot be done easily, before the paper is published, we will work on making it available with the cruise reports.

Why only discuss a selection of cruises in section 5.4? All cruises had adjustments. I recommend expanding this section to cover all cruises.

We have expanded this section to cover all cruises.

Minor comments: Line 67: I suggest changing "profiles" for "observations

Done, in the revised version.

Line 116 The CARIMED data product is not yet published and available

We added a sentence about CARIMED data product (not yet available). The CARIMED initiative lead by M. Álvarez is a compilation of carbon and carbon relevant data for the MedSea that is taking longer than expected to be published, hopefully in 2020.

Line 115: Please refer to the GO-SHIP nutrient manual

Done.

Line 188: I am not sure if this is a useful metric. The authors discuss the influence having observations in different sub-basins have on this statistic later. Why not create statistic that is for sub-basin by sub-basin?

This point was raised by referee#2 as well.

The standard deviation of data deeper than 1000db was defined as a first assessment to get indications about the precision of the measurements in each cruise following (Olsen et al., 2016). Statistics in different sub-basins has been added to check all cruises that have measurements in different subregions (Table 4).

Line 221: The 2_ influence radius is probably fine for the Atlantic Ocean, but mostly not for the Mediterranean Sea. How did the author handle crossovers that were influenced by observations from nearby other sub-basins where a different nutrient concentration could be expected?

The reviewer is correct that we did not separate the analysis by sub-basin. The choice of the 2° was also partly for practical reasons since the number of reference cruises is too low to allow to restrict this radius. If we had more reference cruises, we could have reduced the 2° influence radius, but given that we only have 5, a relatively large influence radius is the only way to ensure statistically relevant results.

Line 226: If you know that the deep water is (potentially) changing fast, why include it in the crossover analysis?
Would it work to have a crossover analysis covering, for instance, 1000 – 2000 meter only? If so, why was that not used, and how did the authors remove temporal natural variability of deep water?
The minimum chosen depth was 1000m, so that all cruises and all areas could be included in the 2nd QC and considering the relative low variability of the deep layer, compared to the intermediate and surface layers (nitrate CV=1.16, phosphate CV=1.005, silicate CV=0.75) the deep (>1000 db) layer (nitrate CV=0.15, phosphate CV=0.22, silicate CV=0.14)). The toolbox we use is not designed and tested to do crossover analyses for a part of the water column (e.g. 1000-2000m as suggested). It can only do it from Xm to the bottom. It would be possible to rewrite the code to do this, but that is beyond the scope of this paper, since we still aim to obtain results that could compare with other regions of the world ocean where the same method has been applied.
The crossover analysis is done in density space. Thus, natural variability in the physics and water mass structure is accounted for in the method. Besides, we have a minimum adjustment limit for a reason and part of that reason is that we should not overcorrect when there is natural variability (which is always there).

Line 260: Here you decide not to include cruises that could not be adjusted in the product. On the other hand, you do include data that had only questionable data in the product (although flagged as such). Why?
An alternative approach could be to include the data with a flag that indicate that the data did not undergo 2nd QC.
Yes, in the final product we included only cruises that underwent a 2nd QC, that is why we removed those that were not subjected to 2ndQC, those cruises are still in the original data collection. We did prefer to leave it up to the users how to appropriately use these data.

Section 6, and possibly elsewhere: GLODAP and CARINA are data products, rather than datasets. The difference being that the products have an additional layer of QC (2nd QC bias adjustment) applied, whereas a data set is a collection of data that are in its original form, possibly with consistent primary QC, unit conversion etc. Not so important perhaps, but a little of semantic difference.
We have changed this in the text, thank you for this important remark.

Line 427: Not a complete list of authors for this paper.
The reference has been corrected.

Table 2: Why have a different format for this table compared to table 1?
We have modified Table 2 to be comparable to Table 1.

Table 4: It would be useful to include the reference cruises in this table
Table of the reference cruises is in the supplementary materials Table 1S, and we have added the number of samples.

Table 5: not a big deal, but the "" sign in this table is applied in column 2, whereas in other tables (4) it is applied to column 1.*
The notation has been revised.

Response to comments from referee #2: Dr. Lipizer

On behalf of all authors, we would like to thank the reviewer for their thorough reading of the manuscript and their constructive remarks and suggestions. Your comments provided valuable insights to refine and clarify the manuscript. We have taken into consideration all suggestions.

In the following, we try to address all issues raised as best as possible.

R : The dataset is complete, with most required metadata, and provided in a user-friendly format. However, the adjusted dataset does not follow exactly WOCE QC flags: missing values are not flagged, while they should be flagged 9 (no data).

A : We did follow the WOCE QC flag during the 1st QC in the original dataset, "flag 9" for missing or non-measured values. As for the adjusted product, we added flags based on the results of the crossover analysis excluding the non-measured one, so there is no "flag 9" in the adjusted product, there is only “flag 2 : adjusted and acceptable“ and “flag 3 : adjusted and recommended questionable”, this based on 2ndQC recommendation in section 4.4. We did clarify it better in table 3 and in the supplementary Materials (Supplementary material – Part 2 (A2)).

R : The dataset can provide a valuable contribution to the main European initiative in charge of assembling and giving access to marine data of the European seas, namely the European Marine Observation and Data network (EMODnet) (see Giorgetti et al., 2018). Surprisingly, there is no reference to the large availability of data in the Western Mediterranean provided by European data infrastructures such as SeaDataNet (https://www.seadatanet.org/) and EMODnet Chemistry (https://www.emodnet-chemistry.eu/).

A : We are aware about the large availability of data in the Western Mediterranean provided by European data infrastructures such as SeaDataNet (https://www.seadatanet.org/) and EMODnet Chemistry. We have now added a reference to the well-known existing nutrient datasets or data products. However, the main purpose of the paper is to make available the CNR data set. In our future studies, we aim at updating and adding other data sources from SeaDataNet and the MOOSE observing network, like Dr. Coppola suggested (Coppola et al., 2019; Tintoré et al., 2019), and integrating the Eastern Mediterranean as well, as far as possible.

R : I am concerned with the choice of the 5 cruises as reference to perform the secondary quality control and the adjustments, given the well known mesoscale dynamics of the Western Mediterranean, the seasonal variability detected also in the deep layers and the changes observed in the deep waters reported in the same period (Manca et al., 2004; Schroeder et al., 2008; Schroeder et al., 2016). It is recommended to compare the profiles of the reference cruises with the outcomes of the extensive analysis of over 40 years of biogeochemical data collected in the Mediterranean and the resulting climatological vertical profiles (Manca et al., 2004) and the full set of spatially averaged vertical profiles available to downloaded at http://nettuno.ogs.trieste.it/medar/climatologies/medz.html), provided for different Mediterranean regions defined according to general circulation patterns.

Giorgetti et al., 2018 EMODnet Chemistry Spatial Data Infrastructure for marine observations and related information. Ocean and Coastal Management 166 (2018) 9–17

Manca et al., 2004 Physical and biochemical averaged vertical profiles in the Mediterranean regions: an important tool to trace the climatology of water masses and to validate incoming data from operational oceanography; Journal of Marine Systems 48, 83–116

Schroeder et al. (2008) An extensive western Mediterranean deep-water renewal between 2004 and 2006, Geophys. Res. Lett., 35, L18605, doi:10.1029/2008GL035146.

A : Reference cruise data were chosen according to a number of criteria:

they are independent from our CNR dataset, they have a large spatial distribution and different time span (we added information about number of observation per reference cruises table 2), Besides, nutrient analysis followed the recommendation of the World Ocean circulation experiment (WOCE) , the GO-SHIP protocols (Hydes et al., 2010; Tanhua et al., 2013) and have undergone rigorous quality control following GLODAP routines, along with cruises that were carried out in the framework of the MedSHIP programme (Schroeder et al., 2015). Observations of these cruises are highly reliable. Based on that, the 5 reference cruises were selected to perform the 2nd QC analysis, as explained in section 2.3. We have added additional details in the text explaining our choice of reference cruises. This work is a starting point for a living data product, the original data collection is available to improve the method/make updates.

We have added a section comparing our results to the Manca et al. (2004) vertical climatological profiles in section 4.5, thank you for the suggestion, which we think is a great addition to the paper.

R : To improve the logical sequence of the information, some sections should be reorganized. The Introduction is not logically organized, there are several citations which are listed, but the connections are not clear. Many important concepts are introduced (eg. Biological pump, N:P ratio) but not introduced and some sentences are not clear or vague (eg. Lines 57- 60).

A : The text has been revised for structure and flow. We thank the reviewer for suggesting the additional references which have now been included.

R : Reference should also be made to the Mediterranean Sea – Eutrophication and Ocean Acidification aggregated datasets 1911/2017 v2018 provided by EMODnet Chemistry (https://doi.org/10.6092/89576629-66d0-4b76-8382- 5ee6c7820c7f) (line 71)
A : Done

R : The use of citations should be revised: some citations do not seem to be appropriate or are not correctly inserted in the text as there are cases of quite vague statements linked to citations (eg. line 57 Boyd; Line 171: Muniz et al 2001)
A : The text has been proofread to ensure proper citation throughout.

R : Reference to published climatologies of biogeochemical properties available for the Mediterranean is missing (eg. Manca et al., 2004; MEDAR/MEDATLAS Climatology)
A : Done, by comparing the product to Medar/MEDATLAS Climatology

R : Section 2.2 should be moved after 4.1.
Section 3 should follow 2.1, after the description of sampling protocols for nutrient measurements.
A : The sections have been modified accordingly.

R : Line 47: the latter: do you mean validation? Can you please explain what you mean?
A: We meant data collection and monitoring, and there are still gaps in the Mediterranean Sea, this is now explained better in the text and refer to dataset and data product previously done.

R : Lines 83-88: there is a not correct comparison among different terms: datasets, databases and large European data infrastructures such as SeaDataNet and EMODnet Chemistry are different things. Throughout the manuscript: check the consistency between the terms dataset and data set.
A : we have made the necessary changes.

R : Is the description at lines 123-130 innovative? If not, the citation to the already consolidated method is enough and the whole part can be removed.

A : It is a summary of the analysis description done in laboratory.

R : On the other hand, a table summarising the laboratories, the instruments, the respective detection limits, together with sample storage and freezing duration used for the different cruises would facilitate the understanding.

A : A table of the sample storage and freezing is added in the revised supplementary materials (Table 1S).

R : Section 4: deals with Quality Assurance rather than QC

A : The section title has been modified accordingly

R : Section 4.1 should be reorganized to clearly explain how primary QC has been carried out;
lines 169 – 172: please explain how were QF assigned to data and the relationships between flagging and CV
Lines 176-179: this sentence is not very clear. Please rephrase it.

A: Section 4.1 has been reorganized as requested.
The CV compares the degree of variation between surface and deep observations and how we can proceed with the flagging. The upper layer (nitrate CV=1.16, phosphate CV=1.005, and silicate CV=0.75) imposed a check of outliers per depth range, here we name it as standard depths (or class of depth) at 0-10, 10-30, 30-60, 60-80, 80-160, 160-260, 260-360, 360-460, 460-560, 560-1000 m. Per cruise, a Median absolute deviation was computed by class of depth, atypical observation was flagged as questionable, in the upper layer we did not strictly follow the criteria of flagging as bad the values higher than three median absolute deviations.
The deep observation is relatively less variable (nitrate CV=0.15, phosphate CV=0.22, silicate CV=0.14).and the flagging was based on a check of nitrate to phosphate (N:P) and nitrate to silicate (N: Si) ratios. We considered as outlier any value that departs from the median ratio (below 1000db) by more than three median absolute deviations.
We did highlight that the primary QC can be subjective depending on the expertise of the person flagging the data, thus flagging could bring in some uncertainties.

R : Lines: 187-206: As shown in fig. 9, most cruises (even cruises #1, 5 and 16) cover different parts of the West Mediterranean basin, which are influenced by heterogeneous physical and biogeochemical processes, different water masses, which are characterised by different nutrient concentrations. The relationship between standard deviation of data collected in different water masses and data precision is not so straightforward. Therefore, the assessment of "precision of each cruise measurements" based on cruise CV is questionable.

A : In order to have a first assessment of the precision of each cruise measurements, the standard deviation of data deeper than 1000db was calculated (Table 4).
When the time span between different cruises is one month or less, then the temporal variation can be excluded below 1000db, and the standard deviation is interpreted as the effect of the natural variability and the precision of the observations. We compared standard deviations of cruises having similar spatial coverage. We add statistics per subregion as an overview of the overall content in nutrient layer (Table 4).

R : The authors use 5 reference cruises carried out in different seasons between 2001 and 2016 to adjust data obtained during a total of 24 cruises carried out between 2004 and 2017. Reference cruises cover a large area but sometimes with just 1 station per sub-area. The use of single stations sampled during a specific season as reference is questionable. Even though only data below 1000 m are involved in the Secondary QC and deep waters are less variable than upper and intermediate *waters, seasonal as well as long term variability in nutrient concentrations in deep waters cannot be ruled out, as also stated by the authors. It is not clear how this is taken into account (lines 226-230).*

A: A valid crossover with the reference cruises should consider at least three stations for the computation to get a valid statistic. If there are not enough stations, there is no crossover.
The computational approach takes this into account if there is a change, weights are given according to the "confidence" in the determined offset of the compared profiles not necessarily the variance of the profiles themselves, i.e. the weighted mean offset of a given crossover-pair is weighted to the depth where the offsets of all compared profiles have the smallest variation, which is the case in deep regions. The summary plot coming out of the 2nd QC toolbox is a function of year. The reason for that is to be able to assess whether a long-term trend exists (it becomes very obvious when the offsets are plotted as a function of time). So long-term trends are taken into account when deciding on an adjustment. Seasonal variability is an issue though, but this is why we go deep.

R : Section 5.4: why only a sub-set of cruises is described?
A : The section has been expanded to discuss all cruises.

R : Line 373: Apart from old MEDAR/MEDATLAS database, reference should be made to the harmonized, aggregated and validated Mediterranean regional dataset of parameters related to eutrophication provided by EMODnet Chemistry (https://doi.org/10.6092/89576629-66d0-4b76-8382-5ee6c7820c7f)
A : We did add it in the revised version.

R : Line 326-327: r2 do not match those in the figures, Line 577: N:P does not match those in the figures
A : We checked it and corrected it in the revised version.

R : A plot showing temporal distribution of cruises and of reference cruises could be appreciated
A : Table 1 is the cruise summary table where cruises were sorted in chronological order and plotted against the reference in Figure 1. Same as table 2 detailing the reference cruises and plotted in figure 2.

R : Fig.1 Map: difficult to identify the different (Blue and red) cruises. The use of larger and filled/open symbols may help.
A : We improved the map.

R : Fig. 8: Numbers in figures do not match with captions. Has the adjustment been done on the whole Profile or only to data > 1000m? This is not clearly described in the paper.
A : The proposed adjustment factor was estimated from observation deeper than 1000db, and we applied it to the whole profile. We clarified it in the revised version (section 3.2).

R : References: The first reference is not complete (journal? Pages?)
A : Done.

Dissolved Inorganic Nutrients in the Western Mediterranean Sea (2004-2017)

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Abstract

Long-term time-series are a fundamental prerequisite to understand and detect climate shifts and trends. Understanding the complex interplay of changing ocean variables and the biological implication for marine ecosystems requires extensive data collection for monitoring ~~and~~ , hypothesis testing and validation of modelling products. In marginal seas, such as Mediterranean Sea, there are still monitoring gaps, both in time and in space. To contribute to filling these gaps, an extensive dataset of dissolved inorganic nutrients ~~profiles~~ observations (nitrate, NO_3; phosphate, PO_4^{3-}; and silicate, SiO_2) have been collected between 2004 and 2017 in the Western Mediterranean Sea and subjected to rigorous quality control techniques to provide to the scientific community a publicly available, long-term, quality controlled, internally consistent biogeochemical data product. The data product~~base~~ includes 870 stations of dissolved inorganic nutrients, including temperature and salinity,

sampled during 24 cruises,~~ including temperature and salinity~~. Details of the quality control (primary and secondary quality control) applied are reported. The data are available in PANGAEA (https://doi.pangaea.de/10.1594/PANGAEA.904172, Belgacem et al. 2019)

Keywords: Mediterranean Sea, Dissolved Inorganic Nutrient, biogeochemistry

1 Introduction

Dissolved inorganic nutrients play a crucial role in marine ecosystem functioning. They ~~are important~~serve as ~~tracers~~ regulators of ocean biological ~~cycles~~productivity, and are trace elements for~~,~~ biogeochemical ~~new production~~cycling as well as ~~,~~ for natural and anthropogenic sources and transport processes (Bethoux, 1989; Bethoux et al., 1992). They are also non-conservative ~~seawater~~ tracers~~constituents~~, since their ~~whose~~ distribution ~~is controlled~~vary according to~~ by~~ both biological (such as primary production and respiration) and physical (such as convection, advection, mixing and diffusion) ~~and biogeochemical (such as primary~~processes~~ production and respiration) processes~~. Very schematically, inorganic nutrients are continuously consumed by phytoplankton (due to primary production) in~~removed from~~ the sea surface ~~(due to primary production)~~ and regenerated in the mesopelagic layer by bacteria and animals (due to respiration). Moreover, the sinking of ~~biogenic~~ organic matter and its decomposition ~~gradation~~ increases the nutrient concentrations in the intermediate and deep-water masses over time. To identify the limiting factors for biological production in the oceans, we need to understand the underlying chemical constraints and especially the macro- and micronutrients spatial and temporal variations. Dissolved inorganic nutrients may be used ~~to~~ as tracers of water masses like salinity and temperature, to assess mixing processes, and to understand the biogeochemical ~~conditions~~ circumstances of their formation regions. Understanding the complex interplay of changing ocean variables and the biological implication for marine ecosystems is a difficult task and requires not only modelling, but also extensive data collection for monitoring, ~~and~~

hypothesis testing and validation. Monitoring gaps still remain in both in time and space, especially ~~.~~ ~~The latter has been done in the open oceans (e.g. GLODAP), but~~ for marginal seas such as the Arctic Ocean or the Mediterranean Sea~~ there are still monitoring gaps ,both in time and in space~~.

The Mediterranean Sea has been identified as a region significantly affected by ongoing climatic changes, like warming and decrease in precipitation (Giorgi, 2006). In addition, it is a region particularly valuable for climate change research because it behaves like a miniature ocean (Bethoux et al., 1999) with a well-defined overturning circulation characterized by spatial and temporal scales much shorter than for the global ocean, with a turnover of only several decades. Being an intercontinental sea, and subjected to more terrestrial nutrient inputs (river runoff, submarine groundwater discharge) and atmospheric deposition, the Mediterranean Sea has a nitrate to phosphate N:P ratio that is anomalously high compared to the “classical” world's oceans Redfield ratio, indicating a general P-limitation regime, which becomes stronger along a west-to-east gradient. The Mediterranean Sea is therefore a potential model to study global patterns that will be experienced in the next decades worldwide, not only regarding ocean circulation, but also the marine biota (Lejeusne et al., 2010). Several environmental variables can act as stressors for marine ecosystems, by which climatically driven ecosystem disturbances are generated (Boyd, 2011). These changes affect, among others, the distribution of biogeochemical elements (including inorganic nutrients) and the functioning of the biological pump and CO_2 regulation.

~~The Mediterranean, compared to the world's oceans, is also more influenced by continental nutrient inputs (Dardanelles, river runoff, submarine groundwater discharge and atmospheric inputs): and since all these inputs go in the same direction of high nitrate to phosphate (N:P) ratios, the N:P ratios in the Mediterranean are anomalously high compared to the “classical” Redfield ratio, indicating a general P-limitation for this sea, which becomes stronger along a west-to-east gradient.~~

Within this context, the aim of this paper is to compile an extensive dataset of dissolved inorganic nutrient~~s~~ observations ~~profiles~~ (nitrate, NO_3; phosphate, PO_4^{3-}; and silicate, SiO_2) collected between 2004 and 2017 in the Western Mediterranean Sea (WMED), to describe the quality control techniques and to provide ~~to~~ the scientific community with a publicly available, long-term, quality controlled, and internally consistent biogeochemical data product, contributing to previously published Mediterranean Sea datasets like the ~~Medar~~MEDAR/Medatlas~~-~~(time period:1908–1999), ~~**dataset**~~ (Fichaut et al., 2003) and the Mediterranean Sea – Eutrophication and Ocean Acidification aggregated datasets v2018 (time period: 1911-2017) provided by EMODnet Chemistry (Giorgetti al.,2018) available at https://www.seadatanet.org/Products/Aggregated-datasets.~~.~~

Both original and quality-controlled data are available in PANGAEA:~~,~~ https://doi.pangaea.de/10.1594/PANGAEA.904172

Coverage: 44°N-35°S; -6°W-14°E

Location Name: Western Mediterranean Sea

Date start: May 2004

Date end: November 2017

2 Dissolved inorganic nutrient data collection

2.1. The CNR dissolved inorganic nutrient data in the WMED

Long-term time-series, such as the OceanSites global time series (www.oceansites.org), are a fundamental prerequisite to understand and detect climate shifts and trends. However, biogeochemical time-series are still ~~restricted~~ limited to the northern western Mediterranean Sea (MOOSE network, Coppola et al., 2019) ~~(three biogeochemical fixed platforms).~~ Yet, inorganic nutrients in the Mediterranean Sea has received more attention in recent years, and various datasets have been compiled to understand its unique characteristics such as the one build by the PERSEUS project Consortium (“Policy-oriented marine environmental research in the southern European seas” - EU FP7 project GA #287600), ~~a database~~ that included 100 cruises collected ~~within~~ during the project’s lifetime, ~~PERSEUS itself~~ in addition to those from other projects like ~~Sesame~~ SESAME, EU FP7 project GA #GOCE-036949), and data products such as the MEDAR/Medatlas. In addition to that, the data assembly system EMODnet Chemistry, a leading infrastructure supported by pan-European directorate General MARE set up (Martin Miguez et al., 2019, Tintoré et al.,2019).

~~or data managing systems as SeaDataNet and EMODnet, or the MEDAR/MEDATLAS (1999-2004) database.~~

The dataset presented here consists of 24 oceanographic cruises (Fig. 1 and Table 1) conducted in the WMED on board of research vessels run by the Italian National Research Council (CNR) and the Science and Technology Organisation Centre for Maritime Research and Experimentation (NATO-STO CMRE). All cruises were merged into a unified dataset with 870 nutrient stations and ~ 9666 data points over a period of 13 years (2004-2017). The overall spatial distribution of the stations covers the whole WMED, but the actual distribution strongly varies depending on the specific cruise ~~(which can be seen on the right side of Fig. 9)~~ and most of the data are collected along sections. At all stations, pressure, salinity and ~~, potential~~ temperature were measured with a CTD-rosette system consisting of a CTD SBE 911 plus and a General Oceanics rosette with 24 12L Niskin Bottles. Temperature measurements were performed with ~~an~~the SBE-3/F thermometer with a resolution of 10^{-3} °C; conductivity measurements were performed with ~~an~~the SBE-4 sensor with a resolution of $3\cdot10^{-4}$ S/m. The probes were calibrated before and after each cruise. During all CNR cruises, redundant sensors were ~~often~~ used for both temperature and salinity measurements.

Seawater samples for dissolved inorganic nutrient measurements were collected during the CTD up-cast at standard depths (with slight modifications according to the depth at which the deep chlorophyll maximum was detected). The standard depths are usually 5, 25, 50, 75, 100, 200, 300, 400, 500, 750, 1000, 1250, 1500, 1750, 2000, 2250, 2500, 2750, 3000 m. No filtration was employed,~~ but~~ nutrient samples were immediately stored at −20 °C. Note that sample storage and freezing duration varied greatly from one cruise to another (Table 3 shows the cruises where this exceeded 1 year).

2.2. Analytical methods for inorganic nutrients

For all cruises, nutrient determination (nitrate, orthosilicate and orthophosphate) was carried out following standard colorimetric methods of seawater analysis, defined by Grasshoff et al. (1999) and Hansen and Koroleff (1999)~~ and (Hansen and Koroleff, 1999)~~. For inorganic phosphate, the method is based on the reaction of the ions with an acidified molybdate reagent to yield a phosphomolybdate heteropoly acid, which is then reduced to a blue-colored compound (absorbance measured at 880 nm). Inorganic nitrate is reduced (with cadmium granules) to nitrite that react with an aromatic amine leading to the final formation of the azo dye (measured at 550 nm). Then, the nitrite separately determined must be subtracted from the total amount measured to get~~have only~~ the nitrate concentration only. The determination of dissolved silicon is based on the formation of a yellow silicomolybdic acid reduced with ascorbic acid to blue-colored complex (measured at 820 nm).~~, see (Hansen and Koroleff, 1999)).~~

~~The analytical method was performed using f~~Nutrient analysis was performed in three laboratories. ~~our different models of autoanalyzer in three laboratories (ENEA analysed all cruises with the following exceptions: cruise #23 and cruise #24 were analysed by CNR-ISMAR.~~ ~~-~~From 2004 to 2013, all cruises nutrients were analysed by ENEA, while for those of 2015 (cruise #23) and 2017 (cruise #24), nutrient concentrations were analysed by CNR-ISMAR. Referring to Table 1S, four different models of autoanalyzer were used. ~~From 2004 to 2013 nutrients were analysed by a continuous-flow system multichannel (Auto Analyzer Bran+Luebbe III Generation) while for those of 2015 (cruise #23) an OI-Analytical (Flow Solution III) flow-segmented autoanalyzer was used, with a detection limit of 0.01µM for nitrate+nitrite, 0.01µM for phosphate and 0.05 for silicate. Nutrient concentrations~~

~~for the 2017 cruise (cruise #24) were measured by the Systea discrete analyzer EasyChem Plus, considering a detection limit of 0.1μM for nitrate, 0.01μM for phosphate and 0.02μM for silicate.~~

Measurements ~~s~~ from the autoanalyzer were reported in μmol L^{-1}. ~~Since measures of salinity and temperature were also available,~~ Inorganic nutrient concentrations were converted to the standard unit μmol kg^{-1}, using sample salinity from CTD and a mean ~~according to the~~ laboratory analytical temperature of ~~(~~20°C~~)~~. Data from nutrient analysis were then merged to ancillary CTD bottle data. ~~Note that sample storage and freezing duration varied greatly from one cruise to another (Table 3 shows the cruises where this exceeded 1 year).~~

~~2.2.~~2.3. Reference inorganic nutrient data

In addition to the data collected during the above-mentioned cruises, and in order to perform the secondary quality control (described below), we identified five reference cruises (Table 2), based on their spatial and temporal distribution of the data and the reliability of the measurements (see Fig. 2 – Table.~~1S~~ 3S Fig.1S). Cruises 06MT20110405 and 06MT20011018 are the only two Mediterranean cruises included in the publicly available Global Ocean Data Analysis Project version 2 (GLODAPv2, ~~(~~Olsen et al.~~,~~ 2016)~~)~~. These cruises, conducted on board the R/V Meteor, provide a reliable reference because nutrient analysis strictly followed the recommendation of the World Ocean circulation experiment (WOCE) and the GO-SHIP protocols (Hydes et al., 2010; ~~-,(~~Tanhua et al., 2013). Cruises 29AH20140426 and 48UR20070528 are to be included in the CARIMED data product (personal communication by M. Álvarez, in preparation but not yet available) and have undergone rigorous quality control following GLODAP routines. Finally, 29AJ20160818 was carried out in the framework of the MedSHIP programme (Schroeder et al., 2015) and its data are available at https://doi.org/10.1594/PANGAEA.902293 (Tanhua, 2019).

~~For all cruises, nutrient determination (nitrate, orthosilicate and orthophosphate) was carried out following standard colorimetric methods of seawater analysis, defined by Grasshoff et al. (1999) and~~

~~(Hansen and Koroleff, 1999). For inorganic phosphate, the method is based on the reaction of the ions with an acidified molybdate reagent to yield a phosphomolybdate heteropoly acid, which is then reduced to a blue-colored compound (absorbance measured at 880 nm). Inorganic nitrate is reduced (with cadmium granules) to nitrite that react with an aromatic amine leading to the final formation of the azo dye (measured at 550 nm). Then, the nitrite separately determined must be subtracted from the total amount measured to have only the nitrate. The determination of dissolved silicon is based on the formation of a yellow silicomolybdic acid reduced with ascorbic acid to blue-colored complex (measured at 820 nm, see (Hansen and Koroleff, 1999)).~~

~~The analytical method was performed using four different models of autoanalyzer in three laboratories (ENEA analysed all cruises with the following exceptions: cruise #23 and cruise #24 were analysed by CNR-ISMAR. From 2004 to 2013 nutrients were analysed by a continuous-flow system multichannel (Auto Analyzer Bran+Luebbe III Generation) while for those of 2015 (cruise #23) an OI-Analytical (Flow Solution III) flow-segmented autoanalyzer was used, with a detection limit of 0.01µM for nitrate+nitrite, 0.01µM for phosphate and 0.05 for silicate. Nutrient concentrations for the 2017 cruise (cruise #24) were measured by the Systea discrete analyzer EasyChem Plus, considering a detection limit of 0.1µM for nitrate, 0.01µM for phosphate and 0.02µM for silicate.~~

~~Measures from the autoanalyzer were reported in µmol L~~$^{-1}$~~. Since measures of salinity and temperature were also available, nutrient concentrations were converted to the standard unit µmol kg~~$^{-1}$~~, according to the laboratory analytical temperature (20°C). Data from nutrient analysis were then merged to CTD bottle data. Note that sample storage and freezing duration varied greatly from one cruise to another (Table 3 shows the cruises where this exceeded 1 year).~~

3 Quality Assurance and quality control methods

Combining inorganic nutrient data from different sources, collected by different operators, stored for different amounts of time, and analysed by multiple laboratories, is not a straightforward task. This is widely recognized in the biogeochemical oceanographic community~~, and~~. S~~s~~ince the 1990s, several studies and programmes (e.g. World Ocean Database, World Ocean Atlas,~~ World Ocean Circulation Experiment~~ WOCE) have been devoted to facilitate the exchange of oceanographic data and develop quality control procedures to compile databases by the estimation of systematic errors (Gouretski and Jancke, 2001) to increase the inter-comparability, generate consistent data sets and accurately observe the long-term change.

An example of a first quality control procedure is the use of ~~certified ~~reference materials ~~standardizations ~~that are available for salinity (IAPSO, salinity standard by OSIL) and temperature (SPRT, Standard~~-~~ Platinum Resistance Thermometer). As for the inorganic carbon, total alkalinity (Dickson et al., 2003) and inorganic nutrients (Aoyama et al., 2016~~; Dickson et al., 2003~~)~~ ~~, certified reference materials (CRM) have been recently made applicable~~vailable~~ for oceanographic cruises. However, since CRM are not always available or used for biogeochemical oceanographic data, ~~(~~Lauvset and Tanhua~~,~~ (2015) developed a secondary quality control tool to identify biases in deep data. ~~ and from that estimate accuracy. ~~The method suggests adjustments that reduce cruise to cruise biases, increase accuracy and allow for the inter-comparison between data from various sources. This approach, based on a crossover and inversion method (Gouretski and Jancke, 2001; Johnson et al., 2001), was used to generate the CARbon IN Atlantic ocean (CARINA, see ~~(~~Hoppema et al., 2009~~)~~), GLODAPv2.2019 (Olsen et al., ~~2016~~2019) and PACIFICA (Suzuki al al.,2013) databases.

3.1 Primary Quality control

Each individual cruise was first subjected to a primary quality control (1st QC) that included a check of apparent and extreme outliers in CTD salinity, nitrate, phosphate and silicate. Each parameter included a quality control flag, following standard WOCE flags (Table 3). Surface, intermediate and deep layer were evaluated separately because nutrient observations evolve differently in each layer. The coefficient of variation (CV, defined as standard deviation over mean) was computed for each depth layer.

~~The surface (0-250 db) layer was difficult to flag since its overall~~ C~~c~~oefficients of variation ~~(CV, defined as standard deviation over mean)~~ in the surface (0-250 db) layer were high (~~for~~ nitrate CV=~~(~~1.16~~)~~, phosphate CV=~~(~~1.005~~)~~ ~~and~~ , silicate CV=~~(~~0.75~~)~~)~~was high~~ due to air-sea interaction ~~and the complexity of biological processes~~ (Muniz et al., 2001) occurring in this layer rendering it difficult to flag. These influences are of reduced importance in the intermediate (250-1000 db) layer (nitrate CV=0.23, phosphate CV=0.31, silicate CV=0.24) and the deep (>1000 db) layer (nitrate CV=0.15, phosphate CV=0.22, silicate CV=0.14), decreasing the total variance. Flags in the upper and intermediate layer were thus set based on outliers within pressure ranges defined according to standard pressures (0-10, 10-30, 30-60, 60-80, 80-160, 160-260, 260-360, 360-460, 460-560, 560-1000 db) ~~These influences are of reduced importance in the intermediate (250-1000 db) layer (nitrate CV=0.23, phosphate CV=0.31, silicate CV=0.24) and the deep (>1000 db) layer (nitrate CV=0.15, phosphate CV=0.22, silicate CV=0.14). Flags in the upper layer were thus set based on atypical distribution of measurements within depth ranges defined according to standard depths (0-10, 10-30, 30-60, 60-80, 80-160, 160-260, 260-360, 360-460, 460-560, 560-1000 m)~~.

Below 1000 db~~, however~~, ~~a rigorous~~ flagging ~~was performed~~ includ~~ing~~ed an ~~check~~inspection of nitrate to phosphate (N:P) and nitrate to silicate (N:Si) ratios~~, since the secondary QC (described in section 4.2) only evaluates measurements with WOCE flag 2~~. The Median and Median Absolute Deviation (MAD) was computed by classes of pressure: we~~We~~ considered as outlier any atypical observation and any value that departs from the median by more than three ~~median absolute deviations~~MADs in the different pressure ranges for each cruise.~~.~~

An overview of the nutrient distribution is provided with scatter plots, showing also the flagged measurements (Fig. 3). Each measurement was flagged 2 (“Acceptable/ measured~~good~~”) or flagged 3 (“~~questionable~~Questionable”): 4.1% of nitrate data, 3.37% of phosphate data, 3.16% of silicate data, and 0.07% of CTD salinity data were considered outliers and flagged 3. As highlighted by ~~(~~Tanhua et al.~~,~~ (2010), the primary QC can be subjective depending on the expertise of the person flagging the data, thus flagging could bring in some uncertainties.

In order to have a first assessment of the precision of each cruise measurements, the standard deviation of ~~data~~ observations deeper than 1000 db was calculated along with averages and standard deviations for each cruise and by subregions to have an overview about nutrient content variability in the deep layer and about the observations spatial spread of individual cruises (Table 4). Following the subdivision of Manca et al. (2004), the WMED has been divided into subregions (Fig.2S, Table 2S) according to the general circulation patterns (details in Manca et al.,2004) ~~–~~. Table 4 displays the comparison of standard deviation of deep measurements for each cruise and within ~~Overall,~~ ~~the~~subregions. The overall standard deviation between cruises in the deep layer varied between 0.51 and 1.41 μmol kg^{-1} for nitrate, between 0.1 and 1.64 μmol kg^{-1} for silicate and between 0.025 and 0.078 μmol kg^{-1} for phosphate. ~~.~~Regional standard deviation of nitrate measurements below 1000 db varied between 0.08 μmol kg^{-1} in the Gulf of Lion (DF2) with cruise #9 and 1.6 μmol kg^{-1} in the Balearic Sea (DS2) observations of cruise #14. Phosphate lowest regional standard deviation was 0.01 μmol kg^{-1} found in the observations of cruise #9 in Gulf of Lion (DF2), cruise #10 in Balearic Sea (DS2) and Algerian West (DS3), cruise #14 and cruise # 15 in Tyrrhenian South (DT3), cruise #18 in Algero-Provençal (DF1) and Sardinia Channel (DI1) while the highest standard deviation was 0.1 μmol kg^{-1} in the observations of cruise #12 in Algerian West (DS3). As for silicate, the lowest standard deviation was 0.02 μmol kg^{-1} observed in cruise #9 measurements of Gulf of Lion subregion (DF2) and the highest deep standard deviation was observed in cruise #6 in its all subregions together with cruise #5 measurement in Tyrrhenian North (DT1) with 1.83 μmol kg^{-1} standard deviation.

Cruises #3, #6 and #9 had the largest spatial extension (~~visible on the~~see right side of Fig. 9) with a high ~~n important~~ number of samples over more than seven subregions (Table 4) ~~the entire area~~ and the geographical variability of the distribution in dissolved inorganic nutrients results thus in the largest standard deviations. Conversely, cruises with smaller spatial coverages have lower standard deviations. Therefore, a relatively small spatial coverage and high standard deviation is considered as indicative of data with low precision (Olsen et al., 2016). This applies to cruises #1, #5, and #16. Despite the small spatial coverage, ~~Samples~~ samples of nitrate and phosphate of cruise #5 have an overall standard deviation of 1.35 μmol kg^{-1} and 0.07 μmol kg^{-1}, respectively, a high standard deviation ~~despite the small spatial coverage (right side of Fig.9),~~ pointed out in also in the regional standard deviation of deep measurements in Tyrrhenian North (DT1) and South (DT3) .

Cruise #1, with few stations in Tyrrhenian North (DT1) and South (DT3) subregions~~the Tyrrhenian Sea~~ and 21 samples below 1000 db, has an overall standard deviation~~s~~ of 1.25 μmol kg^{-1} for nitrate, 0.06 μmol kg^{-1} for phosphate and 1.64 μmol kg^{-1} for silicate. The regional standard deviation was relatively high for nitrate (0.51-1.32μmol kg^{-1}) phosphate (0.02-0.065μmol kg^{-1}) and silicate (0.53-1.83μmol kg^{-1}). A comparison with the deviations from e.g. cruise # 2, carried out in the same year and e.g. cruise #17 (with a similar cruise track), confirms the lower precision of the data of cruise#1. Similar considerations apply to the quality of nitrate samples (0.87-1.02 μmol kg^{-1}).and silicate (0.87-0.9 μmol kg^{-1}) ~~samples~~ from cruise #16, covering a small area in Tyrrhenian North (DT1) and South (DT3)~~the Sicily Channel~~, compared to cruise #~~14~~ 17, carried out in the same ~~year but with a larger spatial coverage~~ regions (right side of Fig. 9 and ~~)~~Table 4).

Deep silicate measurements of cruise #6 have twice the overall standard deviation of silicate data of cruise #8 from the same year. Adding to that, in the seven subregions, the regional standard deviation of deep silicate observations was the highest, between 1.04-2 μmol kg^{-1} which was relatively high compared to the surrounding cruises that have observations in the same subregions. This is again suggestive of the limited precision. On the other hand, trying to explain the source of relatively high standard deviations in specific cruises is not always straightforward, as they could stem from a variety of sources, sampling, conservation and analysis. The bottom water in the WMED exhibits a high nutrient content below 1000 db (Table 4), due to the longer residence time. Dividing the WMED into subregions, has effectively removed the natural spatial change in nutrients, making the interpretation of the standard deviation a matter of the precision of the measurements only.

In Table 4, deep averages by subregions showed that overall nutrient fluctuated around 7.4 ±0.9μmol kg^{-1} for nitrate, 0.3 ±0.06 μmol kg^{-1} for phosphate and 7.7 ±0.8μmol kg^{-1} for silicate, similar findings were reported by Manca et al. (2004). Comparing cruise averages in each region enabled the identification of “suspect” cruises. Cruise #24 has the lowest deep average in nitrate in Algéro-Provençal (DF1), Tyrrhenian North (DT1) subregions and Sardinia Channel (DI1). As for silicate of cruises #24 and #16 was very low compared to the overall regional average in Liguro-Provençal (DF3) and Tyrrhenian South (DT3) subregions. Deep average of phosphate did not show any outlier cruises in all subregions. Different reasons could explain the low precision in the samples, freezing is one. Although it is a valid preservation method (Dore at al.,1995), the error is higher when samples were not analysed immediately (Segura-Noguera et al., 2011), so the storage time could influence.

3.2 Secondary Quality control: the crossover analysis

The method used to perform the secondary QC on the dissolved inorganic nutrient dataset in the WMED makes use of the quality-controlled reference data~~ described in section 2.2~~, and the crossover analysis toolbox developed by ~~(~~Tanhua ~~,~~ (2010) and ~~(~~Lauvset and Tanhua ~~,~~ (2015). The computational approach is based on comparing the cruise data set to a high-quality reference data set to quantify biases, described in detail ~~by~~ in ~~(~~Tanhua et al.~~,~~ (2010). Here, we summarize the technique with emphasis on inorganic nutrient.

The first step consisted of selecting reference data, as described in section 2.~~2~~3. The second step is the crossover analysis that was carried out using a MATLAB Toolbox (available online: https://cdiac.ess-dive.lbl.gov/ftp/oceans/2nd_QC_Tool_V2/) where crossovers are generated as difference between two cruises using the “running cluster” crossover routine. Each cruise is thus compared to the chosen set of reference cruises. For each crossover, samples deeper than 1000 db are selected within a predefined maximum distance set to 2°arc distance, defined as a crossing region, to ensure the quality of the offset with a minimum number of crossovers and to minimize the effect of the spatial change. The reason to select measurements deeper than 1000 db, is to remove the high frequency variability associated to mesoscale features, biological activity and the atmospheric forcing acting in the upper layers, that might induce changes in biogeochemical properties of water masses. On the other hand, also the deep Mediterranean cannot be considered truly "unaffected" by changes, as it is intermittently subjected to ventilation (Schroeder et al., 2016; Testor et al., 2018) and the real variability can be altered in adjusting data. The computational approach takes this into account, since weights are given to the less variant profile in the crossing region, according to the "confidence" in the determined offset of the compared profiles (i.e. the weighted mean offset of a given crossover-pair is weighted to the depth where the offsets of all compared profiles have the smallest variation (which indeed is strongly interlinked with the degree of variance of each profile) (for further details see Lauvset and Tanhua, 2015).

~~since weights are given to the less variant profile in the crossing region within each cruise so that the natural variation is not altered (for further details see (Lauvset and Tanhua, 2015)).~~

Before identifying crossovers, each profile was interpolated using the piecewise cubic Hermite method and the distance criteria outlined in ~~(~~Lauvset and Tanhua~~,~~ (2015), their Table 1, and detailed in ~~(~~Key et al.~~,~~ (2004). The crossover is a comparison between each interpolated profile of the cruise being evaluated and the interpolated profile of the reference cruise. The result is a weighted offset (defined as difference cruise/reference) and a standard deviation of the offset. The standard deviation is indicative of the precision; however, it is important to note that this assumption only works because it is a comparison to a reference, and the absolute offset is indicative of accuracy.

The third step consists in evaluating and selecting the suggested correction factor ~~to be~~that was applied to the whole water column. The correction factor~~, that~~ was calculated from the weighted mean offset of all crossovers found between the cruise and the reference data set, involving a somewhat~~how~~ subjective process.

For inorganic nutrients, offsets are multiplicative so that a weighted mean offset > 1 means that the measurements of the corresponding cruise are higher than the measurements of the reference cruise in the crossing region and applying the adjustment would decrease the measured values. The magnitude of an increase or a decrease is the difference of the weighted offset from 1. In general, no adjustment smaller than 2% (accuracy limit for nutrient measurements) is applied (detailed description is found in ~~(~~Hoppema et al., 2009; Lauvset and Tanhua, 2015; Olsen et al., 2016; Sabine et al., 2010; Tanhua et al., 2010~~)~~).

The last step is the computation of the weighted mean (WM) to determine the internal consistency and quantify the overall accuracy of the adjusted ~~inorganic nutrient dataset~~product (~~, referring to what has been described by (~~Hoppema et al., 2009; Sabine et al., 2010; Tanhua et al., 2009), with the difference that our assessment is based on the offsets with respect to a set of reference cruises. This WM reflects the absolute weighted mean offset of the data set compared to the reference data set, hence the smaller the WM the higher the internal consistency. The accuracy was computed from the individual absolute weighted offsets. The ~~weighted mean~~WM, which will be discussed in section 4~~5~~.4., was computed using the individual weighted absolute offset (D) of number of crossovers (L) and the standard deviation (σ): WM= $\frac{\sum_{i=1}^{L} D(i)/(\sigma(i))^2}{\sum_{i=1}^{L} 1/(\sigma(i))^2}$

4 Results of the secondary QC and recommendations

The results of the secondary QC revealed ~~various~~ the ~~multiplicative~~ necessary corrections ~~necessary~~ for nitrate, phosphate and silicate. Four cruises ~~(#7, #11, #19, and #21)~~ were not considered in the crossover analysis: cruises #7 and #11 do not have enough stations > 1000 db (at least 3 to get valid statistics)~~ stations > 1000 db~~, while cruises#19 and #21 were outside the spatial coverage of the reference cruises. Cruises that were not used for the crossover analysis ~~are~~ are made available in the original dataset but were not included in the ~~adjusted dataset~~final data product (see Supplementary material – Part 2 (A2)).~~.~~

Overall, we found a total number of 73 individual crossovers for nitrate, 72 for phosphate and 54 for silicate. An example of the running cluster crossover output is ~~displayed~~ shown in Fig.4. Results of the crossover analysis is an adjustment factor ~~by~~ for each cruise and each nutrient, that are shown in Table~~s~~ 5 and Fig. 5-6-7~~ that~~. The adjustment factor was calculated from the weighted mean of absolute offset summarized in Table 6 and Fig. ~~2S~~3S-~~3S~~4S-~~4S~~5S. Table 6 details the improvement of the weighted mean of absolute offset by cruise prior to and after adjustments, the information is also displayed graphically in Fig. ~~2S~~3S-~~3S~~4S-~~4S~~5S. Cruises are in chronological order in all figures and tables.

4.1 Nitrate

The crossover analysis suggests a significant adjustment~~s~~ for nitrate concentrations on 15 cruises, ~~from~~ between 0.94 ~~to~~ and 0.98 (for adjustments <1) and ~~from~~ between 1.02 ~~to~~ and 1.34 (for adjustments >1) (Table 5 and Fig.5). Offsets suggest that the deep measurements of cruises #1, #3, #4, #5, #6, #8, #12, #13, #15, #16, #23 and #24 need to be adjusted towards higher concentrations, when compared to the respective reference (Fig.~~2S~~3S).

Nitrate ~~data~~ observations ~~from~~ of cruises #2, #9 and #10 on the other hand were higher than the reference cruises and exhibit variation outside the accepted accuracy limit, thus~~and~~ requires a downward adjustment.

Finally, five cruises (#14, #17, #18, #20, and #22) were consistent with the reference data and no adjustment was necessary. Considering the weighted mean of absolute offset after adjustments shown in Table 6, two cruises (#5 and #24) required large correction factors ~~and~~ but ~~are~~ still remain outside the accuracy threshold~~: cruises #5 and #24~~ (Fig. 5). These cruises are considered in detail later (section ~~5~~4.4).

4.2 Phosphate

For phosphate the crossover analysis suggests adjustments for 20 cruises, as shown in Fig. 6. Deep phosphate measurements of 15 cruises (Table 6) appear to be lower than the respective reference measurements (i.e. phosphate data of these cruises require an upward adjustment~~increase~~), while the data of five cruises (#2, #3, #4, #6, #24) are higher (i.e. they need ~~to ~~a downward adjustment~~be decreased~~) (Fig.~~3S~~4S). Applying all the indicated adjustments, the large offsets of cruises #2, #3, #4, #6, #8, #9, #10, #18, #20, #23 and #24 are reduced and become consistent with the reference. Cruises #1, #5, #12, #13, #14, #15, #16, #17, and #22 retain an offset even after applying the indicated adjustment. These cruises are considered in detail later.

According to Olsen et al. (2016), if a temporal trend is detected in the offsets, no adjustments should be applied. There is indeed a decreasing trend between 2008 and 2017 in the phosphate correction factor (Fig. 6), and thus an increasing one in the weighted mean offset (Fig.~~3S~~4S), implying a temporal increase of phosphate. Therefore, phosphate data of the cruises being part of the trend were not flagged as questionable, except some cruises that are discussed further in section ~~5~~4.4.

Comparing phosphate before and after adjustments, the corrections did minimise the difference with the reference, while the actual variation with time was preserved (Fig.6). The temporal trend towards higher phosphate concentrations in the Mediterranean Sea is considered to be real, even though studies concerning the biogeochemical trends in the deep layers of the WMED are scarce (Pasqueron et al., 2015). However, this variation could be consistent with the findings of Béthoux et al.(1998, 2002) and the modelling studies by Moon et al. (2016) and Powley et al. (2018) who indeed found an increasing trend in phosphate concentrations over time, due to the increase in the atmospheric and terrestrial inputs.

4.3 Silicate

The results of the crossover analysis for silicate suggests corrections for all cruises (Fig.7). The crossovers indicate that deep silicate measurements are lower in the evaluated cruises than in the corresponding reference cruises (i.e. they need to be adjusted upward~~increased~~) (Fig.~~4S~~5S). This is likely to be a direct result of freezing the ~~samples freezing before~~samples before analysis, since the reactive silica polymerizes when frozen (Becker et al., 2019). After applying the adjustment (Table 5), as expected, the offsets are reduced (Table 6), but five cruises (#1, #5, #6, #15, and #16) remain outside the accuracy envelope. Due to the large offsets, these cruises will be discussed further in section ~~5~~4.4.

4.4 Discussion and recommendation

Adjustments were evaluated for each cruise separately. As a general rule no correction was applied when the suggested adjustment is strictly within the 2% limit (indicated with NA in Table 5). The average correction factors were 1.06 for nitrate, 1.14 for phosphate and 1.14 for silicate, respectively. To verify the results, we re-ran the crossover analysis and re-computed offsets and adjustment factors using the adjusted data (as shown in blue in Fig. ~~2S~~3S-~~3S~~4S-~~4S~~ 5S and Fig. 5-6-7). Most of the new adjustments are within the accuracy envelope and ~~only~~ few are outside the limit, except for the cruises belonging to the above mentioned “phosphate-trend” and the other outlying cruises which are detailed hereafter. By the application of adjustments, the deep-water offsets were reduced. This can be seen in the decrease of the weighted mean offset between the data before adjustments (after 1st QC, Fig. 3S-4S-5S, in grey) and the adjusted data (after 2nd QC, Fig. 3S-4S-5S, in blue).

Referring to the analysis detailed in section ~~4~~3.2, the internal consistency of the nutrient data set has improved and increased significantly after the adjustment, from ~~0.98~~4% for nitrate, ~~0.83~~19% for phosphate and ~~0.86~~13% for silicate, to a more unified dataset with ~~1.004~~3 % for nitrate, ~~0.97~~6 % for phosphate and ~~0.98~~3% for silicate.

A comparison between the original and the adjusted ~~vertical~~ nutrient ~~profiles~~ observations is shown in Fig. 8A-B-C, indicating an improvement in the accuracy based on the reference measurement and a relatively reduced range particularly for phosphate (Fig. 8B). Figure 8. D-E scatterplots show that after the ~~performed~~ quality control, nutrient stoichiometry slopes obtained from regressions, between tracers along the water column show a strong coupling and provide a nitrate to phosphate ratio of ~22.09~~1~~ and a nitrate to silicate ratio of ~0.94. These values are consistent with nutrient ratios range found in the WMED as reported in Lazzari et al. (2016); Pujo-Pay et al., (2011) and Segura-Noguera et al. (2016).

The regression model is more accurate after adjustments with an improved r^2 for N:P (from 0.81 to 0.90) and for N: Si (from 0.85 to 0.~~86~~87).

~~A~~One of the main reasons for an upward/ downward bias would be the lack of use of CRM for nutrients in all cruises as also noted in CARINA (Tanhua et al., 2009) or in the most recent global comparability study by Aoyama (2020).

In the following some details on the adjustment of specific cruises are given:

Cruise #2 [48UR20041006] needed an adjustment of 0.98 for nitrate, 0.9 for phosphate and 1.06 for silicate. Most of the crossover profiles occur in the Tyrrhenian sea (Tyrrhenian North and Tyrrhenian South subregions). After adjustment, the cruise is inside the 2% envelope.

Cruise #3 [48UR20050412] appeared to be outside the 2% envelope before adjustments. Its offsets with five reference cruises, crossing the Tyrrhenian sea, Sardinia channel, Gulf of Lion and Algero-Provençal subregions, showed that nitrate and silicate values to be relatively low, and thus an adjustment of 1.08 and 1.15 was applied respectively. On the other hand, phosphate values were relatively high, and a 0.93 adjustment was applied.

Cruise #4 [48UR20050529] correction factor estimate was based on five crossovers that covered five subregions: Tyrrhenian South, Sardinian channel, Algerian East and West and the Alboran sea. Table 4) show that there are no large differences between regional averages within the cruise which justify an adjustment of 1.04 for nitrate, 0.85 for phosphate and 1.183 for silicate.

Cruise #8 [48UR20060928] was adjusted by 1.03 for nitrate, 1.14 for phosphate and 1.1 for silicate, because it showed values to be low compared to four references. After adjustment, the data were inside the acceptable range.

Cruise #9 [48UR20071005] values of nitrate were slightly outside the 2% envelope before adjustments, similar to phosphate and silicate that were lower compared to the reference. The adjustments of 0.97 for nitrate, 1.14 for phosphate and 1.115 for silicate suggested by the mean offset against the reference cruises were recommended.

Cruise #13 [48UR20090508] has three crossovers in the common crossing zone that included Tyrrhenian North, Tyrrhenian South and Sardinia Channel subregions. The crossover suggests that this cruise has too low values and needs an adjustment of 1.05 for nitrate, 1.33 for phosphate and 1.15 for silicate.

Cruise #14 [48UR20100430] has a mean offset with four reference cruises that suggests an adjustment for phosphate of 1.34 and silicate of 1.123. Nitrate did fall within the accuracy envelope.

Cruise #10 [48UR20080318] has only three crossovers in the Algero-Provençal subregion, showing that nitrate is too high compared to the reference while phosphate and silicate are slightly lower. We therefore applied the adjustments of Table 5, since the deep averages for each region (table 4) did not show large regional difference.

Cruise #17 [48UR20110421] crossover analysis did not suggest any correction for nitrate, However, for phosphate and silicate with an offset based on two crossovers in the Tyrrhenian North and South subregions, adjustments were recommended for phosphate (1.25) and silicate (1.12), for being lower than the reference cruises.

Cruise #18 [48UR20111109] is similar to cruise #17, since it was suggested to correct phosphate by 1.14 and silicate by 1.09, based on four crossovers in the Tyrrhenian North and South, Sardinia channel and Algero-Provençal subregions.

Cruise #20 [48UR20120111] has four crossovers over the Tyrrhenian North and South and Algero-Provençal subregions. Its measurements were slightly lower than the reference cruises suggesting a correction factor of 1.17 for phosphate and 1.08 for silicate.

Cruise #22 [48UR20131015] has similar correction factors as cruise#20, based on three crossovers in the Sardinia channel and Tyrrhenian North and South subregion, with measurements being lower than the reference.

Cruise #23 [48QL20150804] showed nutrient values slightly lower than the reference cruises as well, suggesting small correction factors of 1.02 for both nitrate and phosphate and 1.08 for silicate that were based on offsets with five cruises.

Below, we discuss the recommended flags in the final product (Table 3) assigned ~~in the adjusted dataset~~ for some cruises that needed further consideration, since they required larger adjustment factors:

Cruise #1 [48UR20040526]: The adjusted values are still lower than the reference (Fig.5-6-7-Fig.~~2S~~3S-~~3S~~4S-~~4S~~5S) and are still outside the 2% accuracy range. This cruise had stations in the Sicily ~~Channel~~Strait, Tyrrhenian North and South and Ligurian East sub-regions.~~Sea and Corsica Channel~~ (Fig. 9, right side) and only 4 stations were deeper than 1000 db (those within the Tyrrhenian Sea). The low precision of this cruise has already been evidenced during the primary QC (section ~~4~~3.1). We recommend flagging this cruise as questionable (flag 3).

Cruise #5 [48UR20051116]: This cruise took place between Sicily ~~Channel~~ Strait and the Tyrrhenian ~~Sea~~ North and South (Fig. 9, right side). Nitrate, phosphate and silicate data were lower than those from other cruises (#3 and #4) run the same year (Fig. 5-6-7-Fig.~~2S~~3S-~~3S~~4S-~~4S~~5S) and are still biased after adjustments. Considering the limited precision and the low number of crossovers, it is recommended to flag the cruise as questionable (flag 3).

Cruise #6 [48UR20060608]: This cruise had an offset with five cruises giving evidence that adjustments of 1.05 for nitrate, 0.86 for phosphate and 1.26 for silicate are needed. The silicate bias was reduced after adjustment but remains large with respect to the accuracy limit (Fig. 7-Fig. ~~4S~~5S). This cruise has a wide geographic coverage, with stations along 9 sections (Fig. 9, right side). Considering also the high standard deviation (Table ~~3~~4), which is partially attributed to the spatial coverage of the cruise, there is still ~~remains~~ uncertainty about the quality of the samples. It is recommended to flag silicate data of cruise #6 as questionable (flag 3).

Cruise #12 [48UR20081103]: Phosphate data have low accuracy with respect to the reference cruises (Fig. 6-Fig. ~~3S~~4S). This cruise has stations along a longitudinal section from the Sicily ~~Channel~~ Strait to the ~~Gibraltar Strait~~Alboran Sea, which might explain the large standard deviation of deep phosphate samples (Table ~~3~~4). ~~-~~Cruise #12 was given a correction of 1.08 for nitrate, 1.12 for silicate and 1.38 for phosphate. The mean offset from five crossovers computed within the Tyrrhenian South, Sardinia Channel, Algerian East, Algerian West and Alboran Sea subregions suggests that this cruise has lower nutrient values than the reference cruise. After adjustment, cruise #12 is within the acceptable range for nitrate and silicate but not for phosphate as highlighted in section 3.2. In addition, considering the relatively high number of stations >1000 db and a plausible trend in phosphate, it is ~~not~~ recommended to flag the phosphate data as good/acceptable~~questionable~~.

Cruise #15 [48UR20100731]: This cruise had 149 station along a similar track as cruise #12~~ and~~but shows larger offsets for phosphate and silicate (Fig. 6-7-Fig. ~~3S~~4S-~~4S~~5S), compared to cruise #12. Considering that deep silicate data was not of low quality (small standard deviation, see Table ~~3~~4), and that deep phosphate fall within the “phosphate-trend” discussed above, these data are flagged good/acceptable~~we do not recommend flagging as questionable~~.

Cruise #16 [48UR20101123]: The cruise shows large offsets for phosphate and silicate (Fig. 6-7- Fig. ~~3S~~4S-~~4S~~5S), similar to cruise #15. Considering that the overall cruise standard deviation of silicate samples below 1000 db was relatively high (1.02 over 14 samples, see Table ~~3~~4), and that it has only one crossover between the Tyrrhenian North and South subregions (Table 6), and that when comparing deep regional averages, this cruise had the lowest average silicate value, it is recommended to flag silicate data of cruise #16 as questionable (flag 3). As for phosphate, the cruise is part of the “phosphate-trend” and is therefore flagged good/acceptable ~~not recommended to be flagged as questionabl~~e.

Cruise #24 [48QL20171023]: This cruise has the largest offset for nitrate even after adjustment. It is very likely due to a difference between laboratories (calibration standards) concerning nitrate, which needs to be flagged as questionable in the final product.

The c~~C~~ruises discussed in this section were not removed from the final product but are retained along with their recommended quality flag~~s~~ (Table 3) detailed above and in the supplementary material – Part 2 (A2)). We have done the evaluation of their overall quality but leave it up to the users how to appropriately use these data.

4.5 Product assessment: Comparison with MEDATLAS

Averages water mass properties have been computed from the adjusted product (Table 7), and compared to the MEDAR/Medatlas annual climatological profiles, downloaded from the Italian NODC website (http://doga.ogs.trieste.it/medar/) given by Manca et al. (2004), in order to evaluate and ~~and~~ asses the new product. Since nutrient properties exhibit differences with depths, we compared average nutrient concentrations of the three main water masses in twelve subregions of the WMED (Table 7, Fig 2S)~~West and~~.

The results of Table 7 compares water mass biogeochemical properties with the reference climatology. The new product agrees well with the Medatlas climatology. However, there are some distinctions. The surface layer (0-150db) is characterized by a low nutrient content. The surface nitrate varies between 0.69 and 2.75 μmol kg^{-1} with a maximum found in the Ligurian East (DF4) and the minimum in the Alboran Sea (DS1) subregions, similar values were recorded in the climatology (0.61- 3.00 μmol kg^{-1}). The differences in nitrate averages in the surface layer are observed in the Gulf of Lion (DF2) where the new product is higher than the climatology and slightly lower in the Liguro-Provençal (DF3). As for, the surface content in phosphate, it varied between 0.04 and 0.16 μmol kg^{-1} with a maximum found in the Ligurian East (DF1) and a minimum in the Alboran Sea (DS1), alike the Medatlas climatology, where phosphate averages fluctuate between 0.05 and 0.19 μmol kg^{-1} .The new product is slightly lower compared to the climatology. As to the average surface in silicate, it varies between 1.36 and 2.91 μmol kg^{-1} with a minimum found in the Ligurian East (DF4), the maximum in the Gulf of Lion (DF2)) while in the climatology it varied between 1.27 and 2.31 μmol kg^{-1} (the minimum in the Ligurian East (DF4) and the maximum in the Alboran Sea (DS1)). The new product is slightly higher in silicate.

Overall, the differences in the surface layer are observed in Gulf of Lion (DF2), Liguro-Provençal (DF3), Ligurian East (DF4), which is due to the intense variability of the vertical mixing occurring in the northern WMED compared to the other regions.

In the intermediate layer, averages were computed from the depth of the salinity maximum (S_{max}) ±100m from a regional average profile, indicative of the Levantine Intermediate Water (LIW) core. Nitrate average varies between 4.94 and 9.32 μmol kg^{-1} where the minimum content is recorded in Sicily strait (DI3) and the maximum in the Algerian West (DS3) while in the in the Medatlas climatology nitrate was between 5.14 and 8.60 μmol kg^{-1} . In average, the lowest content in nitrate was in Tyrrhenian North (DT1), South (DT3), Sardinia Channel (DI1) and Sicily Strait (DI3) while LIW of Gulf of Lion (DF2), Liguro-Provençal (DF3), Ligurian East (DF4), Balearic Sea (DS2), Algero-

Provençal (DF1), Alboran Sea (DS1), Algerian West (DS3) and East (DS4) subregions is relatively rich in nitrate. Compared to the Medatlas product, though the new product is slightly higher mainly in the Gulf of Lion (DF2), Ligurian East (DF4) and Balearic Sea (DS2). As for phosphate, LIW averages show similar behavior as nitrate, the lowest phosphate content (0.21- 0.27 μmol kg^{-1}) is observed in the Eastern subregions of WMED (Sicily Strait (DI3),Sardinia Channel (DI1), Tyrrhenian South (DT3) and North (DT1), when the maximum concentrations (0.4-0.37 μmol kg^{-1}) were reported in the Western subregions of the WMED (the Alboran Sea (DS1), Algerian West (DS3) and East (DS4), Balearic Sea (DS2) and Gulf of Lion (DF2)). The large differences between the two products were in Ligurian East (DF4) and the Alboran Sea (DS1), subregions of few number of observations.

Concerning silicate, the lowest average concentration (5.25 μmol kg^{-1}) is observed in LIW core of the Sicily Strait (DI3,) and the maximum concentrations (8.66 - 8.77 μmol kg^{-1}) are in Alboran Sea (DS1) and Gulf of Lion (DF2), similar values were recorded in the Medatlas climatology (4.86-7.95 μmol kg^{-1}). There are some discrepancies, where the new product is higher particularly in the Gulf of Lion (DF2), Liguro-Provençal (DF3) and Algerian West (DS3) subregions. This difference is explained by the limited number of observations within depth range in the new product compared to the observations used in the climatology in these subregions.

Referring to Manca et al.,(2004), the LIW core salinity values are relatively more pronounced in Sicily strait (DI3), Sardinia channel (DI1) and in the Tyrrhenian South (DT3), North (DT1) subregions, where nutrients were lower than the Western subregions (DS3,DS4, DS1 , DF1, DS2, DF4, DF3, DF2). The averages of nutrient within the LIW core ties well with the Medatlas climatology averages (Table 7), except in subregions with important vertical mixing.

We have verified also average biochemical properties in the deep layer (below 1500db). The new product is slightly higher in nitrate averages (7.74 -8.37 μmol kg^{-1}) than the Medatlas climatology (7.12 - 8.06 μmol kg^{-1}) (Table 7). The largest difference is found in Tyrrhenian South (DT3) and North (DT1) subregions. This difference could be due to the fact that, we are comparing two different time periods (2004-2017 and 1908-2001). As for the deep layer phosphate, average concentrations vary between 0.35 and 0.37 μmol kg^{-1} and are within the climatology limits (0.31 - 0.40 μmol kg^{-1}). In all subregions, there is not large differences. Overall, phosphate is in accordance with the Medatlas climatology. Similar to nitrate, deep average silicate in the new product (8.64 -9.21 μmol kg^{-1}) is higher than the climatology (7.51 to 9.04 μmol kg^{-1}). The largest difference in average silicate is observed in Tyrrhenian North (DT1), South (DT3) and Liguro-Provençal (DF3) subregions.

~~7~~ We then used the Root Mean Squared Error (RMSE) as statistical index to quantify the difference between averaged regional profiles from the new products and Medatlas product. The climatology annual profiles were interpolated to the regional average profiles of the new product, and the average RMSE for each layer and subregion was calculated. Fig. 10 shows the regional evolution of RMSE in the main water masses for the three nutrients. For nitrate (Fig. 10 A), the RMSE vary between 0.12 μmol kg^{-1} in Tyrrhenian North (DT1) and 1.36 μmol kg^{-1} Gulf of Lion (DF2) in the surface layer, between 0.07 μmol kg^{-1} in the Sardinia Channel (DI1) and 2.35 μmol kg^{-1} in Gulf of Lion (DF2) in the intermediate layer, and between 0.11 μmol kg^{-1} Algerian East (DS4) and 0.79 μmol kg^{-1} Gulf of Lion (DF2). The RMSE decreases in the Algerian East (DS4), Tyrrhenian North (DT1), Tyrrhenian South (DT3), Sardinia Channel (DI1) and Sicily Strait (DI3). This illustrates the low difference between the two products.

For phosphate (Fig. 10 B), the RMSE ranges between 0.0022 μmol kg^{-1} in the Tyrrhenian South (DT3) and 0.12 μmol kg^{-1} in the Ligurian East (DF4) in the surface layer, and between 0.003 μmol kg^{-1} in the Liguro-Provençal subregion (DF3) and 0.048 μmol kg^{-1} in the Alboran Sea (DS1), while in the deep layer RMSE varied between 0.0087 in the Gulf of Lion (DF2) and 0.057 μmol kg^{-1} in the Tyrrhenian North (DT1).

Silicate RMSE (Fig. 10 C) is between 0.13 μmol kg^{-1} in the Algero-Provençal subregion (DF1) and 3.5 μmol kg^{-1} in the Ligurian East subregion (DF4) in the surface layer, between 0.10 μmol kg^{-1} in the Sardinia Channel (DI1) and 2.54 μmol kg^{-1} in the Gulf of Lion (DF2) in the intermediate layer, and in deep layer, RMSE ranges between 0.33 μmol kg^{-1} in the Algerian East (DS4) and 1.43 μmol kg^{-1} in the Liguro-Provençal subregion (DF3).

The best agreement between the two products was observed in the intermediate and deep layer. The lowest RMSE was confined to the deep layer in most of the subregions while the highest difference was found in the surface layer since it is subjected to intense vertical mixing mainly in the northern WMED. Comparing averages in subregions, showed similar differences in nutrient between the two products particularly in the Gulf of Lion (DF2), the Liguro-Provençal (DF3), Ligurian East (DF4) and Algerian East (DS4), due to the relative high variability in nutrient concentrations in these subregions. These differences are not significant as there is discrepancy on the number of observations used in the two products. Overall, inorganic nutrients of the new product agree very well with the MEDAR/Medatlas climatology. The main features of the spatial distribution in the inorganic nutrients were in accordance with the findings of Manca et al., (2004), where the relative high content in nutrient was found in the intermediate layer of the Algerian subregions (DF1, DS3, DS4) than in other subregions (table 7). Besides, the highest concentrations in deep layer silicate were reported in the Algerian subregions (9.21 μmol kg^{-1} (DS3) in the new product; 9.04 μmol kg^{-1} (DS4) in the climatology) in the two products, which is indicative of the poor regional ventilation and of the longer residence time of deep water especially in these subregions.

5 Final remarks

An internally consistent data set of dissolved inorganic nutrients has been generated for the WMED (2004-2017). The accuracy envelope for nitrate and silicate was set to ~2%, a predefined limit used in GLODAP and CARINA data products~~sets~~. Regarding phosphate data, these were almost entirely outside this limit, because of its natural variations and overall very low concentrations in the WMED, a highly P-limited basin. Using a crossover analysis (2nd QC toolbox) to compare cruises with respect to reliable reference data, improved the accuracy of the measurements by bias-minimizing the individual cruises~~.~~ the new product was broadly in consistent with the earlier climatology MEDAR/Medatlas.

The publication of a quality-controlled extensive (spatially and temporally) database of inorganic nutrients in the WMED was timely ~~,~~and fills a gap in information that prevented baseline assessments on spatial and temporal variability of biogeochemical tracers in the Mediterranean. In combination with older databases in the same region (e.g. bottle data available in the MEDAR/Medatlas~~EDATLAS~~ database), this new database will thus constitute a pillar on which the Mediterranean marine scientific community will be able to build on original research topics on biogeochemical fluxes and cycles and their relation to hydrological changes that occurred in the period covered by the dataset. The dataset is also relevant for the modelling community as it can be used as an independent~~ dataset~~ data product to assess reanalysis products or it can be assimilated in new reanalysis products.

6 Data availability

The final ~~dataset~~ product is available as a .csv merged file~~s~~ from PANGAEA, and can be accessed at https://doi.pangaea.de/10.1594/PANGAEA.904172 (Belgacem et al. 2019).

Ancillary information is in the supplementary materials with the list of variables included in original and final product. Table 1 summarizes all cruises included in the dataset. The dataset include frequently measured stations and key transects of the WMED with in situ physical and chemical oceanographic observations. As mentioned, two files are accessible, both include oceanographic variables observed at the standard depths (see supplementary ~~m~~Materials Part-2).

- *Original dataset: CNR_DIN_WMED_20042017_original.csv:* This is the original dataset with flag variable for each of the following parameter: CTD salinity, nitrate, phosphate and silicate from the primary quality control (detailed in section 3~~4~~.1).

- *Adjusted dataset: CNR_DIN_WMED_20042017_adjusted.csv*: This is the product after primary quality control and after applying the adjustment factors from the secondary quality control. Recommendations of section ~~5~~4.4 are included, as well as quality flags.

Author contribution: MB, MA, SL, JC and KS substantially contributed to write the manuscript. SC, GC and FA run the chemical analysis and contributed to the manuscript. MB coordinated the technical aspects of most of the cruises. SC, GC, FA, AR, BP contributed in specific part of the manuscript.

Acknowledgements. The data have been collected in the framework of several of national and European projects, e.g.: KM3NeT, EU GA #011937; SESAME, EU GA #GOCE-036949; PERSEUS, EU GA #287600; OCEAN-CERTAIN, EU GA #603773; COMMON SENSE, EU GA #228344; EUROFLEETS, EU GA #228344; EUROFLEETS2, EU GA # 312762; JERICO, EU GA #262584; the Ital~~a~~ian PRIN 2007 program “Tyrrhenian Seamounts ecosystems”, and the Italian RITMARE Flagship Project, both funded by the Italian Ministry of University and Research. We thank Sarah Jutterström from the Swedish Environmental Research institute for the invaluable help in Quality Control discussions. We would like to express our appreciation to the INOCEN laboratory team at IEO for their help and collaboration during MB’s stay there. The authors are deeply indebted to all investigators and analysts who contributed to data collection at sea during so many years, as well as to the PIs of the cruises (S. Aliani, M. Astraldi, M. Azzaro, M. Dibitetto, G. P. Gasparini, A. Griffa, J. Haun, L. Jullion, G. La Spada, E. Manini, A. Perilli, C. Santinelli, S. Sparnocchia), the captains and the crews for allowing the collection of this enormous dataset; without them, this work would not have been possible.

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Figure Captions

Figure 1. Map of the Western Mediterranean Sea showing the biogeochemical stations (in blue) and the five reference cruise stations (in red).

Figure 2. Overview of the reference cruise spatial coverage and vertical distributions of the inorganic nutrients. Top left: geographical distribution map, top right: vertical profiles of nitrate in μmol kg^{-1}, bottom left: vertical profiles of phosphate in μmol kg^{-1}, bottom right: vertical profiles of silicate in μmol kg^{-1}.

Figure 3. Scatter plots of (A.) phosphate vs nitrate (in μmol kg^{-1}) and (B.) silicate vs. nitrate (in μmol kg^{-1}). Data that have been flagged as "questionable" (flag=3) are in red, the colour bar indicates the pressure (in dbar). The black lines represent the best linear fit between the two parameters, and the corresponding equations and r^2 values are shown on each plot. Average resulting N:P ratio is 20.~~91~~87, average resulting N:Si ratio is 1.05 (whole depth).

Figure 4. An example of the calculated offset for silicate between cruise 48UR20131015 and cruise 29AJ2016818 (reference cruise). Above: location of the stations being part of the crossover and statistics. Bottom left: vertical profiles of silicate data in (μmol kg^{-1}) of the two cruises that fall within the minimum distance criteria (the crossing region), below 1000 dbar. Bottom right: vertical plot of the difference between both cruises (dotted black line) with standard deviations (dashed black lines) and the weighted average of the offset (solid red line) with the weighted standard deviations (dotted red line).

Figure 5. Results of the crossover analysis for nitrate, before (grey) and after adjustment (blue). Error bars indicate the standard deviation of the absolute weighted offset. The dashed lines indicate the accuracy limit 2% for an adjustment to be recommended.

Figure 6. The same as Fig. 5 but for phosphate.

Figure 7. The same as Fig. 5 but for silicate.

Figure 8. Dataset comparison before (black) and after (blue) adjustment, showing vertical profiles of (A.) nitrate (in μmol kg^{-1}), (B.) phosphate (in μmol kg^{-1}) and (C.) silicate (in μmol kg^{-1}). Scatter plots of the adjusted data from all depths after 1st and 2nd quality control for (D.) phosphate vs nitrate (in μmol kg^{-1}) and (E.) silicate vs. nitrate (in μmol kg^{-1}). The black lines represent the best linear fit between the two parameters, and the corresponding equations and r^2 values are shown on each plot. Average resulting N:P ratio is 22.~~17~~09, average resulting N:Si ratio is 0.94 (whole depth).

Figure 9. Vertical profiles of the inorganic nutrients in the dataset after adjustments and spatial coverage of each cruise (reference to cruise ID is above each map). The whole WMED adjusted ~~dataset~~ product is shown in black while the data of each individual cruise are shown in blue (flag=2) and green (flag=3).

Figure 10. RMSE regional averages of water mass properties computed between the new adjusted product and MEDAR/Medatlas climatology for nitrate (A.), phosphate (B.) and silicate (C.).

Table captions

Table 1. Cruise summary table and parameters listed with number of stations and samples. Cruises were identified with an ID number and expedition code ('EXPOCODE' of format AABBYYYYMMDD with AA: country code, BB: ship code, YYYY: year, MM: month, DD: day indicative of cruise starting day)

Table 2. Cruise summary table of the reference cruises collection used in the secondary quality control, collected from 2001 to 2016.

Table 3. WOCE flags used in the original data product and in the adjusted product.

Table 4. Average and Standard deviations of nitrate, phosphate and silicate measurements by cruise and for each region with number of samples deeper than 1000db included in the 2nd QC. Average storage time: the minimum storage time defined as time difference between the cruise ending day and the 1st day of the laboratory analysis.

Table 5. Summary of the suggested adjustment for nitrate, phosphate and silicate resulting from the crossover analysis. Adjustments for inorganic nutrient are multiplicative. NA: denotes not adjusted, i.e. data of cruises that could not be used in the crossover analysis, because of the lack of stations or data are outside the spatial coverage of reference cruises.

Table 6. Secondary QC toolbox results: improvements of the weighted mean of absolute offset per cruise of unadjusted and adjusted data; (n) is the number of crossovers per cruise. The numbers in red (less than 1) indicate that the cruise data are lower than the reference cruises. NA: not adjusted.

Table 7. Water mass properties and regional average concentrations of inorganic nutrients: comparison between the new adjusted product and the MEDAR/Medatlas climatology (with standard deviations and number of observations in brackets).

Figure 1

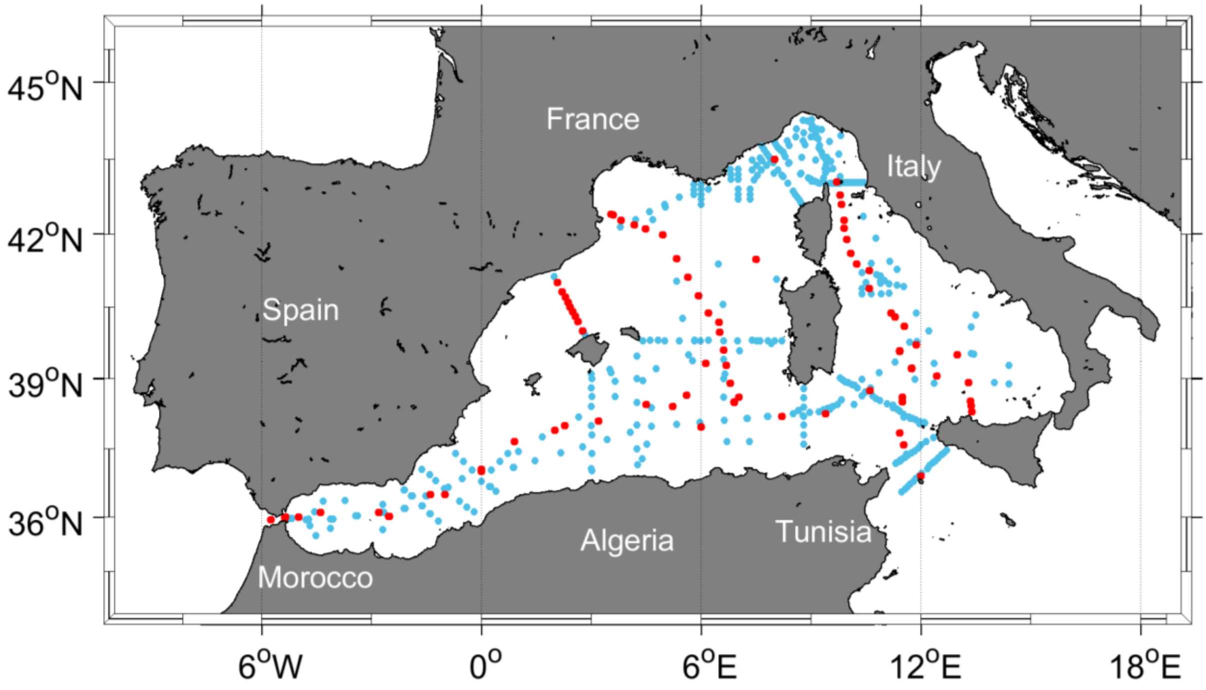
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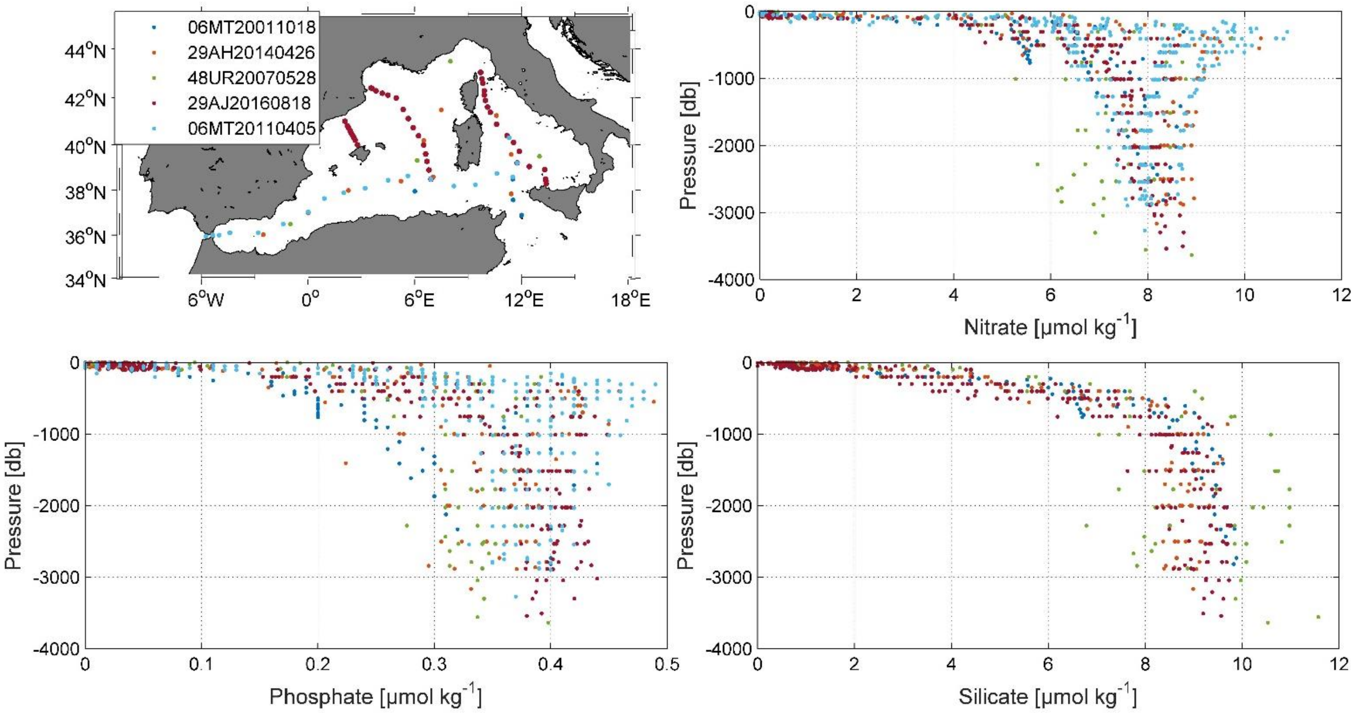
Figure 2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38°N
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34°N
6°W
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6°E
12°E
18°E
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Nitrate [µmol kg^{-1}]
Phosphate [µmol kg^{-1}]
Silicate [µmol kg^{-1}]
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-2000
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Figure 3

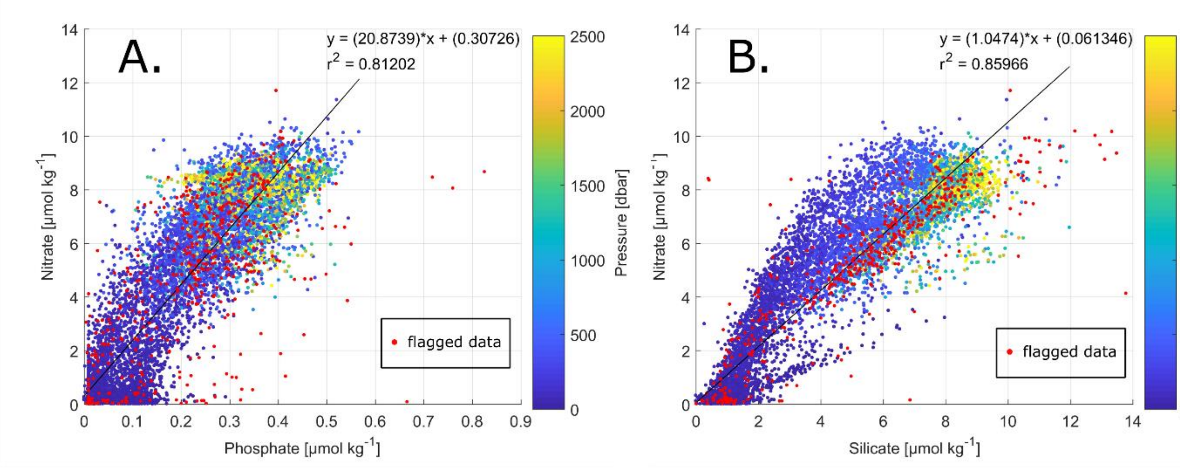

Figure 4

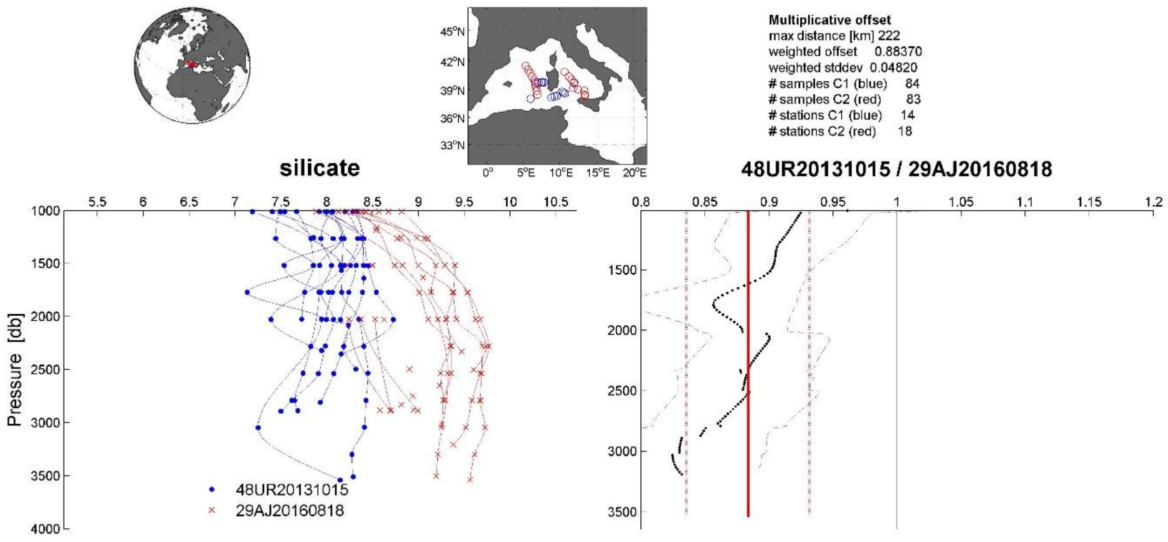

Figure 5

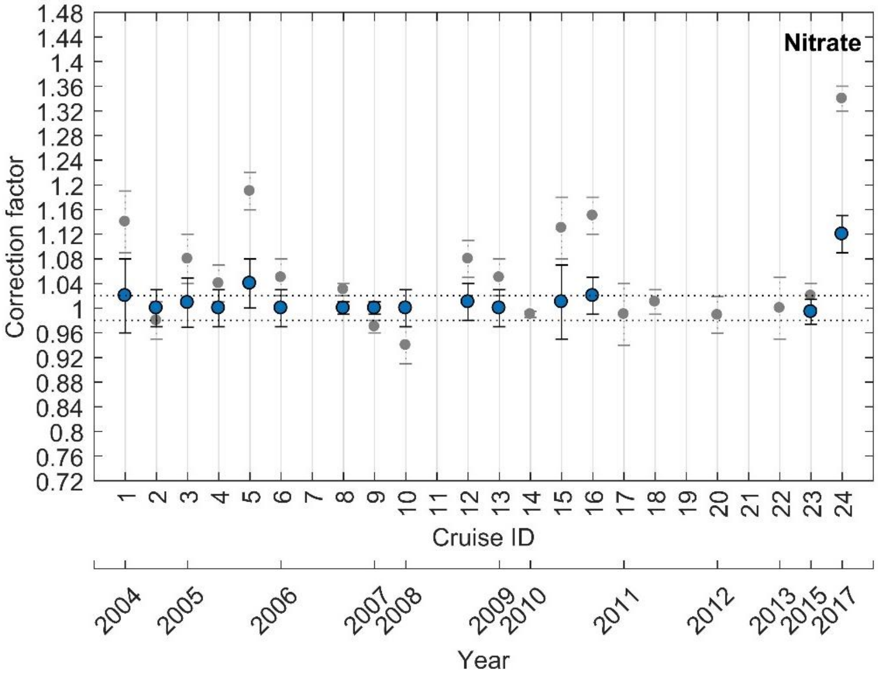
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Figure 6

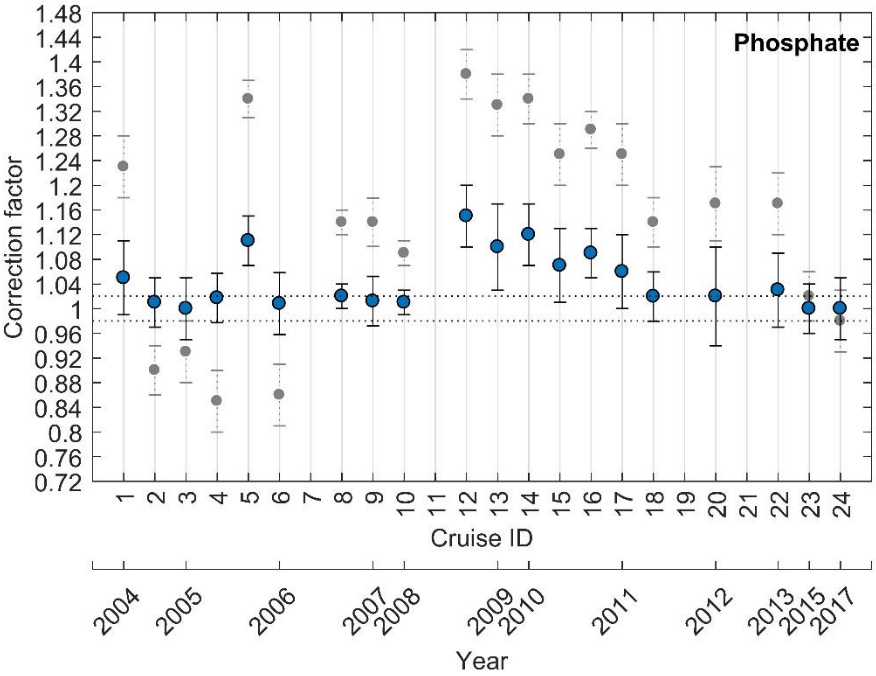
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Figure 7

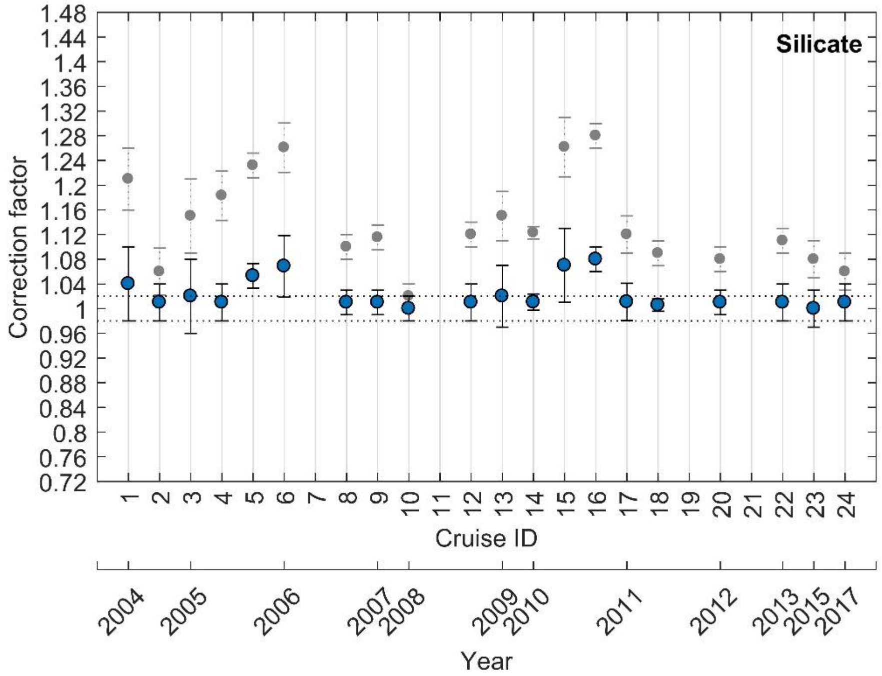
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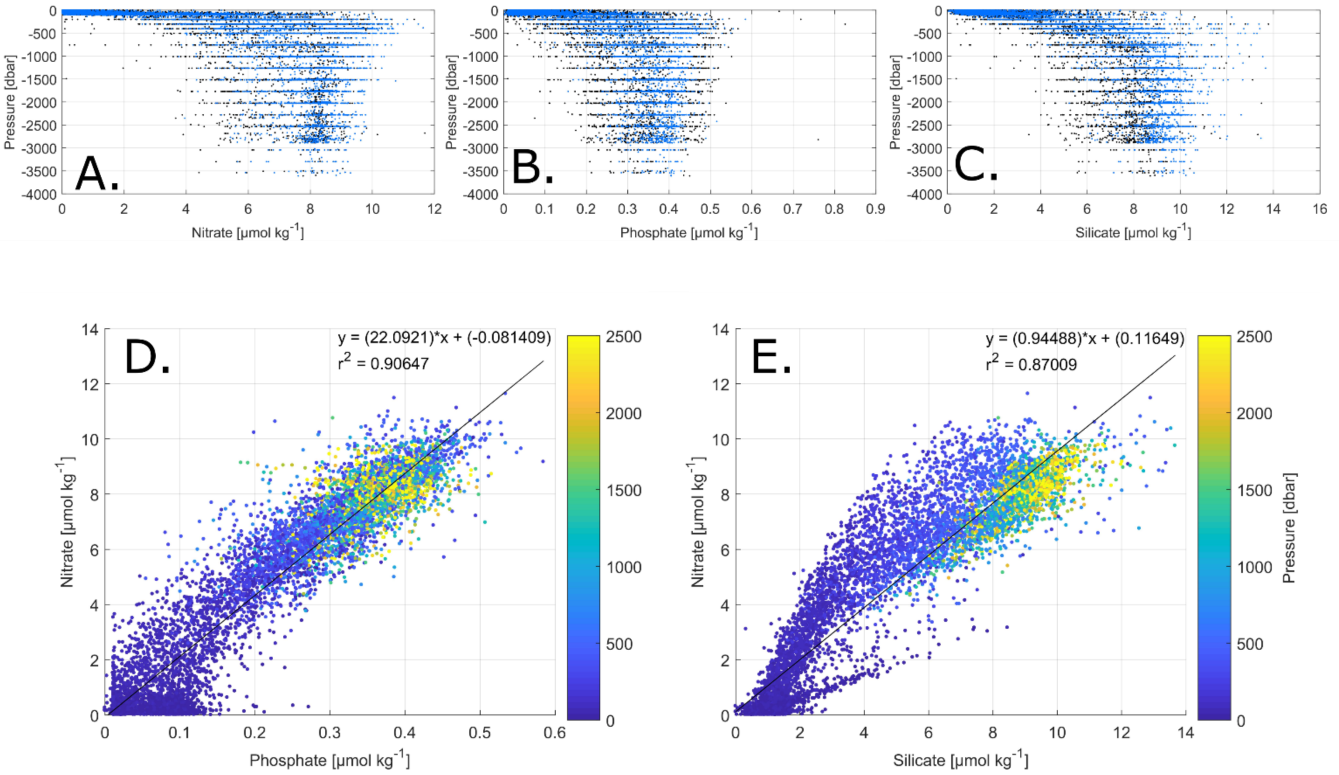
Figure 8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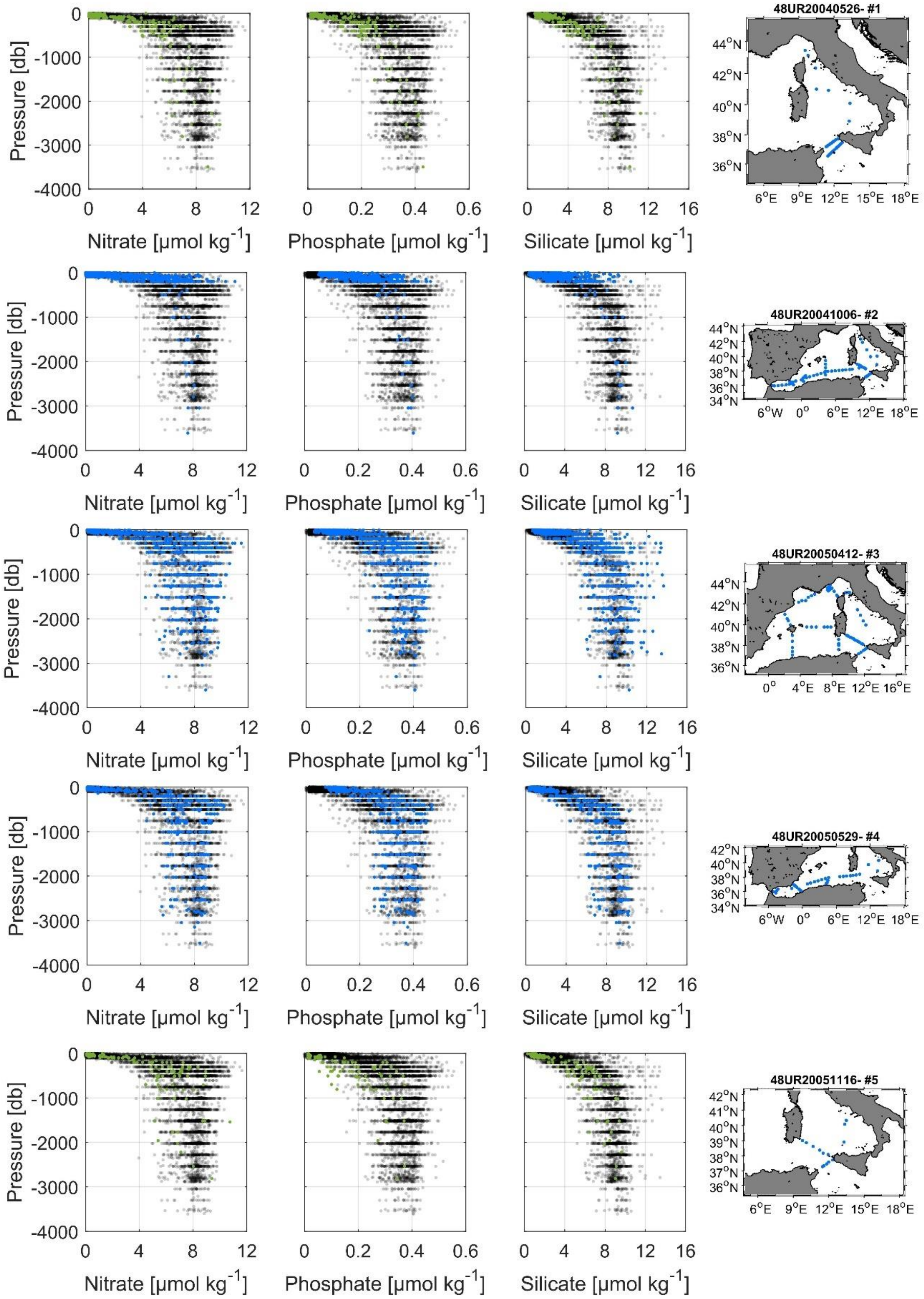
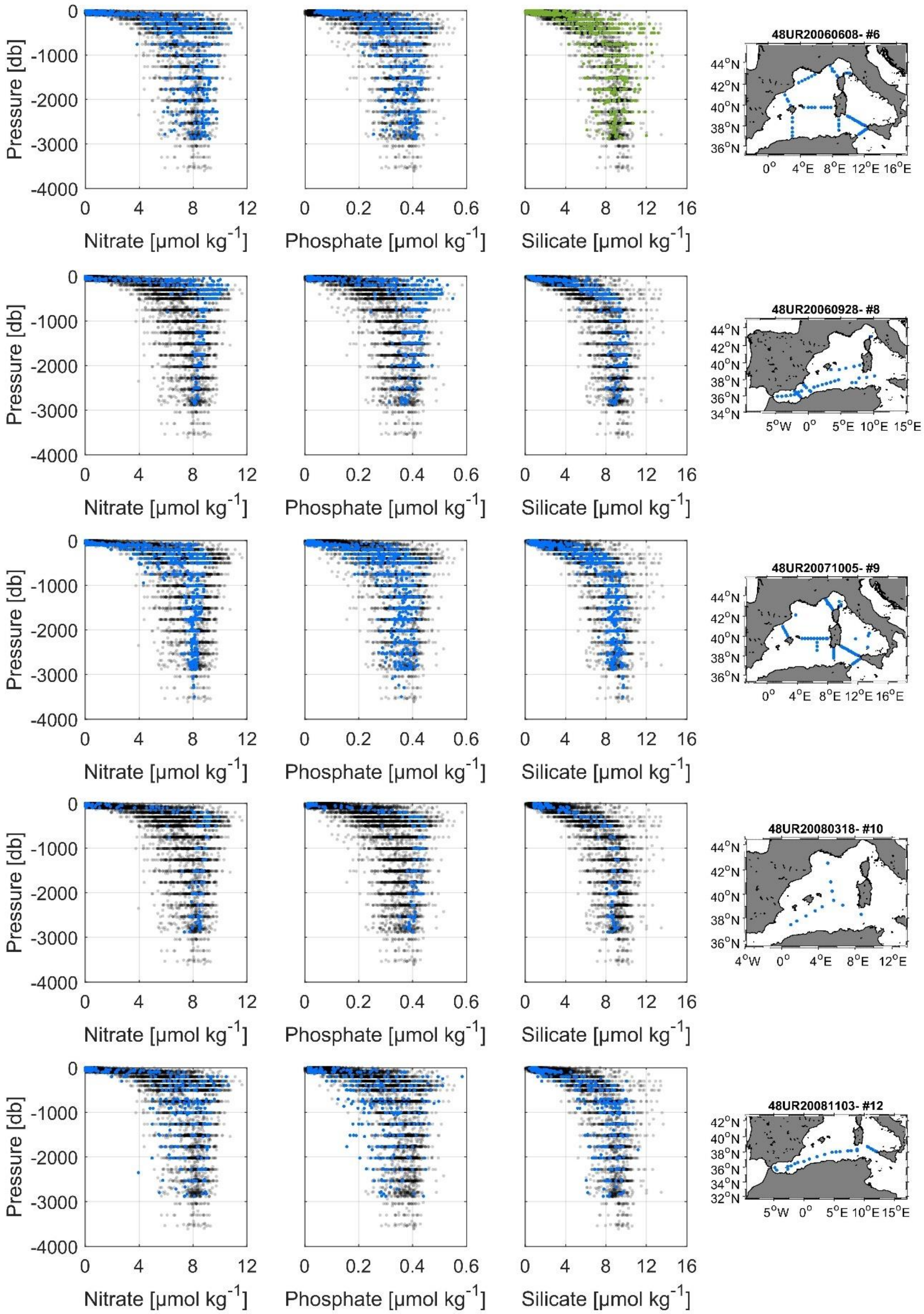
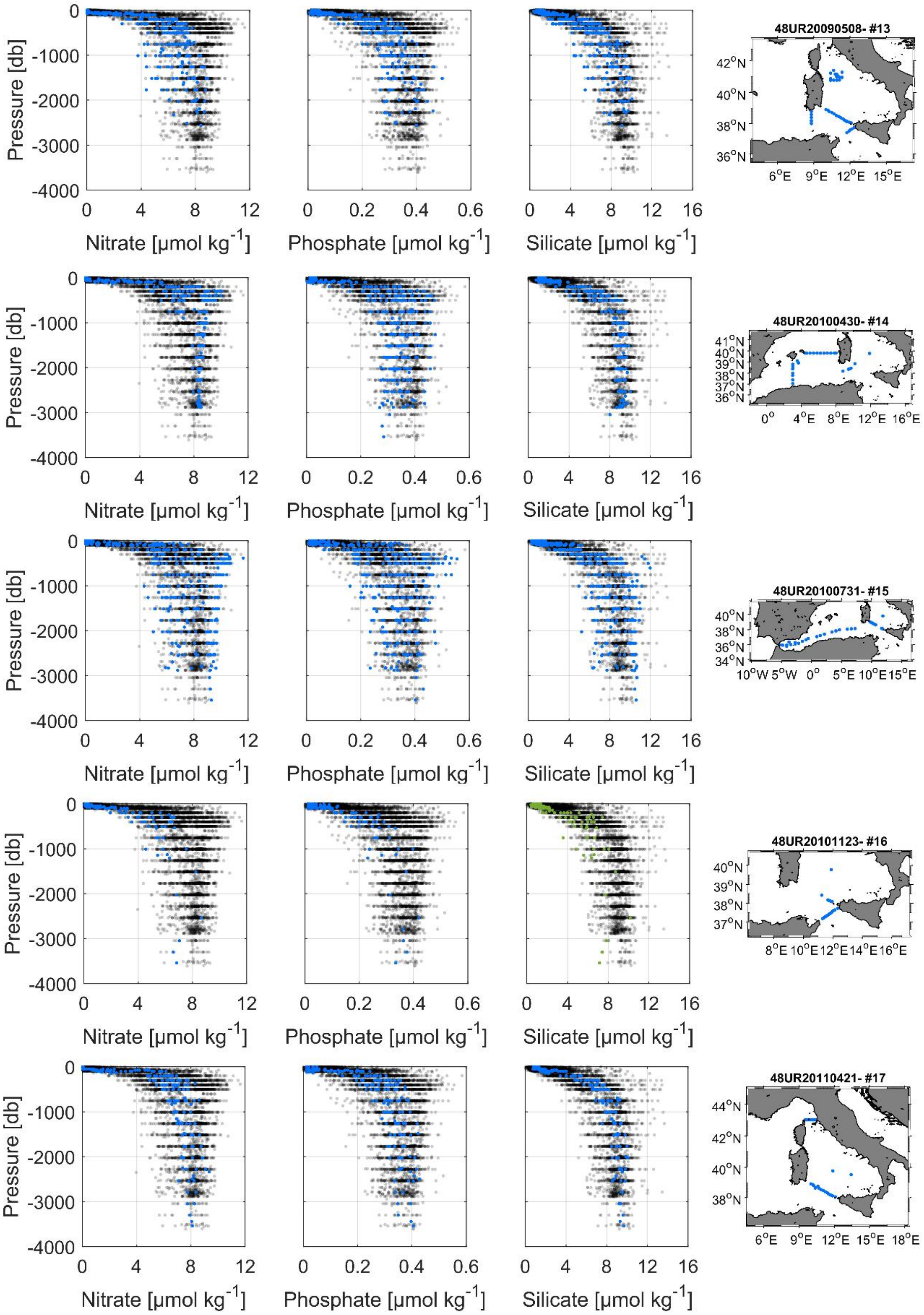
-2500
-3000
-3500
-4000
Nitrate [µmol kg^{-1}]
0 2 4 6 8 10 12
Phosphate [µmol kg^{-1}]
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9
Silicate [µmol kg^{-1}]
0 2 4 6 8 10 12 14 16
D.
y = (22.0921)*x + (-0.081409)
r^2 = 0.90647
Nitrate [µmol kg^{-1}]
0 2 4 6 8 10 12 14
Phosphate [µmol kg^{-1}]
0 0.1 0.2 0.3 0.4 0.5 0.6
0 500 1000 1500 2000 2500
E.
y = (0.94488)*x + (0.11649)
r^2 = 0.87009
Nitrate [µmol kg^{-1}]
0 2 4 6 8 10 12 14
Silicate [µmol kg^{-1}]
0 2 4 6 8 10 12 14
0 500 1000 1500 2000 2500
Pressure [dbar]

Figure 9


Pressure [db]
0
-1000
-2000
-3000
-4000
0 4 8 12
Nitrate [µmol kg^{-1}]
0 0.2 0.4 0.6
Phosphate [µmol kg^{-1}]
0 4 8 12 16
Silicate [µmol kg^{-1}]
48UR20040526- #1
48UR20041006- #2
48UR20050412- #3
48UR20050529- #4
48UR20051116- #5
34°N 35°N 36°N 37°N 38°N 39°N 40°N 41°N 42°N 44°N
6°W 0° 4°E 6°E 8°E 9°E 12°E 15°E 16°E 18°E


Pressure [db]
Nitrate [µmol kg^{-1}]
Phosphate [µmol kg^{-1}]
Silicate [µmol kg^{-1}]
48UR20060608- #6
48UR20060928- #8
48UR20071005- #9
48UR20080318- #10
48UR20081103- #12


Pressure [db]
Nitrate [µmol kg^{-1}]
Phosphate [µmol kg^{-1}]
Silicate [µmol kg^{-1}]
48UR20090508- #13
48UR20100430- #14
48UR20100731- #15
48UR20101123- #16
48UR20110421- #17
0
-1000
-2000
-3000
-4000
0 4 8 12
0 0.2 0.4 0.6
0 4 8 12 16

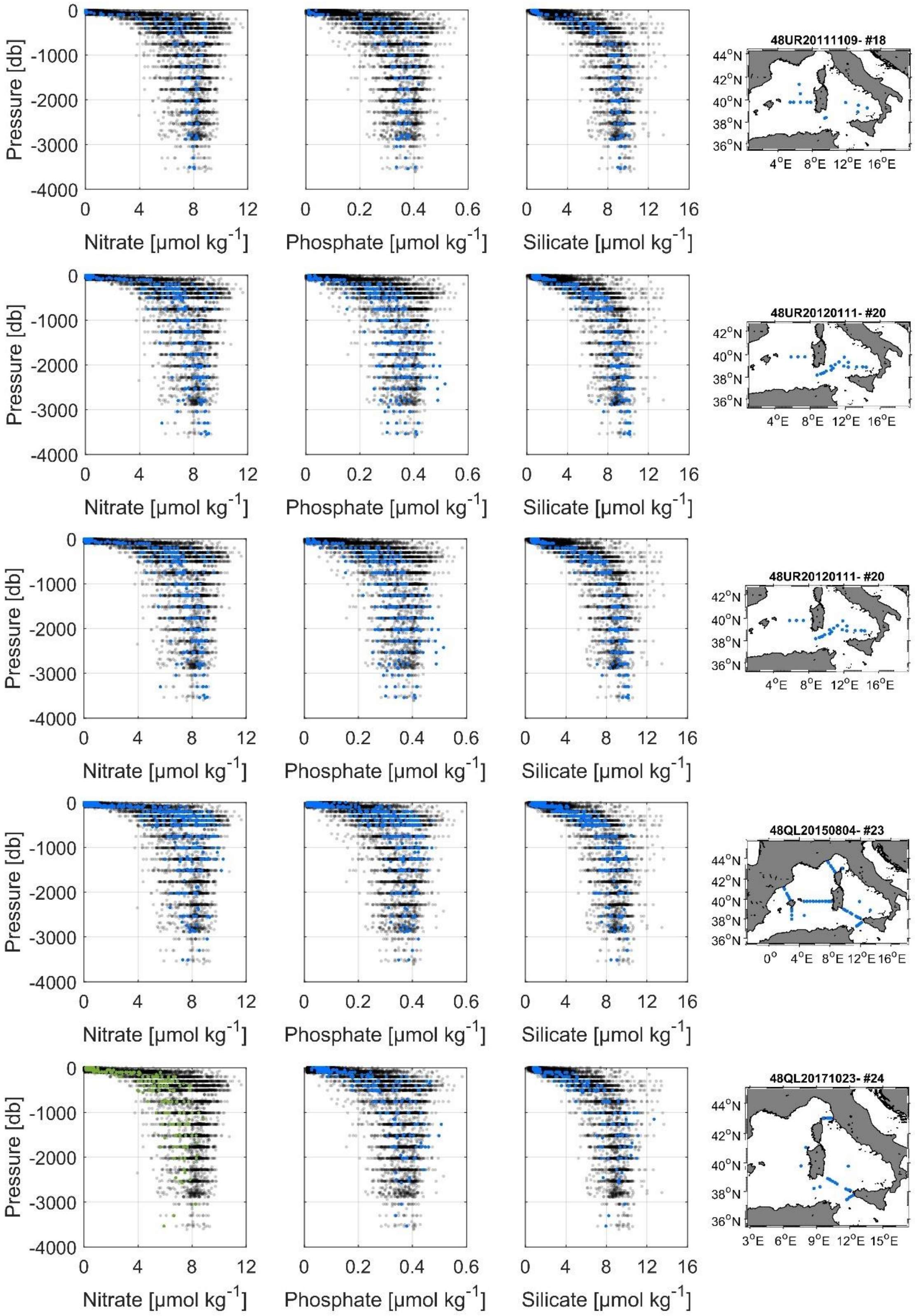

48UR20111109- #18
48UR20120111- #20
48UR20120111- #20
48QL20150804- #23
48QL20171023- #24
Pressure [db]
0
-1000
-2000
-3000
-4000
Nitrate [µmol kg^{-1}]
0
4
8
12
Phosphate [µmol kg^{-1}]
0
0.2
0.4
0.6
Silicate [µmol kg^{-1}]
0
4
8
12
16
44°N
42°N
40°N
38°N
36°N
0°
3°E
4°E
6°E
8°E
9°E
12°E
15°E
16°E

Figure 10

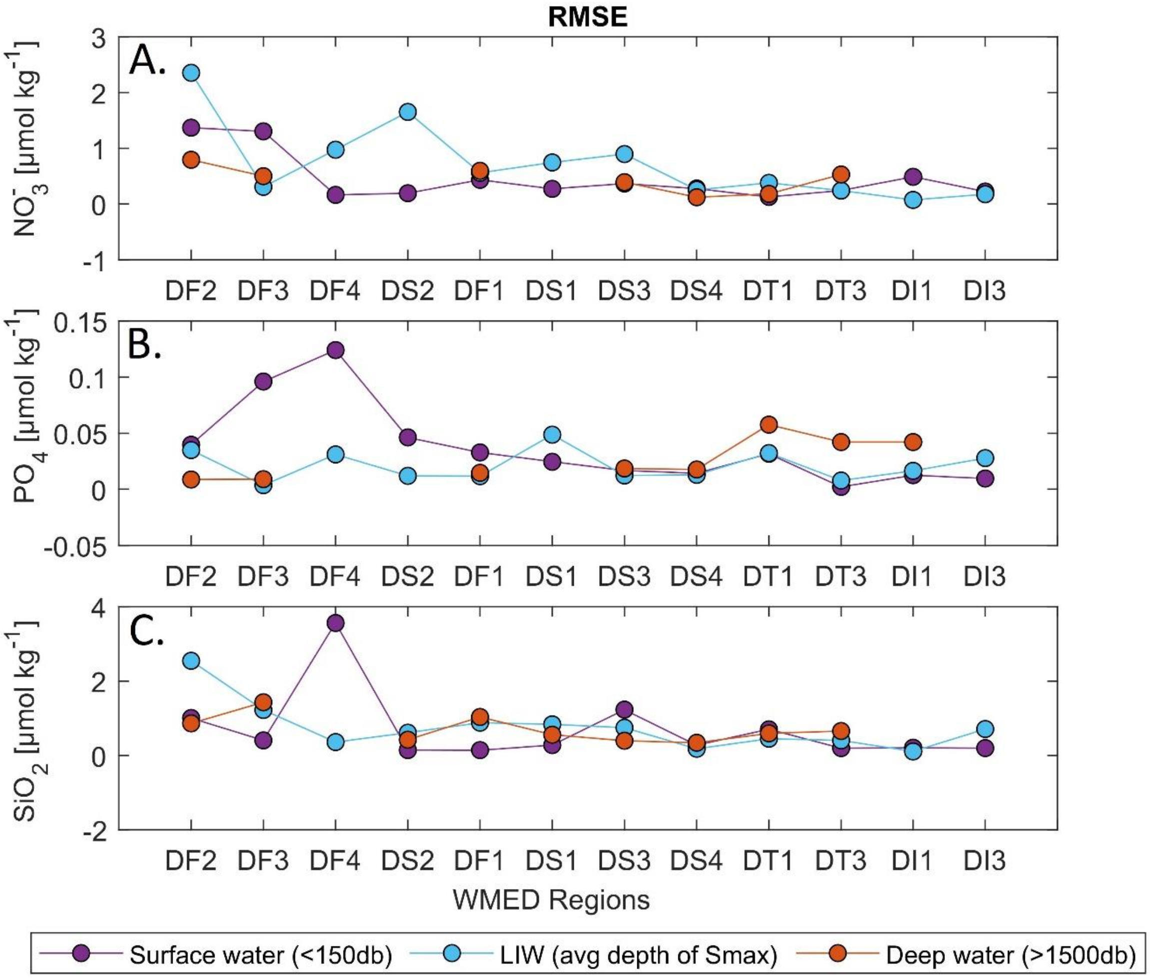

RMSE
A.
NO_3^- [μmol kg^{-1}]
3
2
1
0
-1
B.
PO_4 [μmol kg^{-1}]
0.15
0.1
0.05
0
-0.05
C.
SiO_2 [μmol kg^{-1}]
4
2
0
-2
DF2 DF3 DF4 DS2 DF1 DS1 DS3 DS4 DT1 DT3 DI1 DI3
WMED Regions
Surface water (<150db)
LIW (avg depth of Smax)
Deep water (>1500db)

Table 1

Cruise ID (#)	Common Name	EXPOCODE	Research vessel (RV)	Date Start/End	Stations	Samples NO_3	Samples PO_4	Samples SiO_2	Maximum bottom depth (m)	Chief scientist
1	TRENDS2004/MEDGOOS8leg2	48UR20040526	Urania	26 MAY - 14 JUN 2004	36	255	253	255	3499	M. Borghini
2	MEDGOOS9	48UR20041006	Urania	6 - 25 OCT 2004	68	627	626	627	3610	M. Borghini
3	MEDOCC05/MFSTEP2	48UR20050412	Urania	12 APR - 16 MAY 2005	68	828	828	828	3598	M. Borghini
4	MEDGOOS10	48UR20050529	Urania	29 MAY - 10 JUN 2005	36	577	577	577	3505	A. Perilli
5	MEDGOOS11	48UR20051116	Urania	16 NOV - 3 DEC 2005	14	143	143	143	2810	A. Perilli, M. Borghini, M. Dibitetto
6	MEDOCC06	48UR20060608	Urania	8 JUN - 3 JUL 2006	66	787	785	787	2881	M. Borghini
7	SIRENA06	06A420060720	NRV Alliance	20 JUL - 6 AUG 2006	35	208	208	209	1854	J. Haun
8	MEDGOOS13/MEDBIO06	48UR20060928	Urania	28 SEP - 8 NOV 2006	37	519	520	520	2862	A. Ribotti
9	MEDOCC07	48UR20071005	Urania	5 - 29 OCT 2007	71	977	977	979	3497	A. Perilli
10	SESAMEIt4	48UR20080318	Urania	18 MAR - 7 APR 2008	11	164	164	164	2882	C. Santinelli
11	SESAMEIT5	48UR20080905	Urania	5 - 16 SEP 2008	12	74	74	74	536	S. Sparnocchia, G.P. Gasparini, M. Borghini
12	MEDCO08	48UR20081103	Urania	3 - 24 NOV 2008	24	342	350	348	2880	A. Ribotti
13	TYRRMOUNTS	48UR20090508	Urania	8 MAY - 3 JUN 2009	41	430	441	440	2559	G.P. Gasparini
14	BIOFUN010	48UR20100430	Urania	30 APR - 17 MAY 2010	26	405	405	405	3540	E. Manini, S. Aliani
15	VENUS1	48UR20100731	Urania	31 JUL - 25 AUG 2010	32	431	432	428	3544	G.P. Gasparini, M. Borghini
16	BONSIC2010	48UR20101123	Urania	23 NOV - 9 DEC 2010	18	144	143	143	3540	A. Ribotti
17	EUROFLEET11	48UR20110421	Urania	21 APR - 8 MAY 2011	28	277	275	277	3540	G.P. Gasparini, M. Borghini
18	BONIFACIO2011	48UR20111109	Urania	9 - 23 NOV 2011	13	180	180	181	3541	A. Ribotti, G. La Spada, M. Borghini
19	TOSCA2011	48MG20111210	Maria Grazia	10 - 20 DEC 2011	21	310	310	309	2728	M. Borghini
20	ICHNUSSA12	48UR20120111	Urania	11 - 27 JAN 2012	21	353	352	323	3551	A. Ribotti
21	EUROFLEET2012	48UR20121108	Urania	8 - 26 NOV 2012	53	429	434	434	2633	M. Borghini
22	ICHNUSSA13	48UR20131015	Urania	15 - 29 OCT 2013	37	405	404	405	3540	A. Ribotti
23	OCEANCERTAIN15	48QL20150804	Minerva Uno	4 - 29 AUG 2015	71	531	531	531	3513	J. Chiggiato
24	ICHNUSSA17/INFRAOCE17	48QL20171023	Minerva Uno	23 OCT- 28 NOV 2017	31	251	254	254	3536	A. Ribotti, S. Sparnocchia, M. Borghini

Table 2

Common name	EXPOCODE	Date Start/End	Stations	NO3 Sample	PO4 Sample	SiO2 Sample	Source	Nutrient PI	Chief scientist
M51/2	06MT20011018	18 OCT - 11 NOV 2001	6	79	79	82	GLODAPv2	B. Schneider	W. Roether
TRANSMED_LEGII	48UR20070528	28 MAY- 12 JUN 2007	4	78	77	78	CARIMED (not yet available)	S. Cozzi, V. Ibello	M. Azzaro
M84/3	06MT20110405	5 - 28 APR 2011	20	339	343	-	GLODAPv2	G. Civitarese	T. Tanhua
HOTMIX	29AH20140426	26 APR- 31 MAY 2014	18	144	140	144	CARIMED (not yet available)	XA Álvarez-Salgado	J. Aristegui
TALPro-2016	29AJ20160818	18 - 28 AUG 2016	42	293	293	293	MedSHIP programme	L. Coppola	L. Jullion, K. Schroeder

Table 3

WOCE flag value	Interpretation in original dataset	Interpretation in adjusted product
2	Acceptable/ measured	Adjusted and acceptable
3	Questionable/not used	Adjusted and recommended questionable
9	~~Sample~~ not measured/no data	-

Table 4

Cruise ID	EXPOCODE/ Region	Regional Avg NO_3	std NO_3	Regional Avg PO_4	std PO_4	Regional Avg SiO_2	std SiO_2	# samples	Avg storage (in days)
1	48UR20040526/		**1.25**		**0.062**		**1.64**	21	131
	DT1-Tyrrhenian North	6.07	1.32	0.26	0.065	6.92	1.83	16	
	DT3-Tyrrhenian South	7.03	0.51	0.31	0.02	7.66	0.53	5	
2	48UR20041006/		**0.59**		**0.029**		**0.81**	21	251
	DT1-Tyrrhenian North	7.68	0.53	0.41	0.031	8.74	0.75	15	
	DT3-Tyrrhenian South	8.17	0.60	0.41	0.025	9.31	0.87	6	
3	48UR20050412/		**1.15**		**0.050**		**1.41**	233	135
	DF2-Gulf of Lion	7.89	0.98	0.40	0.044	8.17	1.065	24	
	DF3-Liguro-Provençal	7.45	1.08	0.41	0.05	7.72	1.10	66	
	DS2-Balearic Sea	7.44	1.14	0.40	0.039	7.68	1.47	21	
	DF1-Algero-Provençal	7.87	1.16	0.41	0.043	8.88	1.96	42	
	DS3-Algerian West	7.7	0.816	0.39	0.048	8.14	0.941	23	
	DT1-Tyrrhenian North	6.57	1.065	0.36	0.047	7.41	1.15	21	
	DT3-Tyrrhenian South	6.52	1.12	0.36	0.05	7.56	1.42	22	
	DI1-Sardinia Channel	7.22	1.065	0.40	0.04	8.08	1.11	14	
4	48UR20050529/		**1.13**		**0.057**		**1.08**	205	314
	DS1-Alboran Sea	6.4	1.15	0.38	0.041	6.26	1.02	32	
	DS3-Algerian West	7.6	1.13	0.41	0.06	7.33	0.99	73	
	DS4-Algerian East	7.48	1.13	0.41	0.06	7.50	1.23	47	
	DT1-Tyrrhenian North	7.24	0.44	0.42	0.03	7.91	0.56	16	
	DT3-Tyrrhenian South	7.70	0.38	0.41	0.03	7.55	0.36	14	
	DI1-Sardinia Channel	7.58	1.08	0.43	0.049	7.42	0.82	23	
5	48UR20051116/		**1.35**		**0.078**		**0.98**	16	738
	DT1-Tyrrhenian North	5.68	1.26	0.19	0.08	6.30	0.92	10	
	DT3-Tyrrhenian South	6.71	1.51	0.20	0.06	6.86	1.065	5	
	DI1-Sardinia Channel	6.29	0	0.26	0	7.53	0	1	
6	48UR20060608/		**1.16**		**0.054**		**1.47**	221	27
	DF2-Gulf of Lion	7.69	1.02	0.42	0.04	7.089	1.04	27	
	DF3-Liguro-Provençal	8.08	0.78	0.43	0.04	7.41	1.21	35	
	DS2-Balearic Sea	8.06	0.9	0.43	0.03	7.07	1.18	30	
	DF1-Algero-Provençal	7.97	1.16	0.44	0.05	7.34	1.32	61	
	DS3-Algerian West	8.39	0.9	0.42	0.03	8.5	2	28	
	DT3-Tyrrhenian South	6.39	1.28	0.36	0.06	6.86	1.7	26	
	DI1-Sardinia Channel	8.04	0.85	0.43	0.04	7.77	1.25	14	
7*	06A420060720		-		-		-	-	1367
8	48UR20060928/		**0.71**		**0.036**		**0.76**	179	606
	DS2-Balearic Sea	7.97	0.17	0.33	0.017	7.84	0.27	4	
	DF1-Algero-Provençal	8.17	0.22	0.33	0.026	8.11	0.3	22	
	DS1-Alboran Sea	8.2	0.14	0.35	0.02	8.59	0.35	47	
	DS3-Algerian West	7.93	0.89	0.33	0.03	8.09	0.91	70	
	DS4-Algerian East	7.98	0.68	0.34	0.04	8.01	0.7	28	
	DT3-Tyrrhenian South	6.2	1.51	0.28	0.04	6.71	1.45	3	
	DI1-Sardinia Channel	7.66	0.6	0.28	0.02	8.00	0.49	5	
9	48UR20071005/		**0.89**		**0.040**		**0.86**	302	751
	DF2-Gulf of Lion	8.41	0.08	0.31	0.01	7.43	0.02	4	
	DF3-Liguro-Provençal	8.17	1.08	0.31	0.03	7.64	1.08	81	
	DS2-Balearic Sea	8.17	0.43	0.31	0.02	7.58	0.39	29	
	DF1-Algero-Provençal	8.33	0.6	0.32	0.03	7.79	0.69	82	
	DS4-Algerian East	8.41	0.2	0.33	0.018	7.90	0.26	19	
	DT1-Tyrrhenian North	7.83	0.41	0.28	0.03	8.26	0.55	26	
	DT3-Tyrrhenian South	7.49	1.22	0.28	0.05	7.71	1.26	38	
	DI1-Sardinia Channel	7.92	1.05	0.33	0.02	8.26	0.41	23	
10	48UR20080318/		**0.51**		**0.026**		**0.34**	66	31
	DF2-Gulf of Lion	8.54	0.6	0.35	0.03	8.62	0.43	5	
	DS2-Balearic Sea	9.12	0.18	0.38	0.01	8.40	0.21	9	
	DF1-Algero-Provençal	9.02	0.36	0.38	0.03	8.65	0.25	15	
	DS3-Algerian West	8.93	0.46	0.36	0.01	8.69	0.35	20	
	DS4-Algerian East	8.43	0.25	0.38	0.02	8.32	0.22	10	
	DI1-Sardinia Channel	7.62	0.6	0.34	0.03	8.49	0.36	3	
11*	48UR20080905		-		-		-	-	211
12	48UR20081103/		**1.11**		**0.077**		**0.10**	110	536
	DS1-Alboran Sea	6.4	1.21	0.21	0.06	7.20	1.43	26	

	DS3-Algerian West	7.58	0.9	0.27	0.1	7.89	0.9	30	
	DS4-Algerian East	7.15	1.04	0.23	0.04	7.38	0.9	35	
	DT3-Tyrrhenian South	7.44	0.5	0.22	0.05	8.28	0.4	10	
	DI1-Sardinia Channel	7.40	1.23	0.17	0.04	8.09	0.45	9	
13	48UR20090508/		**1.41**		**0.051**		**1.42**	88	164
	DT1-Tyrrhenian North	5.95	1.55	0.24	0.05	6.28	1.58	46	
	DT3-Tyrrhenian South	6.76	0.77	0.24	0.03	7.37	0.77	29	
	DI1-Sardinia Channel	7.62	1.1	0.28	0.05	7.76	0.9	13	
14	48UR20100430/		**1.06**		**0.036**		**1.03**	159	213
	DS2-Balearic Sea	7.66	1.6	0.25	0.03	7.38	1.75	33	
	DF1-Algero-Provençal	8.43	0.29	0.26	0.03	8.06	0.31	61	
	DS3-Algerian West	8.5	0.14	0.26	0.03	8.25	0.3	26	
	DT1-Tyrrhenian North	6.88	0.8	0.23	0.022	7.17	0.77	11	
	DT3-Tyrrhenian South	6.38	1.35	0.22	0.01	6.76	1.56	7	
	DI1-Sardinia Channel	7.71	0.87	0.23	0.02	7.80	0.74	21	
15	48UR20100731/		**1.34**		**0.053**		**0.14**	149	213
	DS1-Alboran Sea	7.30	1.18	0.29	0.05	7.21	1.11	25	
	DS3-Algerian West	7.67	1.15	0.28	0.045	7.24	1.16	54	
	DS4-Algerian East	7.38	0.89	0.29	0.03	7.00	0.78	29	
	DT1-Tyrrhenian North	7.66	0.96	0.29	0.05	7.89	1.07	10	
	DT3-Tyrrhenian South	5.4	0.67	0.22	0.01	5.52	1.56	30	
	DI1-Sardinia Channel	4.92	0	0.20	0	5.55	0	1	
16	48UR20101123/		**1.02**		**0.045**		**1.02**	14	170
	DT1-Tyrrhenian North	6.34	0.87	0.27	0.02	6.12	0.87	8	
	DT3-Tyrrhenian South	5.43	1.02	0.22	0.04	5.08	0.9	6	
17	48UR20110421/		**0.62**		**0.029**		**0.52**	56	160
	DT1-Tyrrhenian North	7.77	0.45	0.28	0.02	8.11	0.35	21	
	DT3-Tyrrhenian South	7.76	0.7	0.28	0.03	8.017	0.6	35	
18	48UR20111109/		**0.68**		**0.025**		**0.70**	77	74
	DF3-Liguro-Provençal	6.68	0	0.33	0	6.26	0	1	
	DF1-Algero-Provençal	8.17	0.5	0.32	0.01	8.16	0.66	43	
	DT1-Tyrrhenian North	7.26	0.93	0.29	0.02	8.15	1.03	12	
	DT3-Tyrrhenian South	7.61	0.37	0.30	0.02	8.18	0.35	11	
	DI1-Sardinia Channel	7.64	0.45	0.29	0.01	8.08	0.41	10	
19*	48MG20111210		-		-		-	-	38
20	48UR20120111/		**0.97**		**0.051**		**0.26**	152	317
	DF1-Algero-Provençal	8.45	0.49	0.31	0.039	7.91	0.53	23	
	DT1-Tyrrhenian North	7.67	0.83	0.27	0.02	8.29	0.8	30	
	DT3-Tyrrhenian South	7.65	1.06	0.31	0.06	8.03	1.26	69	
	DI1-Sardinia Channel	7.65	0.96	0.31	0.03	7.86	0.78	30	
21*	48UR20121108		-		-		-	-	72
22	48UR20131015/		**1.03**		**0.043**		**0.79**	98	76
	DF1-Algero-Provençal	8.54	0.64	0.33	0.02	7.96	0.38	36	
	DS4-Algerian East	7.67	1.28	0.27	0.04	6.82	1.07	8	
	DT1-Tyrrhenian North	6.47	0.83	0.24	0.025	7.12	0.84	10	
	DT3-Tyrrhenian South	7.81	0.71	0.30	0.03	8.09	0.65	28	
	DI1-Sardinia Channel	7.32	0.99	0.27	0.02	7.47	0.89	16	
23	48QL20150804/		**0.84**		**0.038**		**0.85**	94	30
	DF3-Liguro-Provençal	8.51	0.96	0.39	0.03	8.06	0.85	23	
	DS2-Balearic Sea	7.75	0.66	0.36	0.02	7.86	0.81	20	
	DF1-Algero-Provençal	7.9	0.59	0.37	0.03	8.34	0.68	23	
	DS3-Algerian West	7.84	0.67	0.36	0.02	7.75	0.68	6	
	DT1-Tyrrhenian North	7.92	0.61	0.37	0.02	8.75	0.4	8	
	DT3-Tyrrhenian South	7.23	0.75	0.34	0.025	8.2	0.94	13	
	DI1-Sardinia Channel	6.30	0	0.25	0	5.36	0	1	
24	48QL20171023/		**0.68**		**0.055**		**1.24**	55	30
	DF3-Liguro-Provençal	6.63	0.41	0.40	0.05	10.76	1.07	3	
	DF1-Algero-Provençal	5.14	0.7	0.43	0.02	7.94	1.19	6	
	DT1-Tyrrhenian North	4.98	0.58	0.36	0.02	8.10	0.87	9	
	DT3-Tyrrhenian South	5.43	0.5	0.36	0.04	9.03	0.87	26	
	DI1-Sardinia Channel	5.16	0.76	0.41	0.07	7.58	1.17	11	

(*) cruise not included in the 2ndQC (Section 4.)

in bold: the overall standard deviation by cruise; in normal font: regional standard deviation by cruise

Table 5

Cruise ID	EXPOCODE	NO_3 (x)	PO_4 (x)	SiO_2 (x)
1	48UR20040526	1.14	1.23	1.21
2	48UR20041006	0.98	0.9	1.06
3	48UR20050412	1.08	0.93	1.15
4	48UR20050529	1.04	0.85	1.183
5	48UR20051116	1.19	1.34	1.232
6	48UR20060608	1.05	0.86	1.261
7	06A420060720*	-	-	-
8	48UR20060928	1.03	1.14	1.1
9	48UR20071005	0.97	1.14	1.115
10	48UR20080318	0.94	1.09	1.02
11	48UR20080905*	-	-	-
12	48UR20081103	1.08	1.38	1.12
13	48UR20090508	1.05	1.33	1.15
14	48UR20100430	NA	1.34	1.123
15	48UR20100731	1.13	1.25	1.262
16	48UR20101123	1.15	1.29	1.28
17	48UR20110421	NA	1.25	1.12
18	48UR20111109	NA	1.14	1.09
19	48MG20111210*	-	-	-
20	48UR20120111	NA	1.17	1.08
21	48UR20121108*	-	-	-
22	48UR20131015	NA	1.17	1.11
23	48QL20150804	1.02	1.02	1.08
24	48QL20171023	1.34	0.98	1.06

(*) cruise not included in the 2nd QC (Section 4.)

Table 6

Cruise ID	EXPOCODE	NO_3 [%]			PO_4[%]			SiO_2[%]		
		n	*unadjusted*	*adjusted*	*n*	*unadjusted*	*adjusted*	*n*	*unadjusted*	*adjusted*
1	48UR20040526	2	0.86	0.98	2	0.77	0.95	1	0.79	0.96
2	48UR20041006	2	1.02	1.00	2	1.10	0.99	1	0.94	0.99
3	48UR20050412	5	0.92	0.99	5	1.07	1.00	4	0.85	0.98
4	48UR20050529	5	0.96	1.00	5	1.15	0.98	4	0.82	0.99
5	48UR20051116	2	0.81	0.96	1	0.66	0.89	1	0.77	0.95
6	48UR20060608	5	0.95	1.00	5	1.14	0.99	4	0.74	0.93
7	06A420060720	0	-	-	0	-	-	0	-	-
8	48UR20060928	4	0.97	1.00	4	0.86	0.98	3	0.90	0.99
9	48UR20071005	5	1.03	1.00	5	0.86	0.98	4	0.88	0.99
10	48UR20080318	3	1.06	1.00	3	0.91	0.99	2	0.98	1.00
11	48UR20080905	0	-	-	0	-	-	0	-	-
12	48UR20081103	5	0.92	0.99	5	0.62	0.85	4	0.88	0.99
13	48UR20090508	3	0.95	1.00	3	0.67	0.90	2	0.85	0.98
14	48UR20100430	4	1.01	NA	4	0.66	0.88	3	0.88	0.99
15	48UR20100731	5	0.87	0.99	5	0.75	0.93	4	0.74	0.93
16	48UR20101123	1	0.85	0.98	1	0.71	0.91	1	0.72	0.92
17	48UR20110421	2	1.01	NA	2	0.75	0.94	1	0.88	0.99
18	48UR20111109	4	0.99	NA	4	0.86	0.98	3	0.91	0.99
19	48MG20111210	0	-	-	0	-	-	0	-	-
20	48UR20120111	4	1.01	NA	4	0.83	0.98	3	0.92	0.99
21	48UR20121108	0	-	-	0	-	-	0	-	-
22	48UR20131015	4	1.00	NA	4	0.83	0.97	3	0.89	0.99
23	48QL20150804	5	0.98	1.00	5	0.98	1.00	4	0.92	1.00
24	48QL20171023	3	0.66	0.88	3	1.02	1.00	2	0.94	0.99

*red: data lower than reference

Table 7

~~Average and standard deviation of inorganic nutrient (the number observation within depth range) for three layers, from the adjusted product and MEDATLAS vertical climatological profiles. Regions are defined according to Manca et al., (2004)(table 0S,Fig.0S)~~

Region/ Water mass	NO3 (µmol kg^{-1})		PO4 (µmol kg^{-1})		SiO2 (µmol kg^{-1})	
	Avg new Product	Avg Medar	Avg new Product	Avg Medar	Avg new Product	Avg Medar
DF2- Gulf of Lion						
surface water (0-150db)	2.68±2.53(68)**	1.7±1.1	0.15±0.06(68)	0.13±0.04	2.91±1.33(68)	1.72±0.64
LIW core (S_{max} depth range: 300-500db)	8.49±0.18(17)	6.13±0.32	0.38±0.02(17)	0.34±0.01	8.67±0.69(17)	6.12±0.61
Deep water (>1500db)	8.03±0.43(33)	7.64±0.31	0.37±0.01(33)	0.37±0.015	8.7±0.67(33)	7.95±0.06
DF3- Liguro-Provençal						
surface water (0-150db)	2.31±2.4(205)	3.0±2.6	0.12±0.07(205)	0.19±0.05	2.45±1.05(205)	2.16±1.05
LIW core (S_{max} depth range: 300-500db)	8.05±0.18(76)	7.74±0.13	0.36±0.01(76)	0.35±0.01	7.49±0.55(76)	6.26±0.60
Deep water (>1500db)	8.18±0.25(142)	7.79±0.04	0.37±0.02(142)	1.03±1.29	8.98±0.39(142)	7.60±0.21
DF4- Ligurian East						
surface water (0-150db)	0.7±0.69(228)	0.61±1.03	0.05±0.02(228)	0.18±0.02	1.37±0.45(228)	1.27±1.86
LIW core (S_{max} depth range: 300-500db)	6.8±0.4(23)	5.54±0	0.3±0.02(21)	0.36±0.06	5.86±0.9(24)	4.86±0
Deep water (>1500db)	-	-	-	-	-	-
DS2- Balearic Sea						
surface water (0-150db)	1.32±1.46(196)	1.19±1.5	0.08±0.04(196)	0.11±0.04	1.61±0.64(196)	1.54±0.78
LIW core (S_{max} depth range: 300-500db)	8.32±0.32(58)	6.92±0.12	0.37±0.02(60)	0.39±0.003	7.31±0.9(60)	7.55±0.62
Deep water (>1500db)	8.2±0.35(88)	-	0.37±0.01(88)	-	8.71±0.51(88)	8.45±0.8
DF1- Algero-Provençal						
surface water (0-150db)	0.87±0.85(372)	1.08±1.7	0.05±0.02(372)	0.07±0.05	1.42±0.3(372)	1.28±0.73
LIW core (S_{max} depth range: 300-500db)	8.07±0.34(126)	7.51±0.18	0.36±0.02(126)	0.34±0.008	6.84±0.95(126)	5.96±0.77
Deep water (>1500db)	8.36±0.27(300)	7.87±0.13	0.38±0.02(300)	0.38±0.001	9.01±0.33(300)	8.18±0.10
DS1- Alboran Sea						
surface water (0-150db)	2.75±2.87(299)	2.51±2.23	0.17±0.11(299)	0.16±0.07	2.07±1.38(299)	2.31±1.14
LIW core (S_{max} depth range: 400-600db)	8.89±0.4(77)	8.14±0.11	0.42±0.02(77)	0.37±0.008	8.77±1.66(76)	7.95±0.34
Deep water (>1500db)	7.72±0.81(65)	-	0.36±0.04(65)	-	8.98±0.63(65)	8.16±0
DS3- Algerian West						
surface water (0-150db)	1.8±1.88(254)	1.82±2.01	0.11±0.05(354)	0.11±0.06	1.71±0.68(354)	2.10±0.91
LIW core (S_{max} depth range: 400-600db)	9.33±0.08(70)	8.28±0.15	0.41±0(73)	0.38±0.012	8.1±0.53(72)	6.68±0.80
Deep water (>1500db)	8.37±0.27(246)	8.047±0.013	0.37±0.02(246)	0.36±0.006	9.22±0.35(246)	8.87±0.23
DS4- Algerian East						
surface water (0-150db)	0.94±0.77(170)	0.75±1.26	0.07±0.02(170)	0.05±0.03	1.53±0.12(170)	1.35±0.52
LIW core (S_{max} depth range: 400-600db)	8.5±0.25(43)	8.60±0.06	0.38±0.03(43)	0.38±0.008	7.27±0.67(42)	7.092±0.55
Deep water (>1500db)	7.94±0.24(132)	8.06±0.06	0.36±0.02(132)	0.38±0.006	8.73±0.38(132)	9.04±0.24
DT1- Tyrrhenian North						
surface water (0-150db)	1.03±1.14(231)	0.88±1.2	0.06±0.02(231)	0.09±0.03	1.64±0.52(231)	2.19±0.59
LIW core (S_{max} depth range: 400-600db)	5.95±0.49(43)	5.86±0.36	0.27±0.03(44)	0.308±0.02	7.06±0.08(44)	6.76±0.59
Deep water (>1500db)	7.75±0.37(194)	7.12±0.47	0.36±0.03(194)	0.40±0.02	9.19±0.47(194)	7.51±0.49
DT3- Tyrrhenian South						
surface water (0-150db)	1.21±1.38(711)	1.23±1.80	0.06±0.03(711)	0.061±0.04	1.58±0.61(711)	1.55±1.05
LIW core (S_{max} depth range: 300-500db)	6.2±0.28(225)	6.42±0.01	0.26±0.02(225)	0.254±0.005	6.28±0.65(224)	6.68±0.44
Deep water (>1500db)	7.88±0.4(227)	7.12±0.26	0.37±0.02(227)	0.31±0.007	9.04±0.52(227)	8.02±0.07
DI1- Sardinia Channel						
surface water (0-150db)	1.22±1.39(271)	1.42±1.95	0.07±0.03(271)	0.064±0.03	1.57±0.68(271)	1.39±1.01
LIW core (S_{max} depth range: 300-500db)	6.52±0.17(89)	6.45±0.22	0.27±0.02(89)	0.250±0.01	6.36±0.67(89)	6.27±0.70
Deep water (>1500db)	7.91±0.62(107)	-	0.37±0.03(107)	0.32±0	8.64±0.91(107)	-
DI3- Sicily Strait						
surface water (0-150db)	0.87±0.68(583)	0.77±0.81	0.06±0.02(583)	0.063±0.02	1.53±0.29(583)	1.44±0.58
LIW core (S_{max} depth range: 200-400db)	4.95±0.47(80)	5.14±0.14	0.21±0.02(78)	0.194±0.004	5.26±0.79(81)	6.744±0.41
Deep water (>1500db)	-	-	-	-	-	-

**Average (Avg) ± standard deviation of inorganic nutrient (the number observation within depth range) for three layers from the adjusted/new product and MEDATLAS vertical climatological profiles (called here Medar). Regions are defined according to Manca et al. (2004) (table 2S, Fig.2S)