https://doi.org/10.5194/essd-2019-136
Preprint. Discussion started: 3 September 2019

Open Access Earth System Science Data Discussions

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

Malek Belgacem[1,2], Jacopo Chiggiato[1,*], Mireno Borghini[1], Bruno Pavoni[2], Gabriella Cerrati[3], Francesco Acri[1], Stefano Cozzi[4], Alberto Ribotti[5], Marta Álvarez[6], Siv K. Lauvset[7,8], Katrin Schroeder[1]

[1] CNR-ISMAR, Arsenale Tesa 104, Castello 2737/F, 30122 Venezia, Italy

2 Dipartimento di Scienze Ambientali Informatica e Statistica, Università Ca' Foscari Venezia, Campus Scientifico Mestre, Italy

3 ENEA, Department of Sustainabiliy, S. Teresa, Marine Environmental center, 19032 Pozzuolo di Lerici (SP), Italy

4 CNR-ISMAR, Area Science Park – Basovizza, 34149 Trieste, Italy

5 CNR-IAS, Loc. Sa Mardini snc, Torregrande, 9170 Oristano, Italy

6 Instituto Español de Oceanografía, IEO, A Coruña, Spain

7 NORCE Norwegian Research Centre, Bjerknes Centre for Climate Research, 5007 Bergen, Norway

8 Geophysical Institute, University of Bergen and Bjerknes Centre for Climate Research, 5007 Bergen, Norway

*Corresponding author's email: jacopo.chiggiato@ismar.cnr.it

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 filling these gaps, an extensive dataset of dissolved inorganic nutrients profiles (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 quality control techniques to provide to the scientific community a publicly available, long-term, quality controlled,

https://doi.org/10.5194/essd-2019-136
Preprint. Discussion started: 3 September 2019

Earth System Science Data Discussions

internally consistent biogeochemical data product. The database includes 870 stations of dissolved inorganic nutrients 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 are important tracers of biological cycles, new production, natural and anthropogenic sources and transport processes (Bethoux, 1989; Bethoux et al., 1992) They are non-conservative seawater constituents, whose distribution is controlled by both physical (such as convection, advection, mixing and diffusion) and biogeochemical (such as primary production and respiration) processes. Very schematically, nutrients are continuously removed from the sea surface (due to primary production) and regenerated in the mesopelagic layer (due to respiration). Moreover, the sinking of biogenic matter and its degradation 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 trace water masses, to assess mixing processes, and to understand the biogeochemical conditions 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. 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.

https://doi.org/10.5194/essd-2019-136
Preprint. Discussion started: 3 September 2019

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. 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 (Boyd, 2011), by which climatically driven ecosystem disturbances are generated. These changes affect, among others, the distribution of biogeochemical elements (including nutrients) and the functioning of the biological pump.

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 nutrients 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 a publicly available, long-term, quality controlled, internally consistent biogeochemical data product, contributing to previously published Mediterranean datasets like the Medar/Medatlas dataset (Fichaut et al., 2003).

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

https://doi.org/10.5194/essd-2019-136
Preprint. Discussion started: 3 September 2019

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 to the northern western Mediterranean Sea (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 PERSEUS (Policy-oriented marine environmental research in the southern European seas), a database that included 100 cruises collected within PERSEUS itself in addition to those from projects like Sesame, 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, 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 SBE-3/F thermometer with a resolution of 10^{-3} °C; conductivity measurements were performed with an SBE-4 sensor with a resolution of $3{\cdot}10^{-4}$ 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.

2.2. 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 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, 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 (Tanhua et al., 2013). Cruises 29AH20140426 and 48UR20070528 are included in the CARIMED data product 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).

3 Analytical methods for inorganic nutrients

https://doi.org/10.5194/essd-2019-136
Preprint. Discussion started: 3 September 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).

4 Quality control methods

https://doi.org/10.5194/essd-2019-136
Preprint. Discussion started: 3 September 2019

Combining 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 since the 1990s several studies and programmes (e.g. World Ocean Database, World Ocean Atlas, World Ocean Circulation Experiment) 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 intercomparability, generate consistent data sets and accurately observe the long-term change.

An example of a first quality control procedure is the use of certified 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 and inorganic nutrients (Aoyama et al., 2016; Dickson et al., 2003) , certified reference materials (CRM) have been recently made available 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 (Olsen et al., 2016) and PACIFICA (Suzuki al al.,2013) databases.

4.1 Primary Quality control

Each individual cruise was first subjected to a primary quality control (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).

https://doi.org/10.5194/essd-2019-136
Preprint. Discussion started: 3 September 2019

The surface (0-250 db) layer was difficult to flag since its overall coefficient of variation (CV, defined as standard deviation over mean) for nitrate (1.16), phosphate (1.005) and silicate (0.75) was high due to air-sea interaction and the complexity of biological processes (Muniz et al., 2001) occurring in this layer. 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 including a check 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. We considered as outlier any value that departs from the median by more than three median absolute deviations.

An overview of the nutrient distribution is provided with scatter plots, showing also the flagged measurements (Fig. 3). Each measurement was flagged 2 (“good”) or flagged 3 (“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 deeper than 1000 db was calculated (Table 4). Overall, the standard deviation 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. Cruises #3, #6 and #9 had the largest spatial extension (visible on the right side of Fig. 9) with an important number of samples over 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

https://doi.org/10.5194/essd-2019-136
Preprint. Discussion started: 3 September 2019

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. Samples of nitrate and phosphate of cruise #5 have a standard deviation of 1.35 µmol kg^{-1} and 0.07 µmol kg^{-1}, respectively, despite the small spatial coverage (right side of Fig.9). Cruise #1, with few stations in the Tyrrhenian Sea and 21 samples below 1000 db, has standard deviations of 1.25 µmol kg^{-1} for nitrate, 0.06 µmol kg^{-1} for phosphate and 1.64 µmol kg^{-1} for silicate. 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 #1. Similar considerations apply to the quality of nitrate samples from cruise #16, covering a small area in the Sicily Channel, compared to cruise #14 carried out in the same year but with a larger spatial coverage (right side of Fig. 9). Deep silicate measurements of cruise #6 have twice the standard deviation of silicate data of cruise #8 from the same year. This is again suggestive of limited precision. On the other hand, trying to explain the source of relatively high standard deviations in specific cruises is not always straightforward

4.2 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 (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. The second step is the crossover analysis that was carried out using a MATLAB Toolbox (available online:

https://doi.org/10.5194/essd-2019-136
Preprint. Discussion started: 3 September 2019

https://www.nodc.noaa.gov/ocads/oceans/2nd_QC_Tool/) 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", 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 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, that was calculated from the weighted mean offset of all crossovers found between the cruise and the reference data set, involving a somehow 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

https://doi.org/10.5194/essd-2019-136
Preprint. Discussion started: 3 September 2019

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, 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. The accuracy was computed from the individual weighted offsets. The weighted mean, which will be discussed in section 5.4., was computed using the individual weighted offset (D) of number of crossovers (L) and the standard deviation (σ): WM= $\frac{\sum_{i=1}^{L} D(i)/(\sigma(i))^2}{\sum_{i=1}^{L} 1/(\sigma(i))^2}$

5 Results of the secondary QC and recommendations

The secondary QC revealed various multiplicative 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 (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 not included in the adjusted dataset.

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 in Fig.4. Results of the crossover analysis is an adjustment factor by cruise that are shown in Tables 5 and Fig. 5-6-7 that was calculated from the weighted mean of absolute offset summarized in Table 6 and Fig. 2S-3S-4S. Table 6 details the improvement of the weighted mean of absolute offset by cruise prior and after

https://doi.org/10.5194/essd-2019-136
Preprint. Discussion started: 3 September 2019

adjustments, the information is also displayed graphically in Fig. 2S-3S-4S. Cruises are in chronological order in all figures and tables.

5.1 Nitrate

The crossover analysis suggests adjustments for nitrate concentrations on 15 cruises, from 0.94 to 0.98 (<1) and from 1.02 to 1.34 (>1) (Table 5 and Fig.5). Offsets suggest that 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). Nitrate data from cruises #2, #9 and #10 on the other hand were higher than the reference cruises and require 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 require large correction factors and are still outside the accuracy threshold: cruises #5 and #24 (Fig. 5). These cruises are considered in detail later (section 5.4).

5.2 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 increase), while the data of five cruises (#2, #3, #4, #6, #24) are higher (i.e. they need to be decreased) (Fig.3S). 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

https://doi.org/10.5194/essd-2019-136
Preprint. Discussion started: 3 September 2019

factor (Fig. 6), and thus an increasing one in the weighted mean offset (Fig.3S), 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.

Comparing phosphate before and after adjustments, the corrections did minimise the difference with the reference, while the actual variation with time was preserved. 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; Moon et al., 2016; Powley et al., 2018) modelling studies, who indeed found an increasing trend in phosphate concentrations over time.

5.3 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 increased) (Fig.4S). This is likely to be a direct result of the samples freezing 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.

5.4 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-4S and Fig. 5-6-7). Most of the new

https://doi.org/10.5194/essd-2019-136
Preprint. Discussion started: 3 September 2019

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.

Referring to the analysis detailed in section 4.2, the internal consistency of the nutrient data set has improved after the adjustment from 0.98% for nitrate, 0.83% for phosphate and 0.86% for silicate, to more unified dataset with 1.004 % for nitrate, 0.97 % for phosphate and 0.98% for silicate.

A comparison between the original and the adjusted vertical nutrient profiles is shown in Fig. 8, 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 regression, between tracers along the water column show a strong coupling and provide a nitrate to phosphate ratio of ~22.1 and 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; 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.

Below we discuss the flags assigned in the adjusted dataset for some cruises that needed further consideration, since they required larger adjustment factors:

<u>Cruise #1 [48UR20040526]</u>: The adjusted values are still lower than the reference (Fig.5-6-7-Fig.2S-3S-4S) and are still outside the 2% accuracy range. This cruise had stations in the Sicily Channel, Tyrrhenian 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 4.1). We recommend flagging this cruise as questionable.

https://doi.org/10.5194/essd-2019-136
Preprint. Discussion started: 3 September 2019

Cruise #5 [48UR20051116]: This cruise took place between Sicily Channel and the Tyrrhenian Sea (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-4S) 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.

Cruise #6 [48UR20060608]: The silicate bias was reduced after adjustment but remains large with respect to the accuracy limit (Fig. 7-Fig. 4S). This cruise has a wide geographic coverage, with stations along 9 sections (Fig. 9, right side). Considering also the high standard deviation (Table 3), which is partially attributed to the spatial coverage of the cruise, there still remains uncertainty about the quality of the samples. It is recommended to flag silicate data of cruise #6 as questionable.

Cruise #12 [48UR20081103]: Phosphate data have low accuracy with respect to the reference cruises (Fig. 6-Fig. 3S). This cruise has stations along a longitudinal section from the Sicily Channel to the Gibraltar Strait, which might explain the large standard deviation of deep phosphate samples (Table 3). 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 questionable.

Cruise #15 [48UR20100731]: This cruise had 149 station along a similar track as cruise #12 and shows large offsets for phosphate and silicate (Fig. 6-7-Fig. 3S-4S), compared to cruise #12. Considering that deep silicate data was not of low quality (small standard deviation, see Table 3), and that deep phosphate fall within the "phosphate-trend" discussed above, 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), similar to cruise #15. Considering that the standard deviation of silicate samples below 1000 db was relatively high (1.02 over 14 samples, see Table 3), and that it has only one crossover (Table 6), it is recommended to flag silicate data of cruise #16 as questionable. As for phosphate, the cruise is part of the "phosphate-trend" and is therefore not recommended to be flagged as questionable.

https://doi.org/10.5194/essd-2019-136
Preprint. Discussion started: 3 September 2019

Open Access Earth System Science Data Discussions

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.

Cruises discussed in this section were not removed from the final product but are retained along with their quality flags detailed above. We have done the evaluation of their overall quality but leave it up to the users how to appropriately use these data.

6 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 datasets. 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 to compare cruises with respect to reference data, improved the accuracy of the measurements by bias-minimizing the individual cruises.

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 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 to assess reanalysis product or it can be assimilated in new reanalysis products.

7 Data availability

https://doi.org/10.5194/essd-2019-136
Preprint. Discussion started: 3 September 2019

Open Access Earth System Science Data Discussions

The final dataset is available as a .csv files 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 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 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 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 Italain 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 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.

References

Aoyama, M., Woodward, E. Malcolm S. Bakker, K., Becker, S., Björkman, K., Daniel, A., Mahaffey, C., Murata, A., Naik, H., Tanhua, T., Rho, T., Roman, R. and Sloyan, B.: Comparability of oceanic nutrient data., 2016.

Becker, S., Aoyama, M., Woodward, E. M. S., Bakker, K. and Coverly, S.: GO-SHIP Repeat Hydrography Nutrient Manual , 2019 : The precise and accurate determination of dissolved inorganic nutrients in seawater ; Continuous Flow Analysis methods and laboratory practices ., , 49, 2019.

Belgacem, M., Chiggiato, J., Borghini, M., Pavoni, B., Cerrati, G., Acri, F; Cozzi, S., Ribotti, A., Álvarez, M., Lauvset, S. K., Schroeder, K. (2019): Quality controlled dataset of dissolved inorganic nutrients in the western Mediterranean Sea (2004-2017) from R/V oceanographic cruises. PANGAEA, https://doi.pangaea.de/10.1594/PANGAEA.904172

Bethoux, J. P.: Oxygen consumption, new production, vertical advection and environmental evolution in the Mediterranean Sea, Deep Sea Res. Part A, Oceanogr. Res. Pap., 36(5), 769–781, doi:10.1016/0198-0149(89)90150-7, 1989.

Bethoux, J. P., Morin, P., Madec, C. and Gentili, B.: Phosphorus and nitrogen behaviour in the Mediterranean Sea, Deep Sea Res. Part A, Oceanogr. Res. Pap., 39(9), 1641–1654, doi:10.1016/0198-0149(92)90053-V, 1992.

Bethoux, J. P., Gentili, B., Morin, P., Nicolas, E., Pierre, C. and Ruiz-Pino, D.: The Mediterranean Sea : a miniature ocean for climatic and environmental studies and a key for the climatic funcioning of the North Atlantic, Prog. Oceanogr., 44, 131–146, 1999.

Béthoux, J. P., Morin, P., Chaumery, C., Connan, O., Gentili, B. and Ruiz-Pino, D.: Nutrients in the Mediterranean Sea, mass balance and statistical analysis of concentrations with respect to environmental change, Mar. Chem., 63(1–2), 155–169, doi:10.1016/S0304-4203(98)00059-0, 1998.

Béthoux, J. P., Morin, P. and Ruiz-Pino, D. P.: Temporal trends in nutrient ratios: Chemical evidence of Mediterranean ecosystem changes driven by human activity, Deep. Res. Part II Top. Stud. Oceanogr., 49(11), 2007–2016, doi:10.1016/S0967-0645(02)00024-3, 2002.

Boyd, P. W.: Beyond ocean acidification, Nat. Geosci., 4(5), 273–274, doi:10.1038/ngeo1150, 2011.

Dickson, A. G., Afghan, J. D. and Anderson, G. C.: Reference materials for oceanic CO2 analysis: A method for the certification of total alkalinity, Mar. Chem., 80(2–3), 185–197, doi:10.1016/S0304-4203(02)00133-0, 2003.

Fichaut, M., Garcia, M. J., Giorgetti, A., Iona, A., Kuznetsov, A., Rixen, M. and Group, M.: MEDAR/MEDATLAS 2002: A Mediterranean and Black Sea database for operational oceanography, Elsevier Oceanogr. Ser., 69, 645–648, doi:10.1016/S0422-9894(03)80107-1, 2003.

Giorgi, F.: Climate change hot-spots, Geophys. Res. Lett., 33(8), 1–4, doi:10.1029/2006GL025734, 2006.

Gouretski, V. V. and Jancke, K.: Systematic errors as the cause for an apparent deep water property variability: Global analysis of the WOCE and historical hydrographic data, Prog. Oceanogr., 48(4), 337–402, doi:10.1016/S0079-6611(00)00049-5, 2001.

Grasshoff, K., Kremling K., Ehrhardt M.: Methods of seawater analysis (3rd ed.), Weinheim Press, WILEY-VCH, 203-273, 1999.

Hansen, H. P. and Koroleff, F.: Chapter 10: Determination of nutrients, Methods Seawater Anal., 159–228, 1999.

Hoppema, M., Velo, A., van Heuven, S., Tanhua, T., Key, R. M., Lin, X., Bakker, D. C. E., Perez, F. F., Ríos, A. F., Lo Monaco, C., Sabine, C. L., Álvarez, M. and Bellerby, R. G. J.: Consistency of cruise data of the CARINA database in the Atlantic sector of the Southern Ocean, Earth Syst. Sci. Data, 1(1), 63–75, doi:10.5194/essd-1-63-2009, 2009.

https://doi.org/10.5194/essd-2019-136
Preprint. Discussion started: 3 September 2019

Johnson, G. C., Robbins, P. E. and Hufford, G. E.: Systematic adjustments of hydrographic sections for internal consistency, J. Atmos. Ocean. Technol., 18(7), 1234–1244, doi:10.1175/1520-0426(2001)018<1234:SAOHSF>2.0.CO;2, 2001.

Key, R. M., Kozyr, A., Sabine, C. L., Lee, K., Wanninkhof, R., Bullister, J. L., Feely, R. A., Millero, F. J., Mordy, C. and Peng, T. H.: A global ocean carbon climatology: Results from Global Data Analysis Project (GLODAP), Global Biogeochem. Cycles, 18(4), 1–23, doi:10.1029/2004GB002247, 2004.

Lauvset, S. K. and Tanhua, T.: A toolbox for secondary quality control on ocean chemistry and hydrographic data, Limnol. Oceanogr. Methods, 13(11), 601–608, doi:10.1002/lom3.10050, 2015.

Lazzari, P., Solidoro, C., Salon, S. and Bolzon, G.: Spatial variability of phosphate and nitrate in the Mediterranean Sea : A modeling approach, Deep. Res. Part I, 108, 39–52, doi:10.1016/j.dsr.2015.12.006, 2016.

Lejeusne, C., Chevaldonné, P., Pergent-Martini, C., Boudouresque, C. F. and Pérez, T.: Climate change effects on a miniature ocean: the highly diverse, highly impacted Mediterranean Sea, Trends Ecol. Evol., 25(4), 250–260, doi:10.1016/j.tree.2009.10.009, 2010.

Moon, J., Lee, K., Tanhua, T., Kress, N. and Kim, I.: Temporal nutrient dynamics in the Mediterranean Sea in response to anthropogenic inputs, , 5243–5251, doi:10.1002/2016GL068788.Received, 2016.

Muniz, K., Cruzado, A., Ruiz De Villa, C. and Villa, C. R. De: Statistical analysis of nutrient data quality (nitrate and phosphate), applied to useful predictor models in the northwestern Mediterranean Sea, Methodology, 17, 221–231, 2001.

Olsen, A., Key, R. M., Heuven, S. Van, Lauvset, S. K., Velo, A., Lin, X., Schirnick, C., Kozyr, A., Tanhua, T., Hoppema, M. and Jutterström, S.: The Global Ocean Data Analysis Project version 2 (GLODAPv2) – an internally consistent data product for the world ocean, , 297–323, doi:10.5194/essd-8-297-2016, 2016.

Pasqueron, O., Fommervault, D., Migon, C., Ortenzio, F. D., Ribera, M. and Coppola, L.: Deep-Sea Research I Temporal variability of nutrient concentrations in the northwestern Mediterranean sea (DYFAMED time-series station), Deep. Res. Part I, 100, 1–12, doi:10.1016/j.dsr.2015.02.006, 2015.

Powley, H. R., Krom, M. D. and Van Cappellen, P.: Phosphorus and nitrogen trajectories in the Mediterranean Sea (1950–2030): Diagnosing basin-wide anthropogenic nutrient enrichment, Prog. Oceanogr., 162, 257–270, doi:10.1016/j.pocean.2018.03.003, 2018.

Pujo-Pay, M., Conan, P., Oriol, L., Cornet-Barthaux, V., Falco, C., Ghiglione, J. F., Goyet, C., Moutin, T. and Prieur, L.: Integrated survey of elemental stoichiometry (C, N, P) from the western to eastern Mediterranean Sea, Biogeosciences, 8(4), 883–899, doi:10.5194/bg-8-883-2011, 2011.

Sabine, C. L., Hoppema, M., Key, R. M., Tilbrook, B., Van Heuven, S., Lo Monaco, C., Metzl, N., Ishii, M., Murata, A. and Musielewicz, S.: Assessing the internal consistency of the CARINA data base in the Pacific sector of the Southern Ocean, Earth Syst. Sci. Data, 2(2), 195–204, doi:10.5194/essd-2-195-2010, 2010.

Schroeder, K., Tanhua, T., Bryden, H., Alvarez, M., Chiggiato, J. and Aracri, S.: Mediterranean Sea Ship-based Hydrographic Investigations Program (Med-SHIP), Oceanography, 28(3), 12–15, doi:10.5670/oceanog.2015.71, 2015.

Schroeder, K., Chiggiato, J., Bryden, H. L., Borghini, M. and Ismail, S. Ben: Abrupt climate shift in the Western Mediterranean Sea, Nat. Publ. Gr., 1–7, doi:10.1038/srep23009, 2016.

Segura-Noguera, M., Cruzado, A. and Blasco, D.: The biogeochemistry of nutrients, dissolved oxygen and chlorophyll a in the Catalan Sea (NW Mediterranean Sea), Sci. Mar., 80(S1), 39–56, doi:10.3989/scimar.04309.20a, 2016.

Suzuki, T., Ishii, M., Aoyama, A., Christian, J. R., Enyo, K., Kawano, T., Key, R. M., Kosugi, N., Kozyr, A., Miller, L. A., Murata, A., Nakano, T., Ono, T., Saino, T., Sasaki, K., Sasano, D., Takatani, Y., Wakita, M., and Sabine, C. L.: PACIFICA Data Synthesis Project, ORNL/CDIAC-159, NDP-092, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U. S. Department of Energy, Oak Ridge, Tennessee, 2013.

Tanhua, Toste (2019): Hydrochemistry of water samples during MedSHIP cruise Talpro. PANGAEA, https://doi.org/10.1594/PANGAEA.902293.

Tanhua, T.: Matlab Toolbox to Perform Secondary Quality Control (2nd QC) on Hydrographic Data, ORNL CDIAC-158. Carbon Dioxide Inf. Anal. Center, Oak Ridge Natl. Lab. U.S. Dep. Energy, Oak Ridge, Tennessee, 158, doi:10.3334/CDIAC/otg.CDIAC_158, 2010a.

Tanhua, T., Brown, P. J. and Key, R. M.: Science Data CARINA : nutrient data in the Atlantic Ocean, Earth, 1, 7–24, doi:10.3334/CDIAC/otg.CARINA.ATL.V1.0, 2009.

Tanhua, T., Heuven, S. van, Key, R. M., Velo, A., Olsen, A. and Schirnick, C.: Quality control procedures and methods of the CARINA database, Earth Syst. Sci. Data, 2, 35–49, 2010b.

Tanhua, T., Hainbucher, D., Schroeder, K., Cardin, V., Álvarez, M. and Civitarese, G.: The Mediterranean Sea system: A review and an introduction to the special issue, Ocean Sci., 9(5), 789–803, doi:10.5194/os-9-789-2013, 2013.

Testor, P., Bosse, A., Houpert, L., Margirier, F., Mortier, L., Legoff, H., Dausse, D., Labaste, M., Karstensen, J., Hayes, D., Olita, A., Ribotti, A., Schroeder, K., Chiggiato, J., Onken, R., Heslop, E., Mourre, B., D'ortenzio, F., Mayot, N., Lavigne, H., de Fommervault, O., Coppola, L., Prieur, L., Taillandier, V., Durrieu de Madron, X., Bourrin, F., Many, G., Damien, P., Estournel, C., Marsaleix, P., Taupier-Letage, I., Raimbault, P., Waldman, R., Bouin, M. N., Giordani, H., Caniaux, G., Somot, S., Ducrocq, V. and Conan, P.: Multiscale Observations of Deep Convection in the Northwestern Mediterranean Sea During Winter 2012–2013 Using Multiple Platforms, J. Geophys. Res. Ocean., 123(3), 1745–1776, doi:10.1002/2016JC012671, 2018.

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, 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 1^{st} and 2^{nd} 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, 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 is shown in black while the data of each individual cruise are shown in blue (flag=2) and green (flag=3).

https://doi.org/10.5194/essd-2019-136
Preprint. Discussion started: 3 September 2019

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.

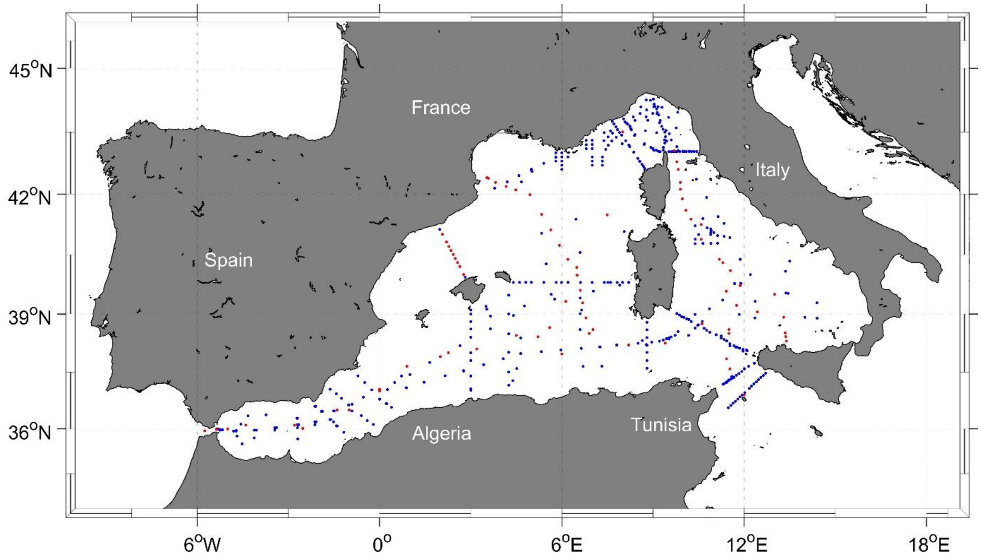
Table 4. Standard deviations of nitrate, phosphate and silicate measurements with number of samples deeper than 1000db included in the 2nd QC. Storage time: the minimum storage time defined as time difference between the cruise ending day and the 1st day of the laboratory analysis

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.

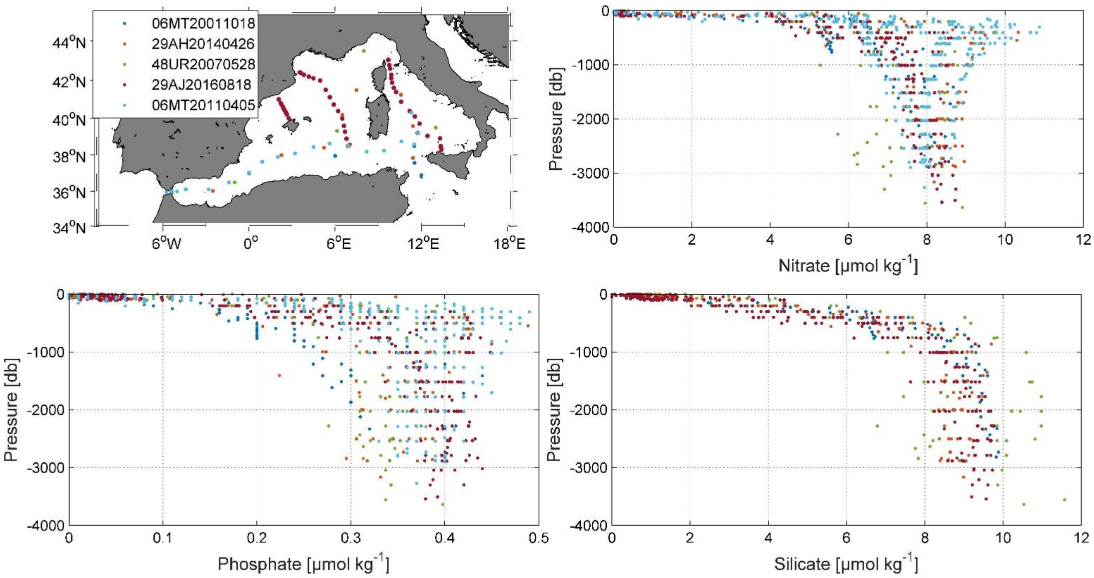
https://doi.org/10.5194/essd-2019-136
Preprint. Discussion started: 3 September 2019

Figure 1



https://doi.org/10.5194/essd-2019-136
Preprint. Discussion started: 3 September 2019

Figure 2



https://doi.org/10.5194/essd-2019-136
Preprint. Discussion started: 3 September 2019

Open Access Earth System Science Data Discussions

Figure 3

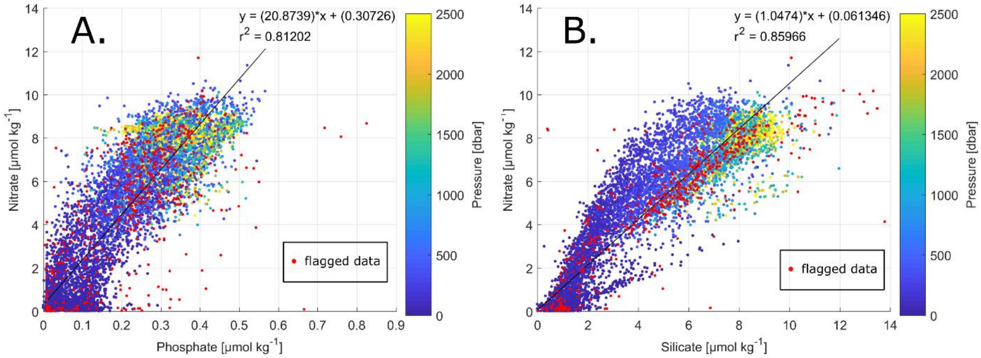
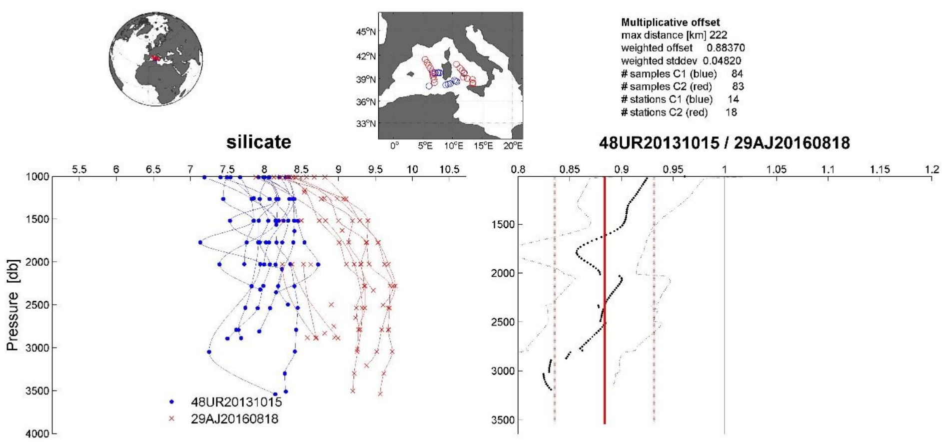
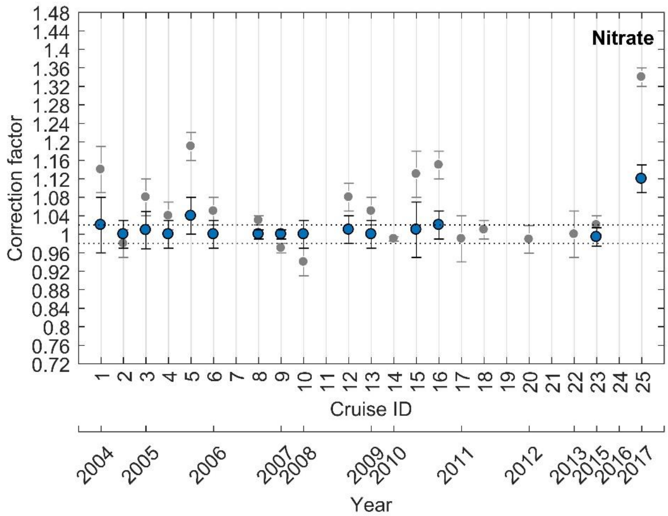


Figure 4



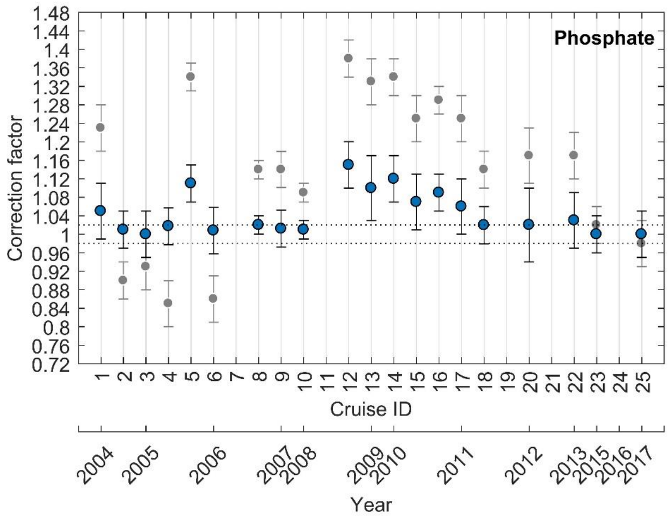
https://doi.org/10.5194/essd-2019-136
Preprint. Discussion started: 3 September 2019

Figure 5



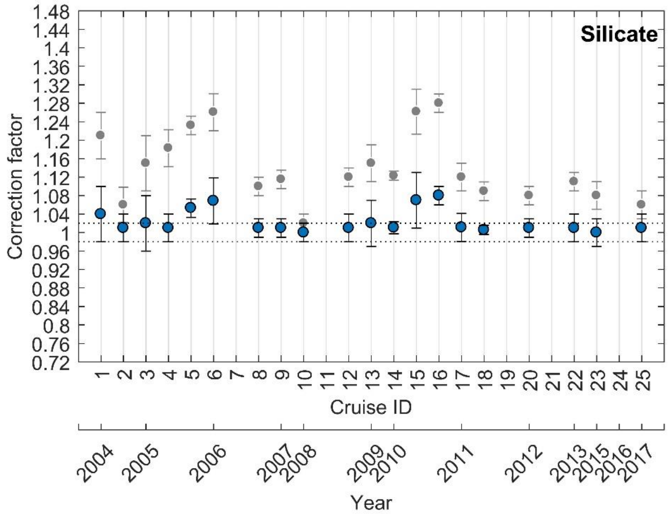
https://doi.org/10.5194/essd-2019-136
Preprint. Discussion started: 3 September 2019

Figure 6



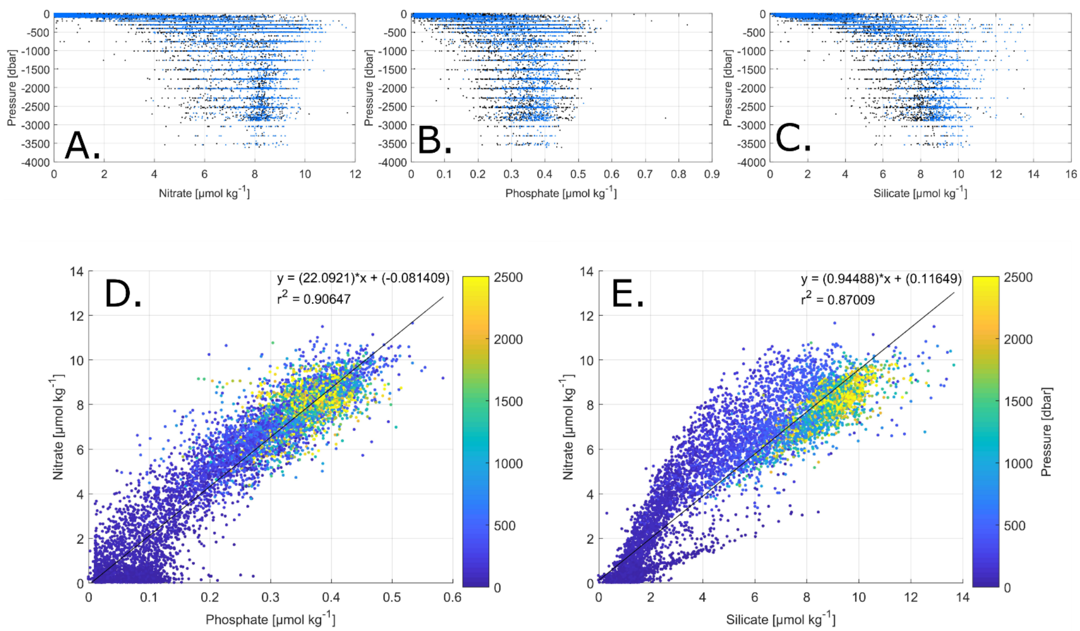
https://doi.org/10.5194/essd-2019-136
Preprint. Discussion started: 3 September 2019

Figure 7

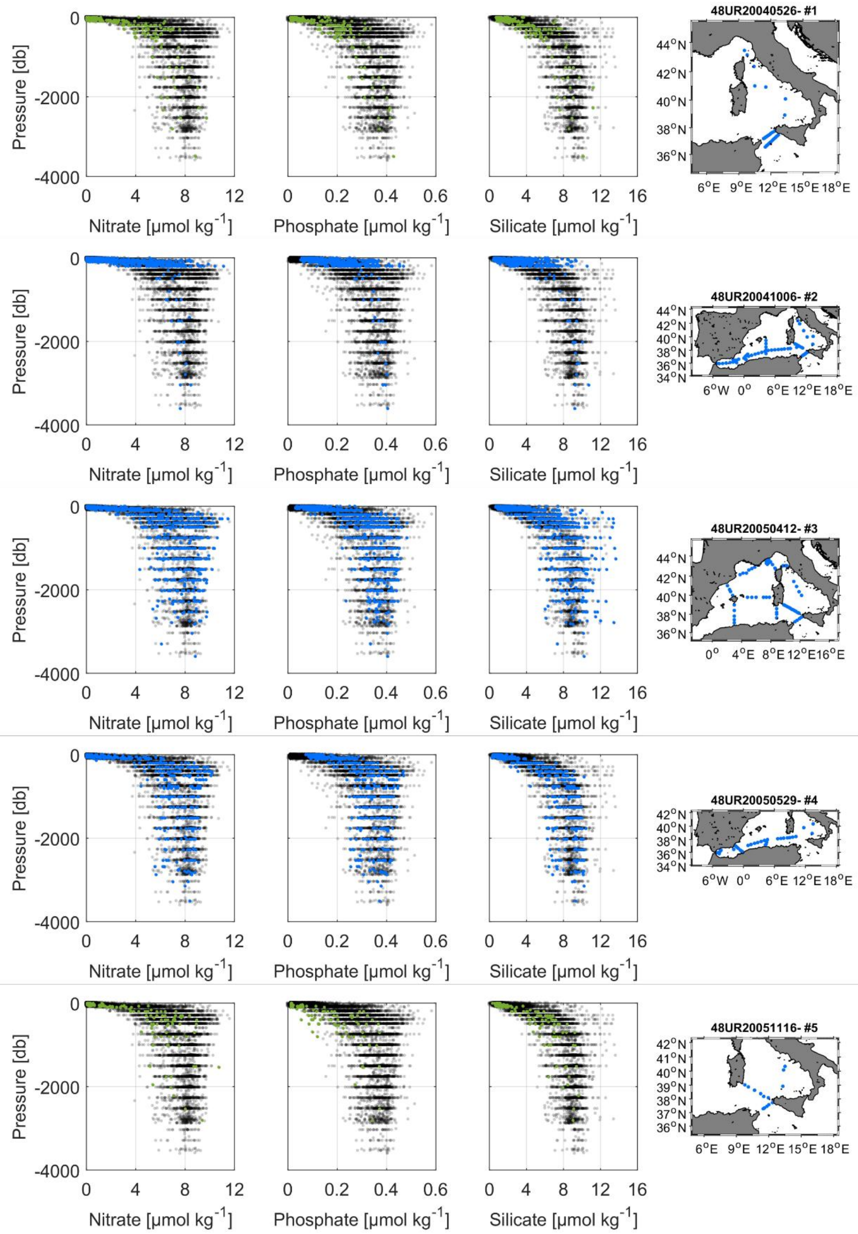


https://doi.org/10.5194/essd-2019-136
Preprint. Discussion started: 3 September 2019

Figure 8



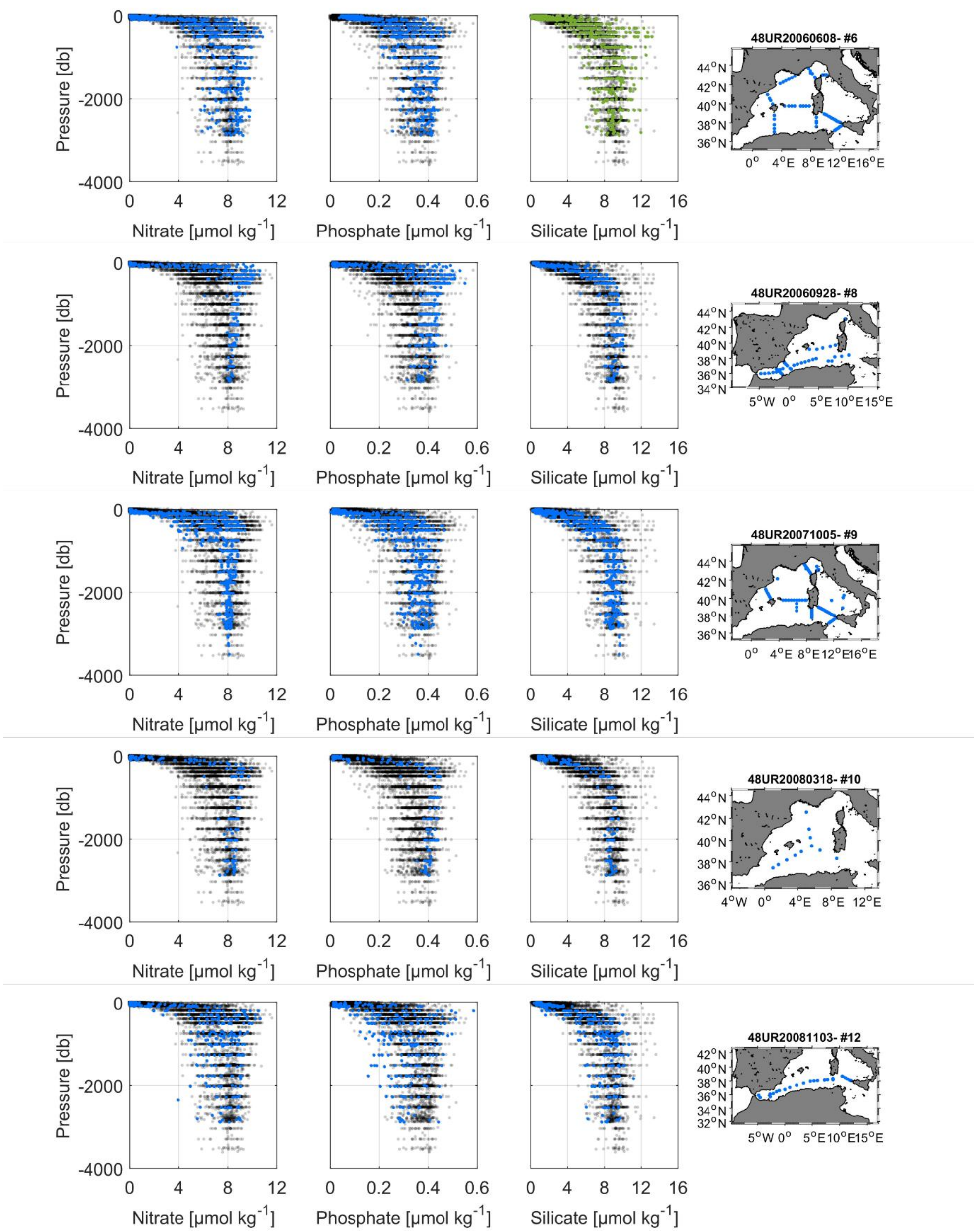
705 **Figure 9**



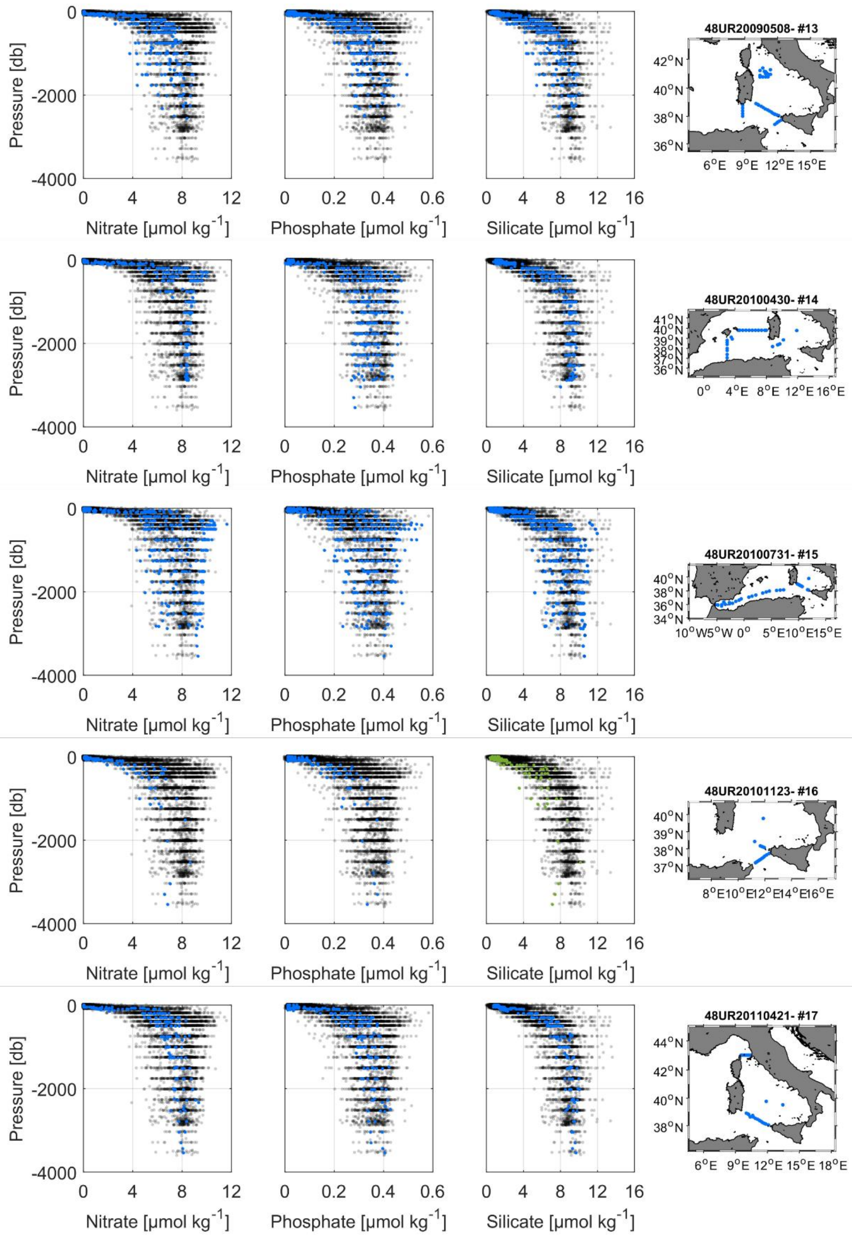
706

https://doi.org/10.5194/essd-2019-136
Preprint. Discussion started: 3 September 2019

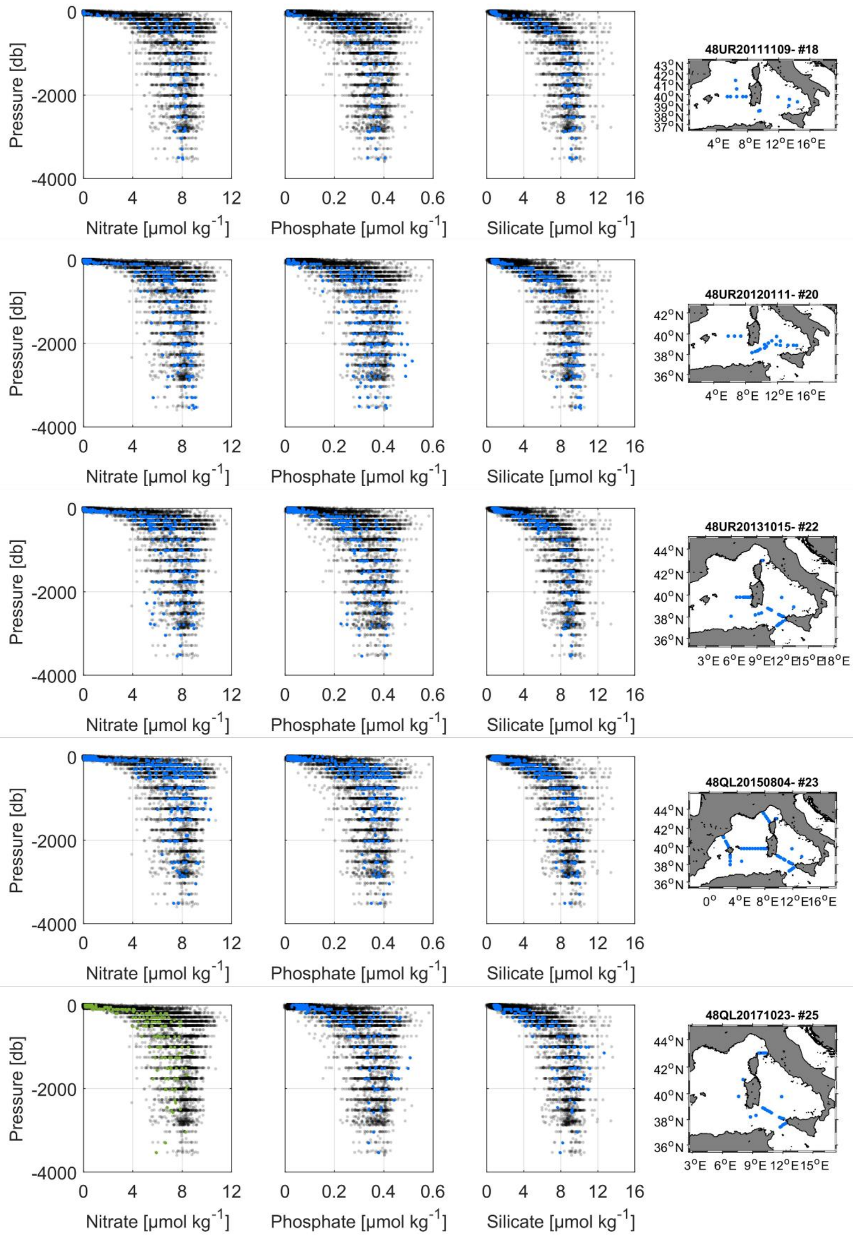
Open Access Earth System Science Data Discussions



https://doi.org/10.5194/essd-2019-136
Preprint. Discussion started: 3 September 2019



https://doi.org/10.5194/essd-2019-136
Preprint. Discussion started: 3 September 2019



https://doi.org/10.5194/essd-2019-136
Preprint. Discussion started: 3 September 2019

Table 1

Cruise ID (#)	Common Name	EXPOCODE	Research vessel	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

https://doi.org/10.5194/essd-2019-136
Preprint. Discussion started: 3 September 2019

Open Access Earth System Science Data Discussions

Table 2

Common name	EXPOCODE	Date Start/End	Source	Nutrient PI	Chief scientist
M51/2	06MT20011018	18 OCT - 11 NOV 2001	GLODAPv2	B. Schneider	W. Roether
TRANSMED_LEGII	48UR20070528	28 MAY- 12 JUN 2007	CARIMED	S. Cozzi, V. Ibello	M. Azzaro
M84/3	06MT20110405	5 - 28 APR 2011	GLODAPv2	G. Civitarese	T. Tanhua
HOTMIX	29AH20140426	26 APR- 31 MAY 2014	CARIMED	XA Álvarez-Salgado	J. Aristegui
TALPro-2016	29AJ20160818	18 - 28 AUG 2016	MedSHIP programme	L. Coppola	L. Jullion, K. Schroeder

Table 3

WOCE flag value	Interpretation in original dataset
2	Acceptable
3	Questionable/not used
9	Sample not measured/no data

Table 4

Cruise ID	EXPOCODE	std NO_3	std PO_4	std SiO_2	# samples
1	48UR20040526	1.25	0.062	1.64	21
2	48UR20041006	0.59	0.029	0.81	21
3	48UR20050412	1.15	0.050	1.41	233
4	48UR20050529	1.13	0.057	1.08	205
5*	48UR20051116	1.35	0.078	0.98	16
6	48UR20060608	1.16	0.054	1.47	221
7*	06A420060720	-	-	-	-
8*	48UR20060928	0.71	0.036	0.76	179
9*	48UR20071005	0.89	0.040	0.86	302
10	48UR20080318	0.51	0.026	0.34	66
11	48UR20080905	-	-	-	-
12*	48UR20081103	1.11	0.077	0.10	110
13	48UR20090508	1.41	0.051	1.42	88
14	48UR20100430	1.06	0.036	1.03	159
15	48UR20100731	1.34	0.053	0.14	149
16	48UR20101123	1.02	0.045	1.02	14
17	48UR20110421	0.62	0.029	0.52	56
18	48UR20111109	0.68	0.025	0.70	77
19	48MG20111210	-	-	-	-
20	48UR20120111	0.97	0.051	0.26	152
21	48UR20121108	-	-	-	-
22	48UR20131015	1.03	0.043	0.79	98
23	48QL20150804	0.84	0.038	0.85	94
24	48QL20171023	0.68	0.055	1.24	55

(-) cruise not included in the 2nd QC

(*) storage time >1 year

https://doi.org/10.5194/essd-2019-136
Preprint. Discussion started: 3 September 2019

Open Access Earth System Science Data Discussions

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 2^{nd}QC but not removed from the final dataset

https://doi.org/10.5194/essd-2019-136
Preprint. Discussion started: 3 September 2019

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