

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

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### 15           **Abstract**

16           Long-term time-series are a fundamental prerequisite to understand and detect climate shifts and  
17           trends. Understanding the complex interplay of changing ocean variables and the biological  
18           implication for marine ecosystems requires extensive data collection for monitoring, hypothesis testing  
19           and validation of modelling products. In marginal seas, such as Mediterranean Sea, there are still  
20           monitoring gaps, both in time and in space. To contribute to filling these gaps, an extensive dataset of  
21           dissolved inorganic nutrients observations (nitrate, NO<sub>3</sub>; phosphate, PO<sub>4</sub><sup>3-</sup>; and silicate, SiO<sub>2</sub>) have  
22           been collected between 2004 and 2017 in the Western Mediterranean Sea and subjected to rigorous  
23           quality control techniques to provide to the scientific community a publicly available, long-term,  
24           quality controlled, internally consistent biogeochemical data product. The data product includes 870  
25           stations of dissolved inorganic nutrients, including temperature and salinity, sampled during 24  
26           cruises. Details of the quality control (primary and secondary quality control) applied are reported.

27 The data are available in PANGAEA (<https://doi.pangaea.de/10.1594/PANGAEA.904172>, Belgacem  
28 et al. 2019)

29 **Keywords:** Mediterranean Sea, Dissolved Inorganic Nutrient, biogeochemistry

30

## 31 **1 Introduction**

32 Dissolved inorganic nutrients play a crucial role in marine ecosystem functioning. They serve as  
33 regulators of ocean biological productivity, and are trace elements for biogeochemical cycling as well  
34 as for natural and anthropogenic sources and transport processes (Bethoux, 1989; Bethoux et al.,  
35 1992). They are also non-conservative tracers, since their distribution vary according to both  
36 biological (such as primary production and respiration) and physical (such as convection, advection,  
37 mixing and diffusion) processes. Very schematically, inorganic nutrients are continuously consumed  
38 by phytoplankton (due to primary production) in the sea surface and regenerated in the mesopelagic  
39 layer by bacteria and animals (due to respiration). Moreover, the sinking of organic matter and its  
40 decomposition increases the nutrient concentrations in the intermediate and deep-water masses over  
41 time. To identify the limiting factors for biological production in the oceans, we need to understand  
42 the underlying chemical constraints and especially the macro- and micronutrients spatial and temporal  
43 variations. Dissolved inorganic nutrients may be used as tracers of water masses like salinity and  
44 temperature, to assess mixing processes, and to understand the biogeochemical circumstances of their  
45 formation regions. Understanding the complex interplay of changing ocean variables and the  
46 biological implication for marine ecosystems is a difficult task and requires not only modelling, but  
47 also extensive data collection for monitoring, hypothesis testing and validation. Monitoring gaps still  
48 remain in both in time and space, especially for marginal seas such as the Arctic Ocean or the  
49 Mediterranean Sea.

50 The Mediterranean Sea has been identified as a region significantly affected by ongoing climatic  
51 changes, like warming and decrease in precipitation (Giorgi, 2006). In addition, it is a region  
52 particularly valuable for climate change research because it behaves like a miniature ocean (Bethoux  
53 et al., 1999) with a well-defined overturning circulation characterized by spatial and temporal scales  
54 much shorter than for the global ocean, with a turnover of only several decades. Being an  
55 intercontinental sea, and subjected to more terrestrial nutrient inputs (river runoff, submarine  
56 groundwater discharge) and atmospheric deposition, the Mediterranean Sea has a nitrate to phosphate  
57 N:P ratio that is anomalously high compared to the “classical” world’s oceans Redfield ratio,  
58 indicating a general P-limitation regime, which becomes stronger along a west-to-east gradient. The  
59 Mediterranean Sea is therefore a potential model to study global patterns that will be experienced in  
60 the next decades worldwide, not only regarding ocean circulation, but also the marine biota (Lejeusne  
61 et al., 2010). Several environmental variables can act as stressors for marine ecosystems, by which  
62 climatically driven ecosystem disturbances are generated (Boyd, 2011). These changes affect, among  
63 others, the distribution of biogeochemical elements (including inorganic nutrients) and the functioning  
64 of the biological pump and CO<sub>2</sub> regulation.

65 Within this context, the aim of this paper is to compile an extensive dataset of dissolved inorganic  
66 nutrient observations (nitrate, NO<sub>3</sub>; phosphate, PO<sub>4</sub><sup>3-</sup>; and silicate, SiO<sub>2</sub>) collected between 2004 and  
67 2017 in the Western Mediterranean Sea (WMED), to describe the quality control techniques and to  
68 provide the scientific community with a publicly available, long-term, quality controlled, and  
69 internally consistent biogeochemical data product, contributing to previously published Mediterranean  
70 Sea datasets like the MEDAR/Medatlas(time period:1908–1999), (Fichaut et al., 2003) and the  
71 Mediterranean Sea – Eutrophication and Ocean Acidification aggregated datasets v2018 (time period:  
72 1911-2017) provided by EMODnet Chemistry (Giorgetti al.,2018) available at  
73 <https://www.seadatanet.org/Products/Aggregated-datasets>.

74 Both original and quality-controlled data are available in PANGAEA:

75 <https://doi.pangaea.de/10.1594/PANGAEA.904172>

76 Coverage: 44°N-35°S; -6°W-14°E

77 Location Name: Western Mediterranean Sea

78 Date start: May 2004

79 Date end: November 2017

## 80 **2 Dissolved inorganic nutrient data collection**

### 81 **2.1. The CNR dissolved inorganic nutrient data in the WMED**

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

93 The dataset presented here consists of 24 oceanographic cruises (Fig. 1 and Table 1) conducted in the  
94 WMED on board of research vessels run by the Italian National Research Council (CNR) and the  
95 Science and Technology Organisation Centre for Maritime Research and Experimentation (NATO-  
96 STO CMRE). All cruises were merged into a unified dataset with 870 nutrient stations and ~ 9666  
97 data points over a period of 13 years (2004-2017). The overall spatial distribution of the stations  
98 covers the whole WMED, but the actual distribution strongly varies depending on the specific cruise

99 and most of the data are collected along sections. At all stations, pressure, salinity and temperature  
100 were measured with a CTD-rosette system consisting of a CTD SBE 911 plus and a General Oceanics  
101 rosette with 24 12L Niskin Bottles. Temperature measurements were performed with the SBE-3/F  
102 thermometer with a resolution of  $10^{-3}$  °C; conductivity measurements were performed with the SBE-4  
103 sensor with a resolution of  $3 \cdot 10^{-4}$  S/m. The probes were calibrated before and after each cruise.  
104 During all CNR cruises, redundant sensors were used for both temperature and salinity measurements.  
105 Seawater samples for dissolved inorganic nutrient measurements were collected during the CTD up-  
106 cast at standard depths (with slight modifications according to the depth at which the deep chlorophyll  
107 maximum was detected). The standard depths are usually 5, 25, 50, 75, 100, 200, 300, 400, 500, 750,  
108 1000, 1250, 1500, 1750, 2000, 2250, 2500, 2750, 3000 m. No filtration was employed, nutrient  
109 samples were immediately stored at  $-20$  °C. Note that sample storage and freezing duration varied  
110 greatly from one cruise to another (Table 3 shows the cruises where this exceeded 1 year).

## 111 **2.2. Analytical methods for inorganic nutrients**

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

122 Nutrient analysis was performed in three laboratories. From 2004 to 2013, all cruises nutrients were  
123 analysed by ENEA, while for those of 2015 (cruise #23) and 2017 (cruise #24), nutrient  
124 concentrations were analysed by CNR-ISMAR. Referring to Table 1S, four different models of  
125 autoanalyzer were used. Measurements from the autoanalyzer were reported in  $\mu\text{mol L}^{-1}$ . Inorganic  
126 nutrient concentrations were converted to the standard unit  $\mu\text{mol kg}^{-1}$ , using sample salinity from CTD  
127 and a mean laboratory analytical temperature of 20°C. Data from nutrient analysis were then merged  
128 to ancillary CTD bottle data.

### 129 **2.3. Reference inorganic nutrient data**

130 In addition to the data collected during the above-mentioned cruises, and in order to perform the  
131 secondary quality control (described below), we identified five reference cruises (Table 2), based on  
132 their spatial and temporal distribution of the data and the reliability of the measurements (see Fig. 2 –  
133 Table.3S Fig.1S). Cruises 06MT20110405 and 06MT20011018 are the only two Mediterranean  
134 cruises included in the publicly available Global Ocean Data Analysis Project version 2 (GLODAPv2,  
135 Olsen et al. 2016). These cruises, conducted on board the R/V Meteor, provide a reliable reference  
136 because nutrient analysis strictly followed the recommendation of the World Ocean circulation  
137 experiment (WOCE) and the GO-SHIP protocols (Hydes et al., 2010; ,Tanhua et al., 2013). Cruises  
138 29AH20140426 and 48UR20070528 are to be included in the CARIMED data product (personal  
139 communication by M. Álvarez, in preparation but not yet available) and have undergone rigorous  
140 quality control following GLODAP routines. Finally, 29AJ20160818 was carried out in the framework  
141 of the MedSHIP programme (Schroeder et al., 2015) and its data are available at  
142 <https://doi.org/10.1594/PANGAEA.902293> (Tanhua, 2019).

### 143 **3 Quality Assurance and quality control methods**

144 Combining inorganic nutrient data from different sources, collected by different operators, stored for  
145 different amounts of time, and analysed by multiple laboratories, is not a straightforward task. This is  
146 widely recognized in the biogeochemical oceanographic community. Since the 1990s, several studies

147 and programmes (e.g. World Ocean Database, World Ocean Atlas, WOCE) have been devoted to  
148 facilitate the exchange of oceanographic data and develop quality control procedures to compile  
149 databases by the estimation of systematic errors (Gouretski and Jancke, 2001) to increase the inter-  
150 comparability, generate consistent data sets and accurately observe the long-term change.

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

### 162 **3.1 Primary Quality control**

163 Each individual cruise was first subjected to a primary quality control (1<sup>st</sup> QC) that included a check of  
164 apparent and extreme outliers in CTD salinity, nitrate, phosphate and silicate. Each parameter included  
165 a quality control flag, following standard WOCE flags (Table 3). Surface, intermediate and deep layer  
166 were evaluated separately because nutrient observations evolve differently in each layer. The  
167 coefficient of variation (CV, defined as standard deviation over mean) was computed for each depth  
168 layer. Coefficients of variation in the surface (0-250 db) layer were high (nitrate CV=1.16, phosphate  
169 CV=1.005, silicate CV=0.75) due to air-sea interaction (Muniz et al., 2001) occurring in this layer  
170 rendering it difficult to flag. These influences are of reduced importance in the intermediate (250-1000  
171 db) layer (nitrate CV=0.23, phosphate CV=0.31, silicate CV=0.24) and the deep (>1000 db) layer

172 (nitrate CV=0.15, phosphate CV=0.22, silicate CV=0.14), decreasing the total variance. Flags in the  
173 upper and intermediate layer were thus set based on outliers within pressure ranges defined according  
174 to standard pressures (0-10, 10-30, 30-60, 60-80, 80-160, 160-260, 260-360, 360-460, 460-560, 560-  
175 1000 db).

176 Below 1000 db, flagging included an inspection of nitrate to phosphate (N:P) and nitrate to silicate (N:  
177 Si) ratios. The Median and Median Absolute Deviation (MAD) was computed by classes of pressure:  
178 we considered as outlier any atypical observation and any value that departs from the median by more  
179 than three MADs in the different pressure ranges for each cruise.

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

186 In order to have a first assessment of the precision of each cruise measurements, the standard deviation  
187 of observations deeper than 1000 db was calculated along with averages and standard deviations for  
188 each cruise and by subregions to have an overview about nutrient content variability in the deep layer  
189 and about the observations spatial spread of individual cruises (Table 4). Following the subdivision of  
190 Manca et al. (2004), the WMED has been divided into subregions (Fig.2S, Table 2S) according to the  
191 general circulation patterns (details in Manca et al.,2004). Table 4 displays the comparison of standard  
192 deviation of deep measurements for each cruise and within subregions. The overall standard deviation  
193 between cruises in the deep layer varied between 0.51 and 1.41  $\mu\text{mol kg}^{-1}$  for nitrate, between 0.1 and  
194 1.64  $\mu\text{mol kg}^{-1}$  for silicate and between 0.025 and 0.078  $\mu\text{mol kg}^{-1}$  for phosphate. Regional standard  
195 deviation of nitrate measurements below 1000 db varied between 0.08  $\mu\text{mol kg}^{-1}$  in the Gulf of Lion  
196 (DF2) with cruise #9 and 1.6  $\mu\text{mol kg}^{-1}$  in the Balearic Sea (DS2) observations of cruise #14.



197 Phosphate lowest regional standard deviation was  $0.01 \mu\text{mol kg}^{-1}$  found in the observations of cruise  
198 #9 in Gulf of Lion (DF2), cruise #10 in Balearic Sea (DS2) and Algerian West (DS3), cruise #14 and  
199 cruise # 15 in Tyrrhenian South (DT3), cruise #18 in Algero-Provençal (DF1) and Sardinia Channel  
200 (DI1) while the highest standard deviation was  $0.1 \mu\text{mol kg}^{-1}$  in the observations of cruise #12 in  
201 Algerian West (DS3). As for silicate, the lowest standard deviation was  $0.02 \mu\text{mol kg}^{-1}$  observed in  
202 cruise #9 measurements of Gulf of Lion subregion (DF2) and the highest deep standard deviation was  
203 observed in cruise #6 in its all subregions together with cruise #5 measurement in Tyrrhenian North  
204 (DT1) with  $1.83 \mu\text{mol kg}^{-1}$  standard deviation.

205 Cruises #3, #6 and #9 had the largest spatial extension (see right side of Fig. 9) with a high number of  
206 samples over more than seven subregions (Table 4) and the geographical variability of the distribution  
207 in dissolved inorganic nutrients results thus in the largest standard deviations. Conversely, cruises with  
208 smaller spatial coverages have lower standard deviations. Therefore, a relatively small spatial  
209 coverage and high standard deviation is considered as indicative of data with low precision (Olsen et  
210 al., 2016). This applies to cruises #1, #5, and #16. Despite the small spatial coverage, samples of  
211 nitrate and phosphate of cruise #5 have an overall standard deviation of  $1.35 \mu\text{mol kg}^{-1}$  and  $0.07 \mu\text{mol}$   
212  $\text{kg}^{-1}$ , respectively, a high standard deviation pointed out in also in the regional standard deviation of  
213 deep measurements in Tyrrhenian North (DT1) and South (DT3) . Cruise #1, with few stations in  
214 Tyrrhenian North (DT1) and South (DT3) subregions and 21 samples below 1000 db, has an overall  
215 standard deviation of  $1.25 \mu\text{mol kg}^{-1}$  for nitrate,  $0.06 \mu\text{mol kg}^{-1}$  for phosphate and  $1.64 \mu\text{mol kg}^{-1}$  for  
216 silicate. The regional standard deviation was relatively high for nitrate ( $0.51\text{-}1.32 \mu\text{mol kg}^{-1}$ ) phosphate  
217 ( $0.02\text{-}0.065 \mu\text{mol kg}^{-1}$ ) and silicate ( $0.53\text{-}1.83 \mu\text{mol kg}^{-1}$ ). A comparison with the deviations from e.g.  
218 cruise # 2, carried out in the same year and e.g. cruise #17 (with a similar cruise track), confirms the  
219 lower precision of the data of cruise#1. Similar considerations apply to the quality of nitrate samples  
220 ( $0.87\text{-}1.02 \mu\text{mol kg}^{-1}$ ).and silicate ( $0.87\text{-}0.9 \mu\text{mol kg}^{-1}$ ) from cruise #16, covering a small area in

221 Tyrrhenian North (DT1) and South (DT3), compared to cruise #17, carried out in the same regions  
222 (right side of Fig. 9 and Table 4).

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

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

### 243 **3.2 Secondary Quality control: the crossover analysis**

244 The method used to perform the secondary QC on the dissolved inorganic nutrient dataset in the  
245 WMED makes use of the quality-controlled reference data, and the crossover analysis toolbox  
246 developed by Tanhua (2010) and Lauvset and Tanhua (2015). The computational approach is based on  
247 comparing the cruise data set to a high-quality reference data set to quantify biases, described in detail  
248 in Tanhua et al. (2010). Here, we summarize the technique with emphasis on inorganic nutrient. The  
249 first step consisted of selecting reference data, as described in section 2.3. The second step is the  
250 crossover analysis that was carried out using a MATLAB Toolbox (available online: [https://cdiac.ess-  
252 dive.lbl.gov/ftp/oceans/2nd\\_QC\\_Tool\\_V2/](https://cdiac.ess-<br/>251 dive.lbl.gov/ftp/oceans/2nd_QC_Tool_V2/)) where crossovers are generated as difference between two  
253 cruises using the “running cluster” crossover routine. Each cruise is thus compared to the chosen set of  
254 reference cruises. For each crossover, samples deeper than 1000 db are selected within a predefined  
255 maximum distance set to 2°arc distance, defined as a crossing region, to ensure the quality of the  
256 offset with a minimum number of crossovers and to minimize the effect of the spatial change. The  
257 reason to select measurements deeper than 1000 db, is to remove the high frequency variability  
258 associated to mesoscale features, biological activity and the atmospheric forcing acting in the upper  
259 layers, that might induce changes in biogeochemical properties of water masses. On the other hand,  
260 also the deep Mediterranean cannot be considered truly “unaffected” by changes, as it is intermittently  
261 subjected to ventilation (Schroeder et al., 2016; Testor et al., 2018) and the real variability can be  
262 altered in adjusting data. The computational approach takes this into account, since weights are given  
263 to the less variant profile in the crossing region, according to the “confidence” in the determined offset  
264 of the compared profiles (i.e. the weighted mean offset of a given crossover-pair is weighted to the  
265 depth where the offsets of all compared profiles have the smallest variation (which indeed is strongly  
266 interlinked with the degree of variance of each profile) (for further details see Lauvset and Tanhua,  
2015).

267 Before identifying crossovers, each profile was interpolated using the piecewise cubic Hermite method  
268 and the distance criteria outlined in Lauvset and Tanhua (2015), their Table 1, and detailed in Key et

269 al. (2004). The crossover is a comparison between each interpolated profile of the cruise being  
270 evaluated and the interpolated profile of the reference cruise. The result is a weighted offset (defined  
271 as difference cruise/reference) and a standard deviation of the offset. The standard deviation is  
272 indicative of the precision; however, it is important to note that this assumption only works because it  
273 is a comparison to a reference, and the absolute offset is indicative of accuracy.

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

278 For inorganic nutrients, offsets are multiplicative so that a weighted mean offset > 1 means that the  
279 measurements of the corresponding cruise are higher than the measurements of the reference cruise in  
280 the crossing region and applying the adjustment would decrease the measured values. The magnitude  
281 of an increase or a decrease is the difference of the weighted offset from 1. In general, no adjustment  
282 smaller than 2% (accuracy limit for nutrient measurements) is applied (detailed description is found in  
283 Hoppema et al., 2009; Lauvset and Tanhua, 2015; Olsen et al., 2016; Sabine et al., 2010; Tanhua et al.,  
284 2010).

285 The last step is the computation of the weighted mean (WM) to determine the internal consistency and  
286 quantify the overall accuracy of the adjusted product (Hoppema et al., 2009; Sabine et al., 2010;  
287 Tanhua et al., 2009), with the difference that our assessment is based on the offsets with respect to a  
288 set of reference cruises. This WM reflects the absolute weighted mean offset of the data set compared  
289 to the reference data set, hence the smaller the WM the higher the internal consistency. The accuracy  
290 was computed from the individual absolute weighted offsets. The WM, which will be discussed in  
291 section 4.4., was computed using the individual weighted absolute offset (D) of number of crossovers

292 (L) and the standard deviation ( $\sigma$ ):  $WM = \frac{\sum_{i=1}^L D(i)/(\sigma(i))^2}{\sum_{i=1}^L 1/(\sigma(i))^2}$

## 293 **4 Results of the secondary QC and recommendations**

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

300 Overall, we found a total number of 73 individual crossovers for nitrate, 72 for phosphate and 54 for  
301 silicate. An example of the running cluster crossover output is shown in Fig.4. Results of the crossover  
302 analysis is an adjustment factor for each cruise and each nutrient, that are shown in Table 5 and Fig. 5-  
303 6-7. The adjustment factor was calculated from the weighted mean of absolute offset summarized in  
304 Table 6 and Fig. 3S-4S-5S. Table 6 details the improvement of the weighted mean of absolute offset  
305 by cruise prior to and after adjustments, the information is also displayed graphically in Fig. 3S-4S-5S.  
306 Cruises are in chronological order in all figures and tables.

### 307 **4.1 Nitrate**

308 The crossover analysis suggests a significant adjustment for nitrate concentrations on 15 cruises,  
309 between 0.94 and 0.98 (for adjustments <1) and between 1.02 and 1.34 (for adjustments >1) (Table 5  
310 and Fig.5). Offsets suggest that the deep measurements of cruises #1, #3, #4, #5, #6, #8, #12, #13, #15,  
311 #16, #23 and #24 need to be adjusted towards higher concentrations, when compared to the respective  
312 reference (Fig.3S).

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

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

## 319 **4.2 Phosphate**

320 For phosphate the crossover analysis suggests adjustments for 20 cruises, as shown in Fig. 6. Deep  
321 phosphate measurements of 15 cruises (Table 6) appear to be lower than the respective reference  
322 measurements (i.e. phosphate data of these cruises require an upward adjustment), while the data of  
323 five cruises (#2, #3, #4, #6, #24) are higher (i.e. they need a downward adjustment) (Fig.4S). Applying  
324 all the indicated adjustments, the large offsets of cruises #2, #3, #4, #6, #8, #9, #10, #18, #20, #23 and  
325 #24 are reduced and become consistent with the reference. Cruises #1, #5, #12, #13, #14, #15, #16,  
326 #17, and #22 retain an offset even after applying the indicated adjustment. These cruises are  
327 considered in detail later.

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

333 Comparing phosphate before and after adjustments, the corrections did minimise the difference with  
334 the reference, while the actual variation with time was preserved (Fig.6). The temporal trend towards  
335 higher phosphate concentrations in the Mediterranean Sea is considered to be real, even though  
336 studies concerning the biogeochemical trends in the deep layers of the WMED are scarce (Pasqueron  
337 et al., 2015). However, this variation could be consistent with the findings of Béthoux et al.(1998,  
338 2002) and the modelling studies by Moon et al. (2016) and Powley et al. (2018) who indeed found an

339 increasing trend in phosphate concentrations over time, due to the increase in the atmospheric and  
340 terrestrial inputs.

### 341 **4.3 Silicate**

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

### 349 **4.4 Discussion and recommendation**

350 Adjustments were evaluated for each cruise separately. As a general rule no correction was applied  
351 when the suggested adjustment is strictly within the 2% limit (indicated with NA in Table 5). The  
352 average correction factors were 1.06 for nitrate, 1.14 for phosphate and 1.14 for silicate, respectively.  
353 To verify the results, we re-ran the crossover analysis and re-computed offsets and adjustment factors  
354 using the adjusted data (as shown in blue in Fig. 3S-4S-5S and Fig. 5-6-7). Most of the new  
355 adjustments are within the accuracy envelope and few are outside the limit, except for the cruises  
356 belonging to the above mentioned “phosphate-trend” and the other outlying cruises which are detailed  
357 hereafter. By the application of adjustments, the deep-water offsets were reduced. This can be seen in  
358 the decrease of the weighted mean offset between the data before adjustments (after 1<sup>st</sup> QC, Fig. 3S-  
359 4S-5S, in grey) and the adjusted data (after 2<sup>nd</sup> QC, Fig. 3S-4S-5S, in blue).

360 Referring to the analysis detailed in section 3.2, the internal consistency of the nutrient data set has  
361 improved and increased significantly after the adjustment, from 4% for nitrate, 19% for phosphate and  
362 13% for silicate, to a more unified dataset with 3 % for nitrate, 6 % for phosphate and 3% for silicate.

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

370 The regression model is more accurate after adjustments with an improved  $r^2$  for N:P (from 0.81 to  
371 0.90) and for N: Si (from 0.85 to 0.87). One of the main reasons for an upward/ downward bias would  
372 be the lack of use of CRM for nutrients in all cruises as also noted in CARINA (Tanhua et al., 2009)  
373 or in the most recent global comparability study by Aoyama (2020).

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

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

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

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



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

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

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

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

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

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

408 Cruise #18 [48UR20111109] is similar to cruise #17, since it was suggested to correct phosphate by  
409 1.14 and silicate by 1.09, based on four crossovers in the Tyrrhenian North and South, Sardinia  
410 channel and Algero-Provençal subregions.

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

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

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

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

422 Cruise #1 [48UR20040526]: The adjusted values are still lower than the reference (Fig.5-6-7-Fig.3S-  
423 4S-5S) and are still outside the 2% accuracy range. This cruise had stations in the Sicily Strait,  
424 Tyrrhenian North and South and Ligurian East sub-regions. (Fig. 9, right side) and only 4 stations  
425 were deeper than 1000 db (those within the Tyrrhenian Sea). The low precision of this cruise has  
426 already been evidenced during the primary QC (section 3.1). We recommend flagging this cruise as  
427 questionable (flag 3).

428 Cruise #5 [48UR20051116]: This cruise took place between Sicily Strait and the Tyrrhenian North and  
429 South (Fig. 9, right side). Nitrate, phosphate and silicate data were lower than those from other cruises  
430 (#3 and #4) run the same year (Fig. 5-6-7-Fig.3S-4S-5S) and are still biased after adjustments.

431 Considering the limited precision and the low number of crossovers, it is recommended to flag the  
432 cruise as questionable (flag 3).

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

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

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

454 Cruise #16 [48UR20101123]: The cruise shows large offsets for phosphate and silicate (Fig. 6-7- Fig.  
455 4S-5S), similar to cruise #15. Considering that the overall cruise standard deviation of silicate samples

456 below 1000 db was relatively high (1.02 over 14 samples, see Table 4), and that it has only one  
457 crossover between the Tyrrhenian North and South subregions (Table 6), and that when comparing  
458 deep regional averages, this cruise had the lowest average silicate value, it is recommended to flag  
459 silicate data of cruise #16 as questionable (flag 3). As for phosphate, the cruise is part of the  
460 “phosphate-trend” and is therefore flagged good/acceptable e.

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

464 The cruises discussed in this section were not removed from the final product but are retained along  
465 with their recommended quality flag (Table 3) detailed above and in the supplementary material – Part  
466 2 (A2)). We have done the evaluation of their overall quality but leave it up to the users how to  
467 appropriately use these data.

#### 468 **4.5 Product assessment: Comparison with MEDATLAS**

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

475 The results of Table 7 compares water mass biogeochemical properties with the reference climatology.  
476 The new product agrees well with the Medatlas climatology. However, there are some distinctions.  
477 The surface layer (0-150db) is characterized by a low nutrient content. The surface nitrate varies  
478 between 0.69 and 2.75  $\mu\text{mol kg}^{-1}$  with a maximum found in the Ligurian East (DF4) and the minimum  
479 in the Alboran Sea (DS1) subregions, similar values were recorded in the climatology (0.61- 3.00

480  $\mu\text{mol kg}^{-1}$ ). The differences in nitrate averages in the surface layer are observed in the Gulf of Lion  
481 (DF2) where the new product is higher than the climatology and slightly lower in the Liguro-  
482 Provençal (DF3). As for, the surface content in phosphate, it varied between 0.04 and 0.16  $\mu\text{mol kg}^{-1}$   
483 with a maximum found in the Ligurian East (DF1) and a minimum in the Alboran Sea (DS1), alike the  
484 Medatlas climatology, where phosphate averages fluctuate between 0.05 and 0.19  $\mu\text{mol kg}^{-1}$ . The new  
485 product is slightly lower compared to the climatology. As to the average surface in silicate, it varies  
486 between 1.36 and 2.91  $\mu\text{mol kg}^{-1}$  with a minimum found in the Ligurian East (DF4), the maximum in  
487 the Gulf of Lion (DF2)) while in the climatology it varied between 1.27 and 2.31  $\mu\text{mol kg}^{-1}$  (the  
488 minimum in the Ligurian East (DF4) and the maximum in the Alboran Sea (DS1)). The new product is  
489 slightly higher in silicate.

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

493 In the intermediate layer, averages were computed from the depth of the salinity maximum ( $S_{\text{max}}$ )  
494  $\pm 100\text{m}$  from a regional average profile, indicative of the Levantine Intermediate Water (LIW) core.  
495 Nitrate average varies between 4.94 and 9.32  $\mu\text{mol kg}^{-1}$  where the minimum content is recorded in  
496 Sicily strait (DI3) and the maximum in the Algerian West (DS3) while in the in the Medatlas  
497 climatology nitrate was between 5.14 and 8.60  $\mu\text{mol kg}^{-1}$ . In average, the lowest content in nitrate was  
498 in Tyrrhenian North (DT1), South (DT3), Sardinia Channel (DI1) and Sicily Strait (DI3) while LIW of  
499 Gulf of Lion (DF2), Liguro-Provençal (DF3), Ligurian East (DF4), Balearic Sea (DS2), Algeo-  
500 Provençal (DF1), Alboran Sea (DS1), Algerian West (DS3) and East (DS4) subregions is relatively  
501 rich in nitrate. Compared to the Medatlas product, though the new product is slightly higher mainly in  
502 the Gulf of Lion (DF2), Ligurian East (DF4) and Balearic Sea (DS2). As for phosphate, LIW averages  
503 show similar behavior as nitrate, the lowest phosphate content (0.21- 0.27  $\mu\text{mol kg}^{-1}$ ) is observed in the  
504 Eastern subregions of WMED (Sicily Strait (DI3), Sardinia Channel (DI1), Tyrrhenian South (DT3)

505 and North (DT1), when the maximum concentrations ( $0.4-0.37 \mu\text{mol kg}^{-1}$ ) were reported in the  
506 Western subregions of the WMED (the Alboran Sea (DS1), Algerian West (DS3) and East (DS4),  
507 Balearic Sea (DS2) and Gulf of Lion (DF2)). The large differences between the two products were in  
508 Ligurian East (DF4) and the Alboran Sea (DS1), subregions of few number of observations.

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

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

521 We have verified also average biochemical properties in the deep layer (below 1500db). The new  
522 product is slightly higher in nitrate averages ( $7.74 -8.37 \mu\text{mol kg}^{-1}$ ) than the Medatlas climatology  
523 ( $7.12 - 8.06 \mu\text{mol kg}^{-1}$ ) (Table 7). The largest difference is found in Tyrrhenian South (DT3) and North  
524 (DT1) subregions. This difference could be due to the fact that, we are comparing two different time  
525 periods (2004-2017 and 1908-2001). As for the deep layer phosphate, average concentrations vary  
526 between  $0.35$  and  $0.37 \mu\text{mol kg}^{-1}$  and are within the climatology limits ( $0.31 - 0.40 \mu\text{mol kg}^{-1}$ ). In all  
527 subregions, there is not large differences. Overall, phosphate is in accordance with the Medatlas  
528 climatology. Similar to nitrate, deep average silicate in the new product ( $8.64 -9.21 \mu\text{mol kg}^{-1}$ ) is

529 higher than the climatology ( $7.51$  to  $9.04 \mu\text{mol kg}^{-1}$ ). The largest difference in average silicate is  
530 observed in Tyrrhenian North (DT1), South (DT3) and Liguro-Provençal (DF3) subregions.

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

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

547 Silicate RMSE (Fig. 10 C) is between  $0.13 \mu\text{mol kg}^{-1}$  in the Algero-Provençal subregion (DF1) and  
548  $3.5 \mu\text{mol kg}^{-1}$  in the Ligurian East subregion (DF4) in the surface layer, between  $0.10 \mu\text{mol kg}^{-1}$  in the  
549 Sardinia Channel (DI1) and  $2.54 \mu\text{mol kg}^{-1}$  in the Gulf of Lion (DF2) in the intermediate layer, and in  
550 deep layer, RMSE ranges between  $0.33 \mu\text{mol kg}^{-1}$  in the Algerian East (DS4) and  $1.43 \mu\text{mol kg}^{-1}$  in  
551 the Liguro-Provençal subregion (DF3).

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

## 567 **5 Final remarks**

568 An internally consistent data set of dissolved inorganic nutrients has been generated for the WMED  
569 (2004-2017). The accuracy envelope for nitrate and silicate was set to 2%, a predefined limit used in  
570 GLODAP and CARINA data products. Regarding phosphate data, these were almost entirely outside  
571 this limit, because of its natural variations and overall very low concentrations in the WMED, a highly  
572 P-limited basin. Using a crossover analysis (2<sup>nd</sup> QC toolbox) to compare cruises with respect to  
573 reliable reference data, improved the accuracy of the measurements by bias-minimizing the individual  
574 cruises the new product was broadly in consistent with the earlier climatology MEDAR/Medatlas.

575 The publication of a quality-controlled extensive (spatially and temporally) database of inorganic  
576 nutrients in the WMED was timely and fills a gap in information that prevented baseline assessments



577 on spatial and temporal variability of biogeochemical tracers in the Mediterranean. In combination  
578 with older databases in the same region (e.g. bottle data available in the MEDAR/Medatlas database),  
579 this new database will thus constitute a pillar on which the Mediterranean marine scientific community  
580 will be able to build on original research topics on biogeochemical fluxes and cycles and their relation  
581 to hydrological changes that occurred in the period covered by the dataset. The dataset is also relevant  
582 for the modelling community as it can be used as an independent data product to assess reanalysis  
583 products or it can be assimilated in new reanalysis products.

## 584 **6 Data availability**

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

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

592 - *Original dataset: CNR\_DIN\_WMED\_20042017\_original.csv*: This is the original dataset with  
593 flag variable for each of the following parameter: CTD salinity, nitrate, phosphate and silicate  
594 from the primary quality control (detailed in section 3.1).

595 - *Adjusted dataset: CNR\_DIN\_WMED\_20042017\_adjusted.csv*: This is the product after  
596 primary quality control and after applying the adjustment factors from the secondary quality  
597 control. Recommendations of section 4.4 are included, as well as quality flags.

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797 **Figure Captions**

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

800 **Figure 2.** Overview of the reference cruise spatial coverage and vertical distributions of the inorganic  
801 nutrients. Top left: geographical distribution map, top right: vertical profiles of nitrate in  $\mu\text{mol kg}^{-1}$ ,  
802 bottom left: vertical profiles of phosphate in  $\mu\text{mol kg}^{-1}$ , bottom right: vertical profiles of silicate in  
803  $\mu\text{mol kg}^{-1}$ .

804 **Figure 3.** Scatter plots of (A.) phosphate vs nitrate (in  $\mu\text{mol kg}^{-1}$ ) and (B.) silicate vs. nitrate (in  $\mu\text{mol}$   
805  $\text{kg}^{-1}$ ). Data that have been flagged as “questionable” (flag=3) are in red, the colour bar indicates the  
806 pressure (in dbar). The black lines represent the best linear fit between the two parameters, and the  
807 corresponding equations and  $r^2$  values are shown on each plot. Average resulting N:P ratio is 20.87,  
808 average resulting N:Si ratio is 1.05 (whole depth).

809 **Figure 4.** An example of the calculated offset for silicate between cruise 48UR20131015 and cruise  
810 29AJ2016818 (reference cruise). Above: location of the stations being part of the crossover and  
811 statistics. Bottom left: vertical profiles of silicate data in ( $\mu\text{mol kg}^{-1}$ ) of the two cruises that fall within  
812 the minimum distance criteria (the crossing region), below 1000 dbar. Bottom right: vertical plot of  
813 the difference between both cruises (dotted black line) with standard deviations (dashed black lines)  
814 and the weighted average of the offset (solid red line) with the weighted standard deviations (dotted  
815 red line).

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

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



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

821 **Figure 8.** Dataset comparison before (black) and after (blue) adjustment, showing vertical profiles of  
822 (A.) nitrate (in  $\mu\text{mol kg}^{-1}$ ), (B.) phosphate (in  $\mu\text{mol kg}^{-1}$ ) and (C.) silicate (in  $\mu\text{mol kg}^{-1}$ ). Scatter plots  
823 of the adjusted data from all depths after 1<sup>st</sup> and 2<sup>nd</sup> quality control for (D.) phosphate vs nitrate (in  
824  $\mu\text{mol kg}^{-1}$ ) and (E.) silicate vs. nitrate (in  $\mu\text{mol kg}^{-1}$ ). The black lines represent the best linear fit  
825 between the two parameters, and the corresponding equations and  $r^2$  values are shown on each plot.  
826 Average resulting N:P ratio is 22.09, average resulting N:Si ratio is 0.94 (whole depth).

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

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

833 **Table captions**

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

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

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

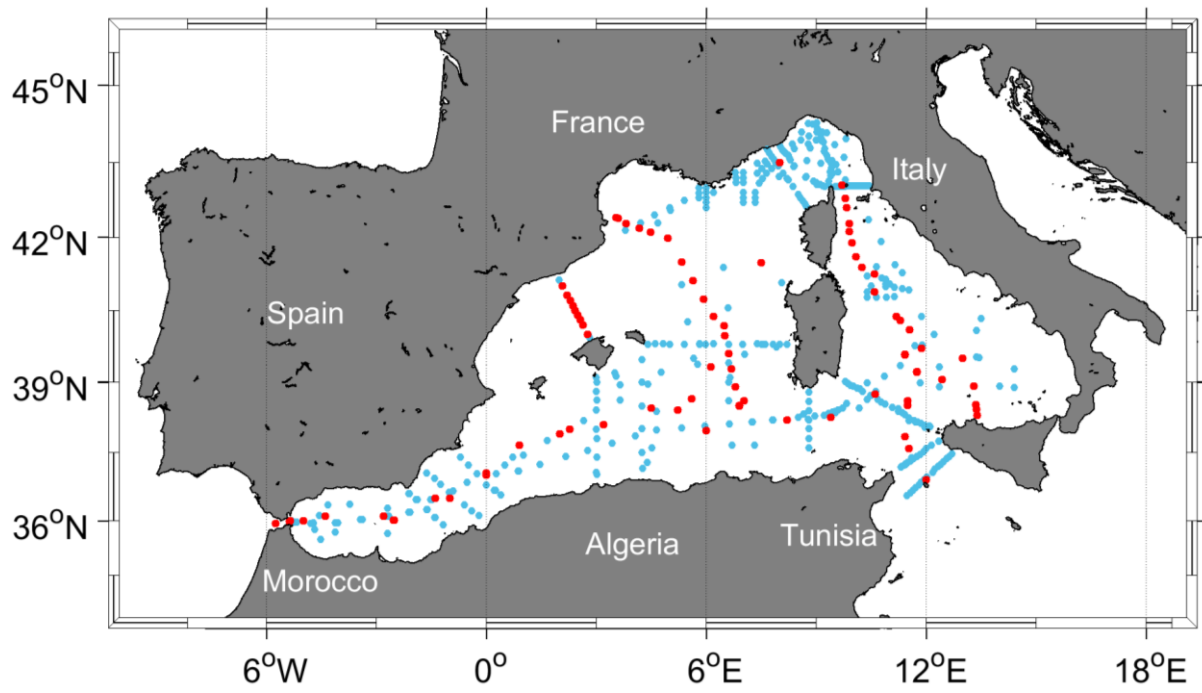
841 **Table 4.** Average and Standard deviations of nitrate, phosphate and silicate measurements by cruise  
842 and for each region with number of samples deeper than 1000db included in the 2<sup>nd</sup> QC. Average  
843 storage time: the minimum storage time defined as time difference between the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

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

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

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

855 **Figure 1**



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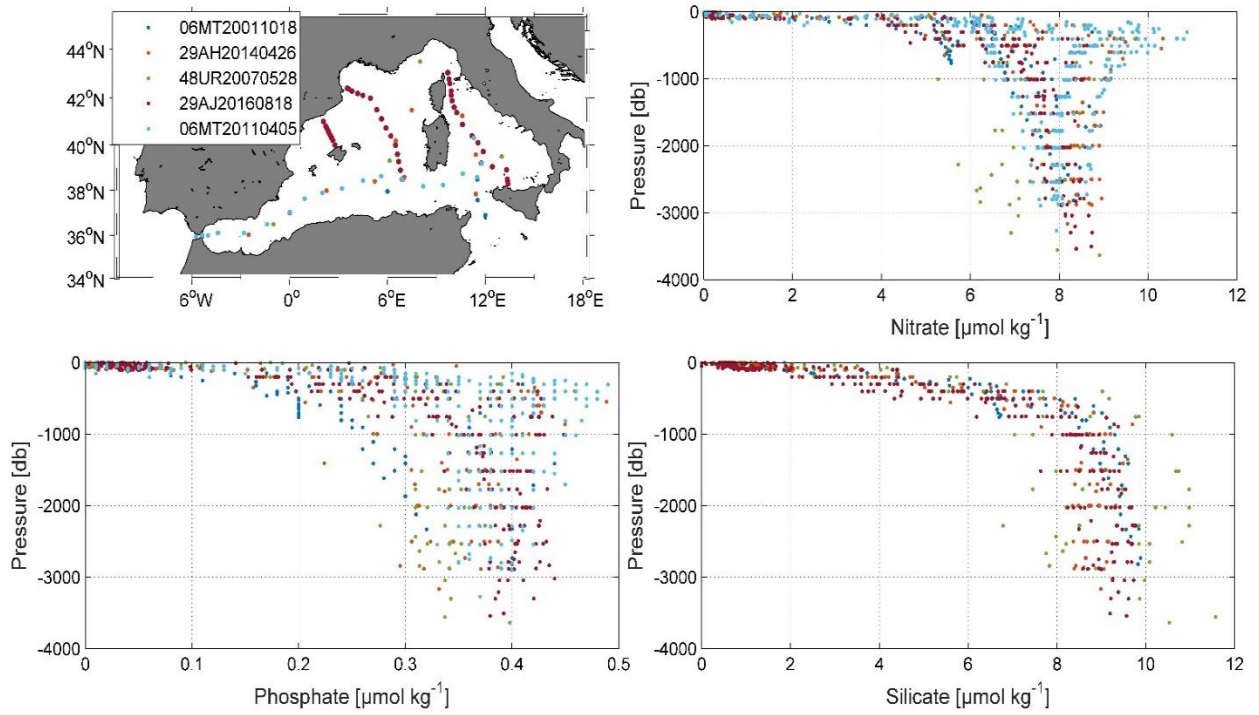
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867 **Figure 2**



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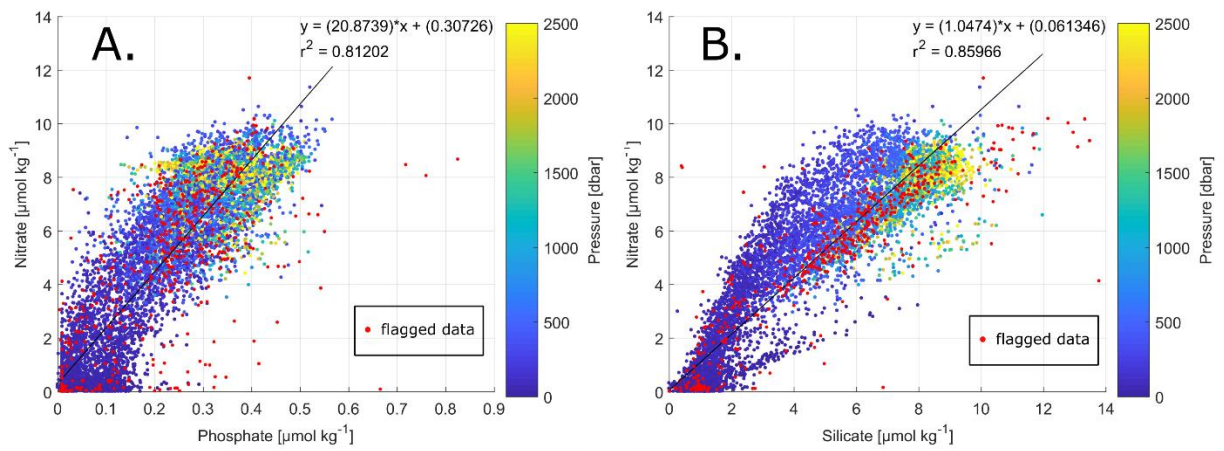
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882 **Figure 3**



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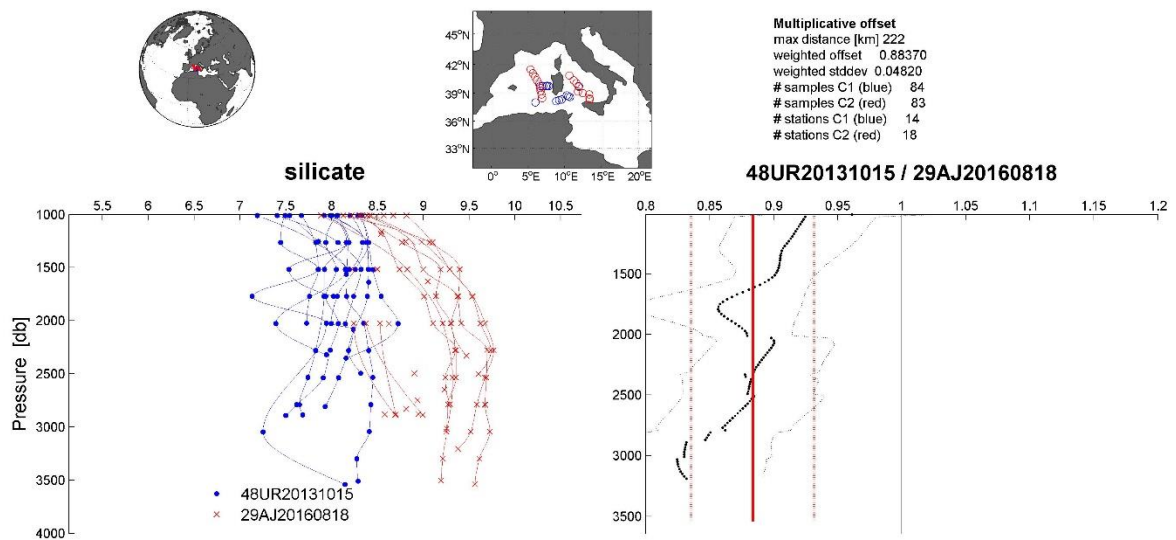
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889 **Figure 4**

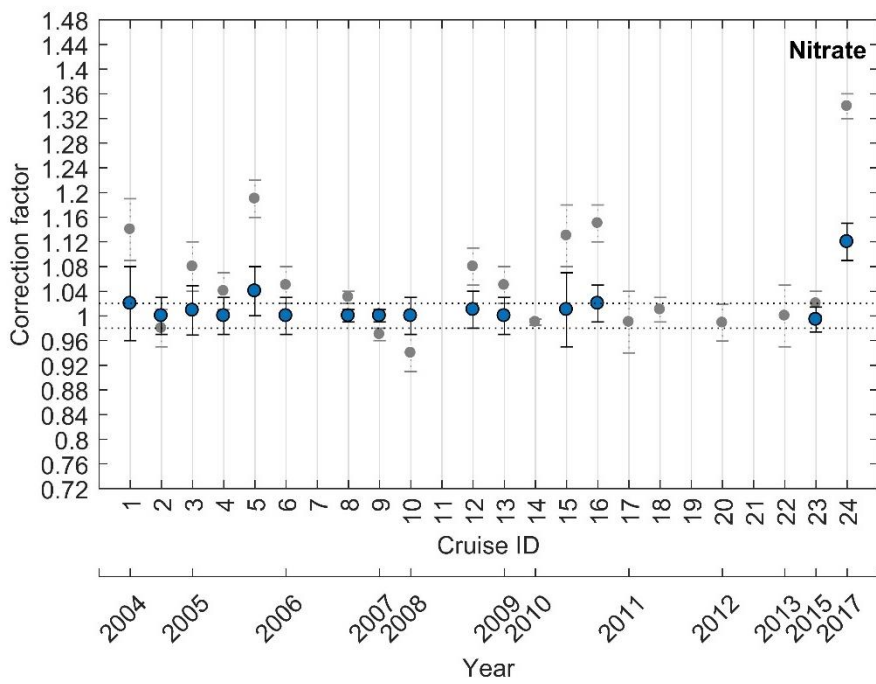


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893 **Figure 5**



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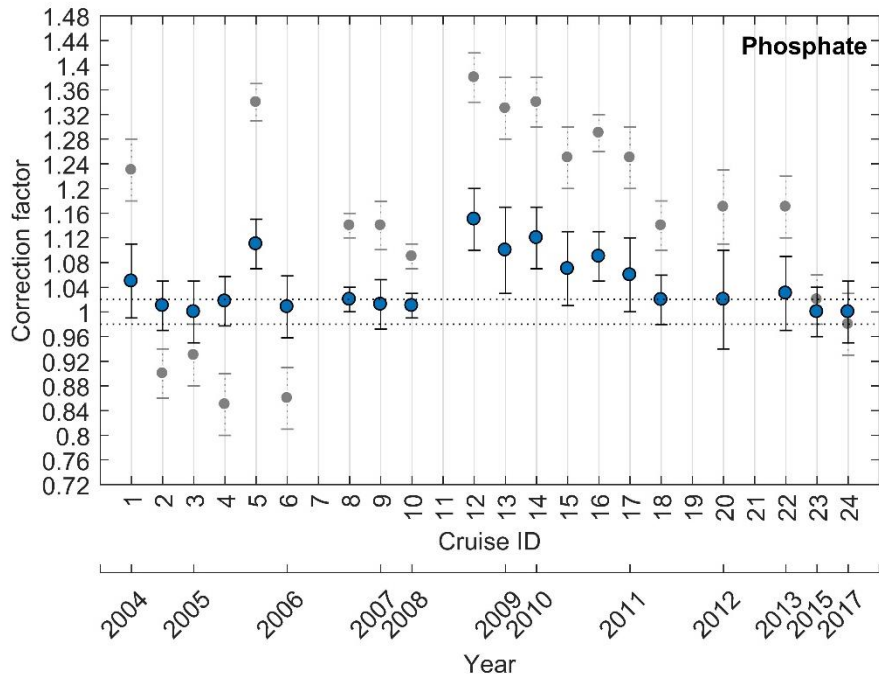
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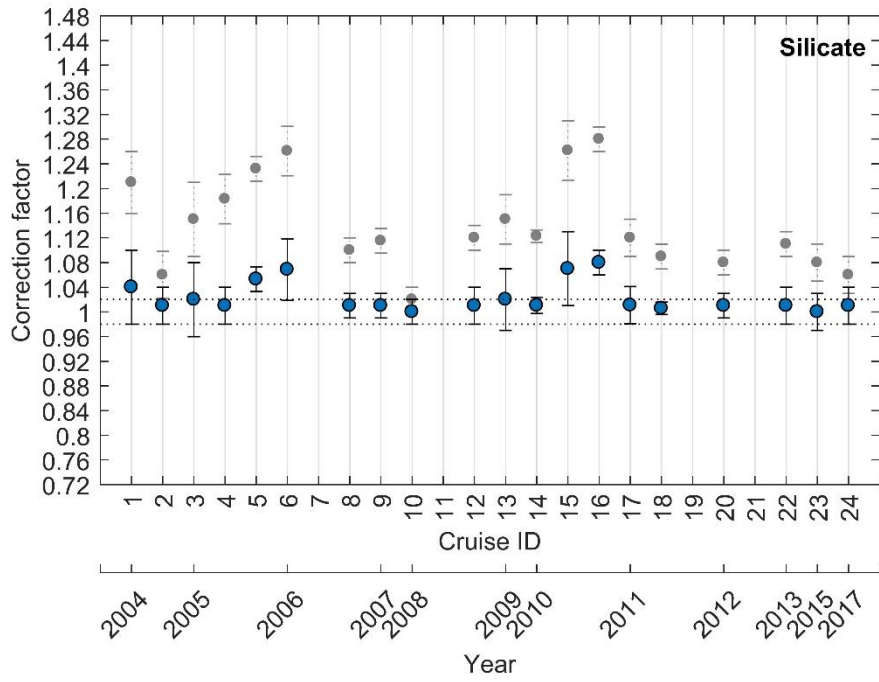
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909 **Figure 6**



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925 **Figure 7**



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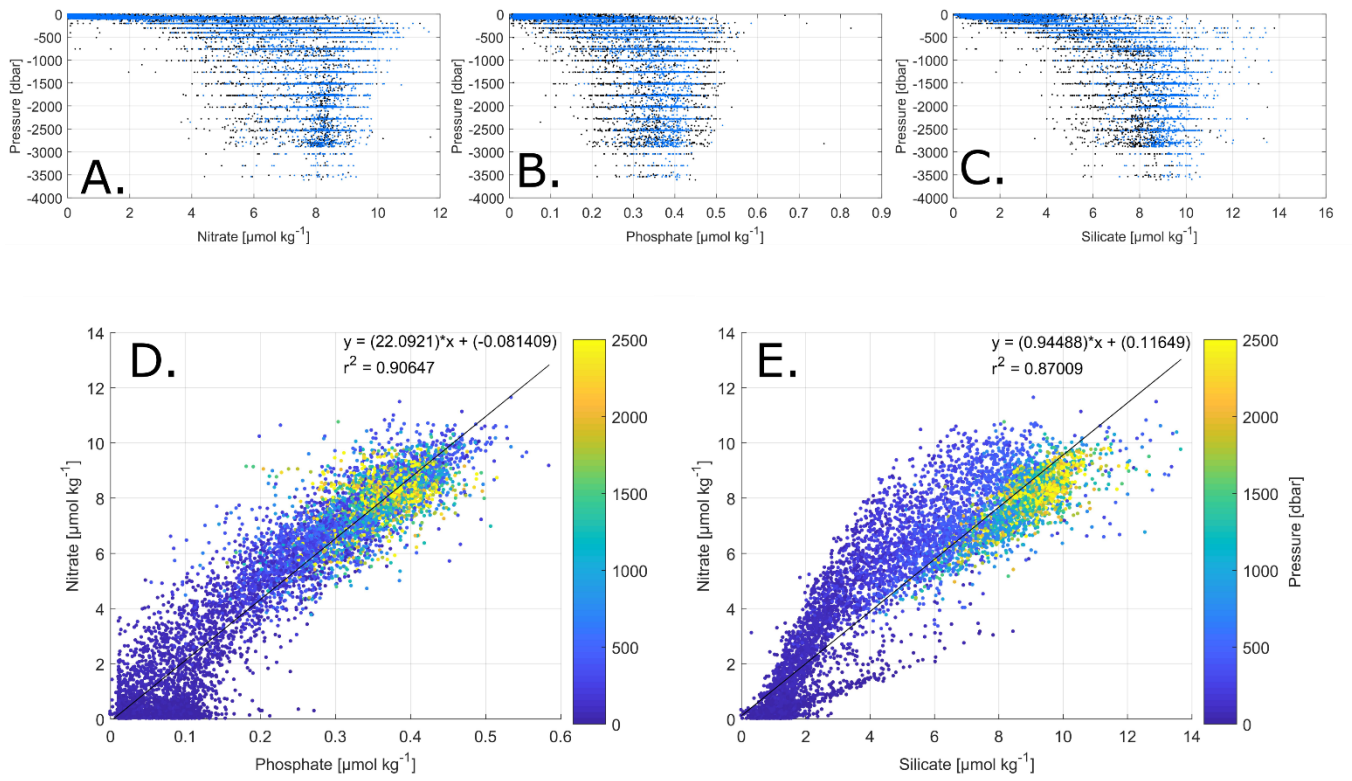
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941 **Figure 8**



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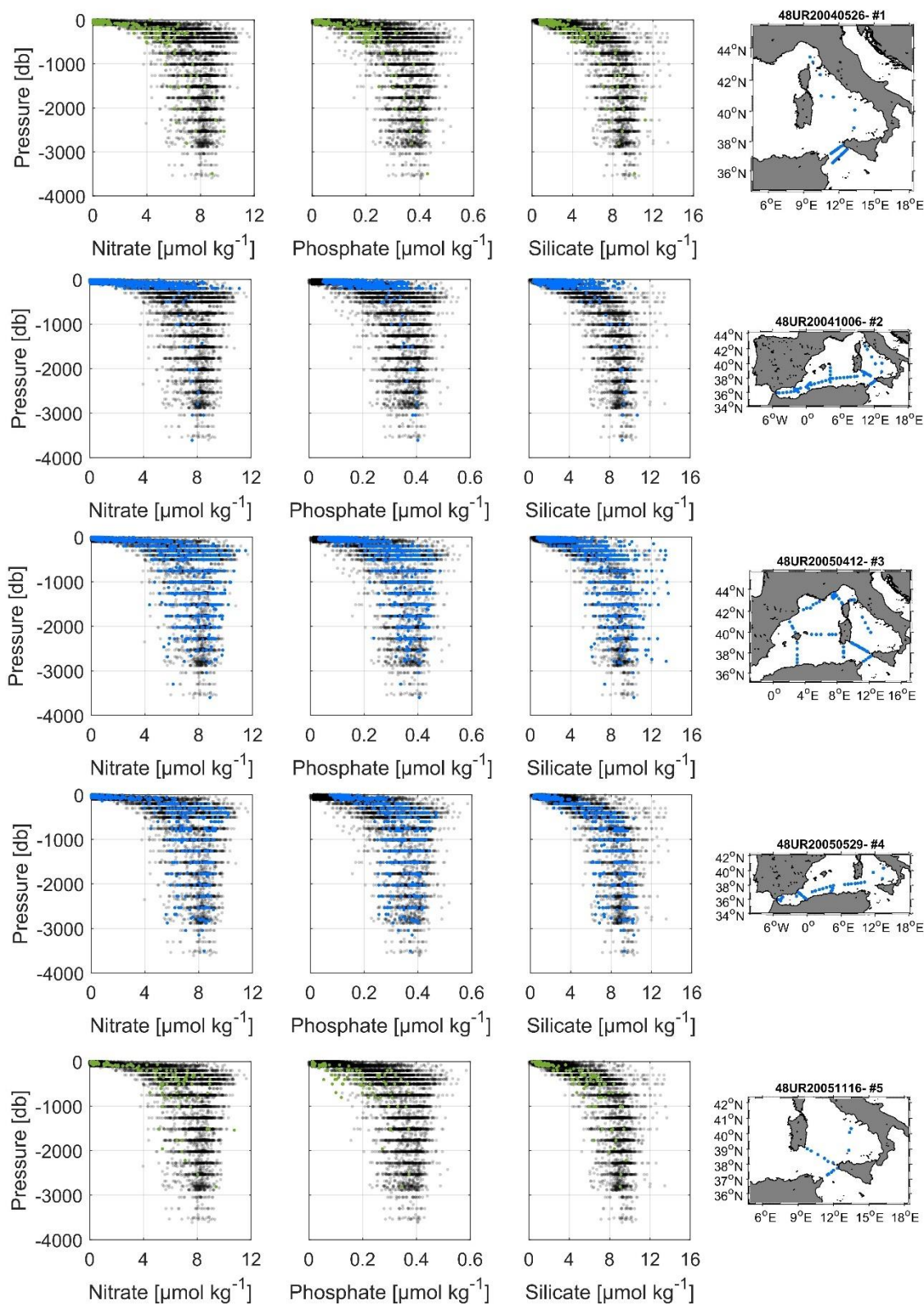
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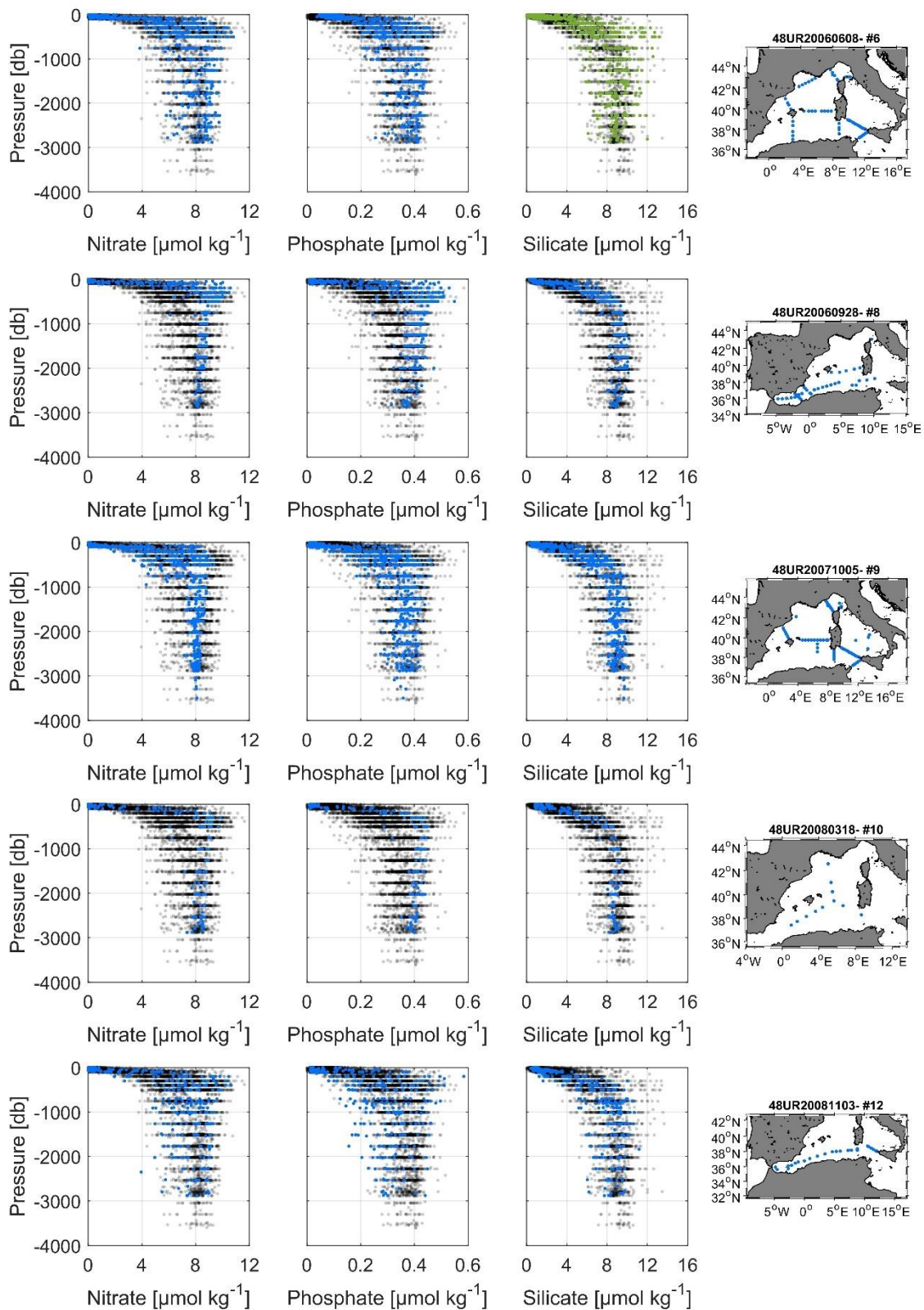
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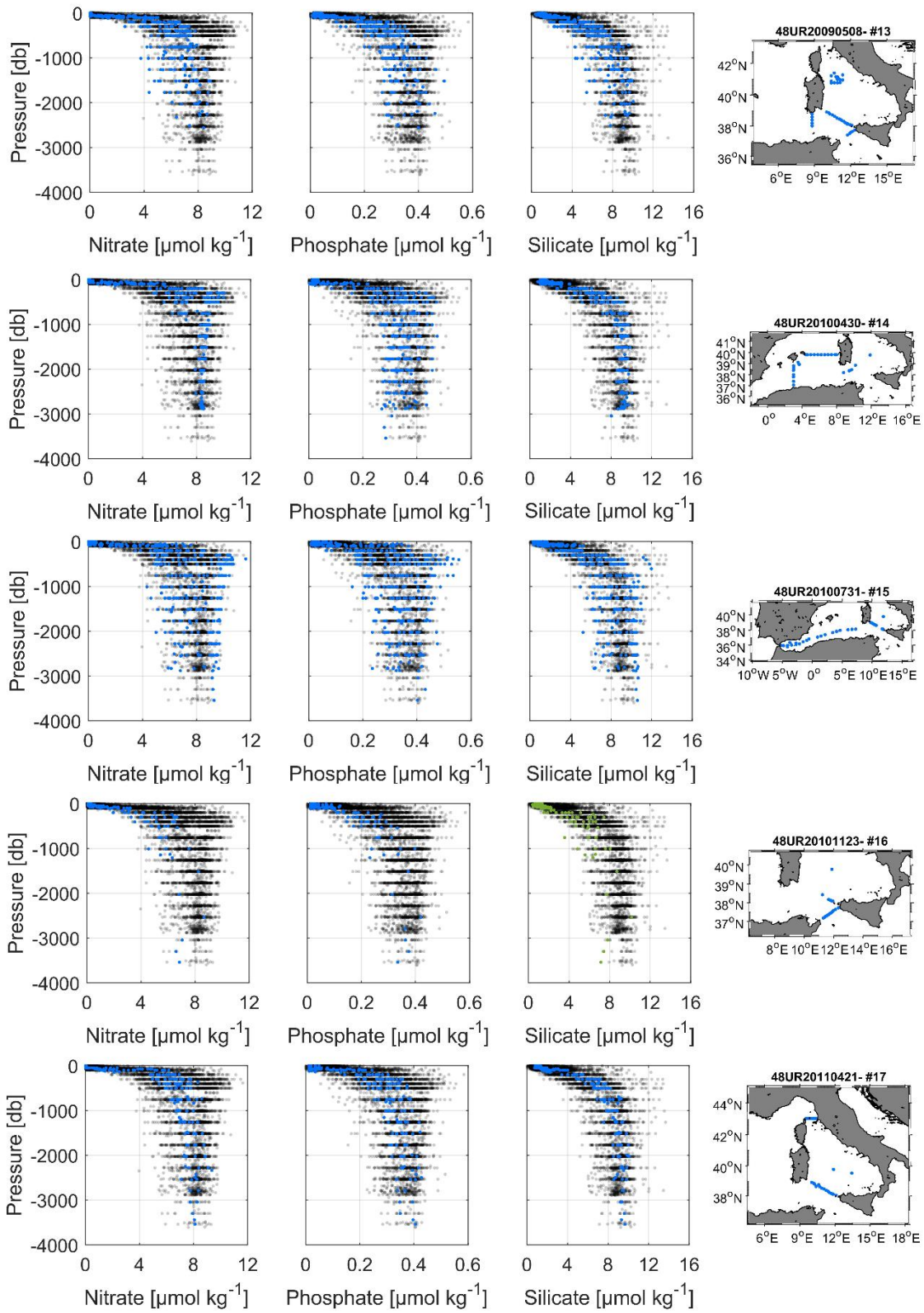
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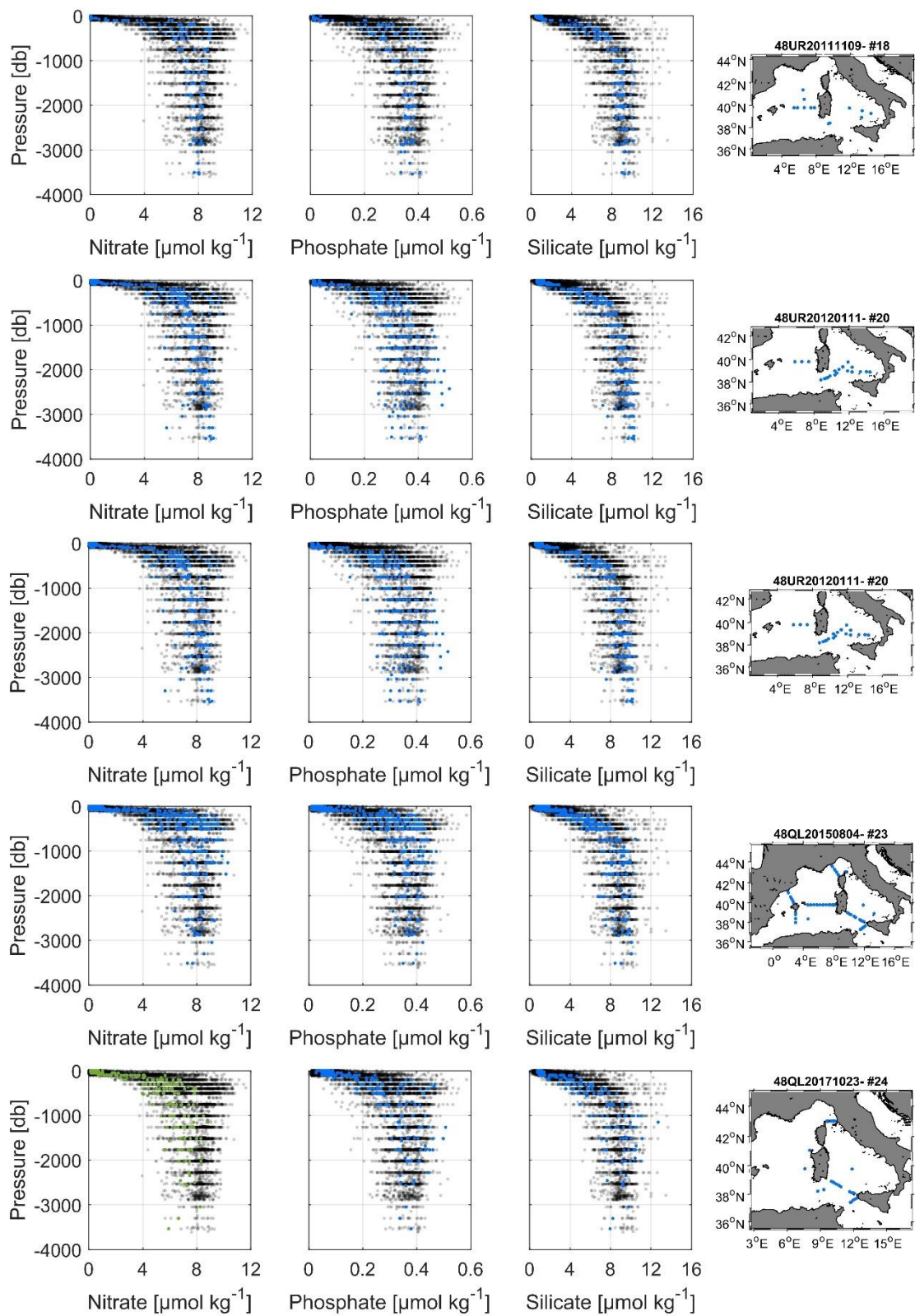






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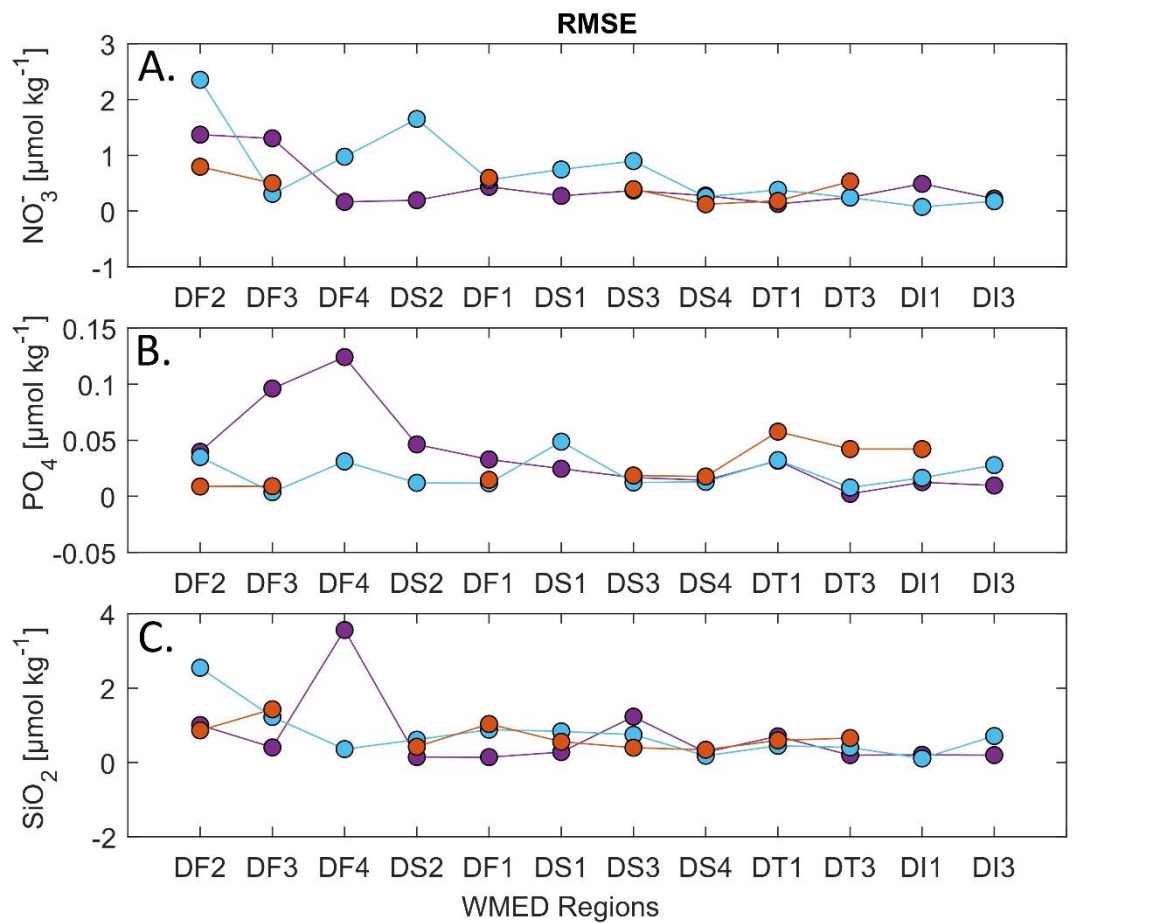
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963 **Figure 10**



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**Table 1**

Cruise ID (#)	Common Name	EXPOCODE	Research vessel (RV)	Date Start/End	Stations	Samples NO <sub>3</sub>	Samples PO <sub>4</sub>	Samples SiO <sub>2</sub>	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
<i>M51/2</i>	06MT20011018	18 OCT - 11 NOV 2001	6	79	79	82	GLODAPv2	B. Schneider	W. Roether
<i>TRANSMED_LEGII</i>	48UR20070528	28 MAY - 12 JUN 2007	4	78	77	78	CARIMED (not yet available)	S. Cozzi, V. Ibello	M. Azzaro
<i>M84/3</i>	06MT20110405	5 - 28 APR 2011	20	339	343	-	GLODAPv2	G. Civitarese	T. Tanhua
<i>HOTMIX</i>	29AH20140426	26 APR - 31 MAY 2014	18	144	140	144	CARIMED (not yet available)	XA Álvarez-Salgado	J. Aristegui
<i>TALPro-2016</i>	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	not measured/no data	-



**Table 4**

Cruise ID	EXPOCODE/ Region	Regional Avg NO <sub>3</sub>	std NO <sub>3</sub>	Regional Avg PO <sub>4</sub>	std PO <sub>4</sub>	Regional Avg SiO <sub>2</sub>	std SiO <sub>2</sub>	# samples	Avg storage (in days)
1	48UR20040526/		<b>1.25</b>		<b>0.062</b>		<b>1.64</b>	21	131
	<i>DT1-Tyrrhenian North</i>	6.07	1.32	0.26	0.065	6.92	1.83	16	
	<i>DT3-Tyrrhenian South</i>	7.03	0.51	0.31	0.02	7.66	0.53	5	
2	48UR20041006/		<b>0.59</b>		<b>0.029</b>		<b>0.81</b>	21	251
	<i>DT1-Tyrrhenian North</i>	7.68	0.53	0.41	0.031	8.74	0.75	15	
	<i>DT3-Tyrrhenian South</i>	8.17	0.60	0.41	0.025	9.31	0.87	6	
3	48UR20050412/		<b>1.15</b>		<b>0.050</b>		<b>1.41</b>	233	135
	<i>DF2-Gulf of Lion</i>	7.89	0.98	0.40	0.044	8.17	1.065	24	
	<i>DF3-Liguro-Provençal</i>	7.45	1.08	0.41	0.05	7.72	1.10	66	
	<i>DS2-Balearic Sea</i>	7.44	1.14	0.40	0.039	7.68	1.47	21	
	<i>DF1-Algero-Provençal</i>	7.87	1.16	0.41	0.043	8.88	1.96	42	
	<i>DS3-Algerian West</i>	7.7	0.816	0.39	0.048	8.14	0.941	23	
	<i>DT1-Tyrrhenian North</i>	6.57	1.065	0.36	0.047	7.41	1.15	21	
	<i>DT3-Tyrrhenian South</i>	6.52	1.12	0.36	0.05	7.56	1.42	22	
	<i>DII-Sardinia Channel</i>	7.22	1.065	0.40	0.04	8.08	1.11	14	
4	48UR20050529/		<b>1.13</b>		<b>0.057</b>		<b>1.08</b>	205	314
	<i>DS1-Alboran Sea</i>	6.4	1.15	0.38	0.041	6.26	1.02	32	
	<i>DS3-Algerian West</i>	7.6	1.13	0.41	0.06	7.33	0.99	73	
	<i>DS4-Algerian East</i>	7.48	1.13	0.41	0.06	7.50	1.23	47	
	<i>DT1-Tyrrhenian North</i>	7.24	0.44	0.42	0.03	7.91	0.56	16	
	<i>DT3-Tyrrhenian South</i>	7.70	0.38	0.41	0.03	7.55	0.36	14	
5	48UR20051116/		<b>1.35</b>		<b>0.078</b>		<b>0.98</b>	16	738
	<i>DT1-Tyrrhenian North</i>	5.68	1.26	0.19	0.08	6.30	0.92	10	
	<i>DT3-Tyrrhenian South</i>	6.71	1.51	0.20	0.06	6.86	1.065	5	
6	48UR20060608/		<b>1.16</b>		<b>0.054</b>		<b>1.47</b>	221	27
	<i>DF2-Gulf of Lion</i>	7.69	1.02	0.42	0.04	7.089	1.04	27	
	<i>DF3-Liguro-Provençal</i>	8.08	0.78	0.43	0.04	7.41	1.21	35	
	<i>DS2-Balearic Sea</i>	8.06	0.9	0.43	0.03	7.07	1.18	30	
	<i>DF1-Algero-Provençal</i>	7.97	1.16	0.44	0.05	7.34	1.32	61	
	<i>DS3-Algerian West</i>	8.39	0.9	0.42	0.03	8.5	2	28	
	<i>DT3-Tyrrhenian South</i>	6.39	1.28	0.36	0.06	6.86	1.7	26	
	<i>DII-Sardinia Channel</i>	8.04	0.85	0.43	0.04	7.77	1.25	14	
	7	06A420060720		-		-		-	-
8	48UR20060928/		<b>0.71</b>		<b>0.036</b>		<b>0.76</b>	179	606
	<i>DS2-Balearic Sea</i>	7.97	0.17	0.33	0.017	7.84	0.27	4	
	<i>DF1-Algero-Provençal</i>	8.17	0.22	0.33	0.026	8.11	0.3	22	
	<i>DS1-Alboran Sea</i>	8.2	0.14	0.35	0.02	8.59	0.35	47	
	<i>DS3-Algerian West</i>	7.93	0.89	0.33	0.03	8.09	0.91	70	
	<i>DS4-Algerian East</i>	7.98	0.68	0.34	0.04	8.01	0.7	28	
	<i>DT3-Tyrrhenian South</i>	6.2	1.51	0.28	0.04	6.71	1.45	3	
	<i>DII-Sardinia Channel</i>	7.66	0.6	0.28	0.02	8.00	0.49	5	
9	48UR20071005/		<b>0.89</b>		<b>0.040</b>		<b>0.86</b>	302	751
	<i>DF2-Gulf of Lion</i>	8.41	0.08	0.31	0.01	7.43	0.02	4	
	<i>DF3-Liguro-Provençal</i>	8.17	1.08	0.31	0.03	7.64	1.08	81	
	<i>DS2-Balearic Sea</i>	8.17	0.43	0.31	0.02	7.58	0.39	29	
	<i>DF1-Algero-Provençal</i>	8.33	0.6	0.32	0.03	7.79	0.69	82	
	<i>DS4-Algerian East</i>	8.41	0.2	0.33	0.018	7.90	0.26	19	
	<i>DT1-Tyrrhenian North</i>	7.83	0.41	0.28	0.03	8.26	0.55	26	
	<i>DT3-Tyrrhenian South</i>	7.49	1.22	0.28	0.05	7.71	1.26	38	
10	48UR20080318/		<b>0.51</b>		<b>0.026</b>		<b>0.34</b>	66	31
	<i>DF2-Gulf of Lion</i>	8.54	0.6	0.35	0.03	8.62	0.43	5	
	<i>DS2-Balearic Sea</i>	9.12	0.18	0.38	0.01	8.40	0.21	9	
	<i>DF1-Algero-Provençal</i>	9.02	0.36	0.38	0.03	8.65	0.25	15	
	<i>DS3-Algerian West</i>	8.93	0.46	0.36	0.01	8.69	0.35	20	
	<i>DS4-Algerian East</i>	8.43	0.25	0.38	0.02	8.32	0.22	10	
	<i>DII-Sardinia Channel</i>	7.62	0.6	0.34	0.03	8.49	0.36	3	
11*	48UR20080905		-		-		-	-	211
12	48UR20081103/		<b>1.11</b>		<b>0.077</b>		<b>0.10</b>	110	536
	<i>DS1-Alboran Sea</i>	6.4	1.21	0.21	0.06	7.20	1.43	26	

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

(\*) cruise not included in the 2<sup>nd</sup>QC (Section 4.)

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

**Table 5**

Cruise ID	EXPOCODE	NO <sub>3</sub> (x)	PO <sub>4</sub> (x)	SiO <sub>2</sub> (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<sup>nd</sup>QC (Section 4.)

**Table 6**

Cruise ID	EXPOCODE	NO <sub>3</sub> [%]			PO <sub>4</sub> [%]			SiO <sub>2</sub> [%]		
		<i>n</i>	<i>unadjusted</i>	<i>adjusted</i>	<i>n</i>	<i>unadjusted</i>	<i>adjusted</i>	<i>n</i>	<i>unadjusted</i>	<i>adjusted</i>
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**

Region/ Water mass	NO3 ( $\mu\text{mol kg}^{-1}$ )		PO4 ( $\mu\text{mol kg}^{-1}$ )		SiO2 ( $\mu\text{mol kg}^{-1}$ )	
	Avg new Product	Avg Medar	Avg new Product	Avg Medar	Avg new Product	Avg Medar
<i>DF2- Gulf of Lion</i>						
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 ( $S_{\text{max}}$ 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
<i>DF3- Liguro-Provençal</i>						
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 ( $S_{\text{max}}$ 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
<i>DF4- Ligurian East</i>						
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 ( $S_{\text{max}}$ 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)	-	-	-	-	-	-
<i>DS2- Balearic Sea</i>						
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 ( $S_{\text{max}}$ 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
<i>DF1- Algero-Provençal</i>						
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 ( $S_{\text{max}}$ 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
<i>DS1- Alboran Sea</i>						
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 ( $S_{\text{max}}$ 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
<i>DS3- Algerian West</i>						
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 ( $S_{\text{max}}$ 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
<i>DS4- Algerian East</i>						
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 ( $S_{\text{max}}$ 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
<i>DT1- Tyrrhenian North</i>						
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 ( $S_{\text{max}}$ 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
<i>DT3- Tyrrhenian South</i>						
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 ( $S_{\text{max}}$ 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
<i>DII- Sardinia Channel</i>						
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 ( $S_{\text{max}}$ 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)	-
<i>DI3- Sicily Strait</i>						
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 ( $S_{\text{max}}$ 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)