Recommendations for enhancement of NO3 QC Methods

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EXECUTIVE SUMMARY

This deliverable presents the enhancements on quality control procedures performed on the NITRATE concentration. The NITRATE concentration is one of the six core variables of the BGC-Argo program. Regarding Real Time quality control procedures (already in place in several DACS), the main outcome relies on the release of the V1.0 of the official documentation endorsed by the international BGC-Argo program. Regarding Delayed Mode Quality control, the approved method is tested with different reference data sets and several ways to validate the results are reported. More than 7300 profiles have been corrected in delayed mode following the presented procedure.

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1 Introduction

The main method used to date to measure dissolved nitrate concentration (NITRATE) in seawater on profiling floats is based on the absorption of light at ultraviolet wavelengths by nitrate ions. Presently, the whole fleet of floats measuring NITRATE is equipped with a SUNA or an ISUS sensors (Johnson and Coletti, 2002; Johnson et al., 2010; 2013; D'Ortenzio et al., 2012). In August 2021, 49502 NITRATE profiles are collected, with 4925 since the beginning of 2021. 149 floats are presently operational.

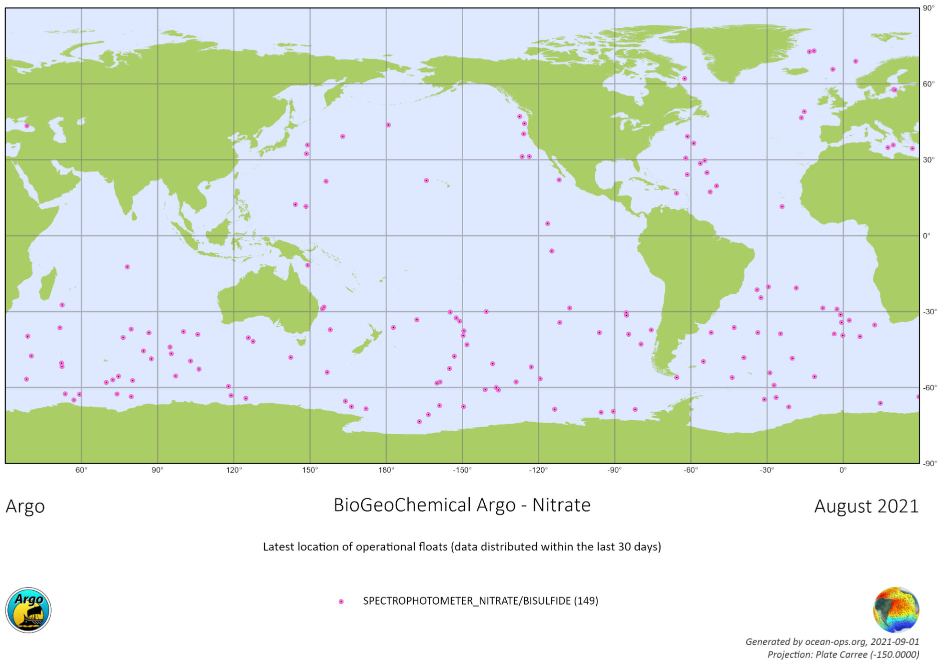

Figure 1: Operational floats measuring NITRATE (August 2021 source https://www.jcommops.org/board)

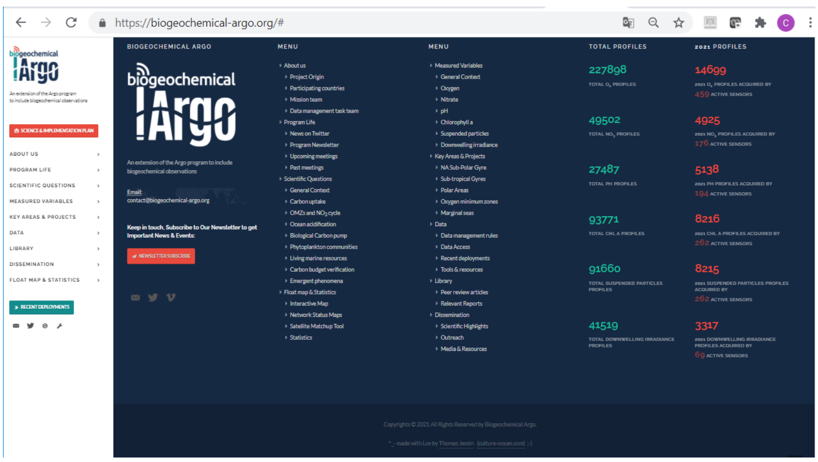

Figure 2: Total number of NITRATE profiles in Argo and number of NITRATE profiles since the beginning of 2021 (https://biogeochemical-argo.org/#)

2 RT

The Real Time (RT) Quality Control (QC) for NITRATE was initially discussed during the ADMT14 in 2013. We managed to get an agreement on the documentation in September 2021, quite lately mainly because of different ways of working at different DACs (mainly Aoml and Coriolis).

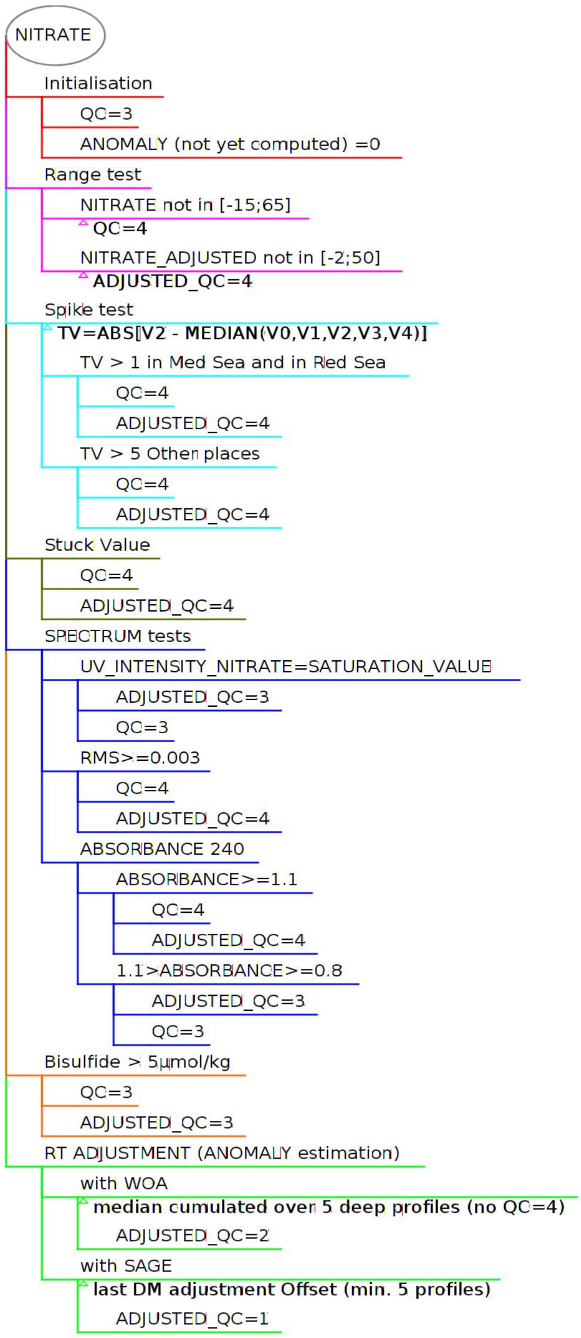

Figure 3: Flowchart of the RT QC and Adjustment for NITRATE

The flowchart, as well as the associated algorithms have been defined, implemented and applied since July 2019 at the Coriolis DAC. The boundaries of the RANGE test are the last point that will be fixed, after the documentation is released. It marks as doubtful some outliers caused by a saturation of the sensor (several channels of the spectrophotometer reach the greatest value of the DC making it impossible to report the dynamic of the NITRATE absorption across the wavelengths, Figure 4).

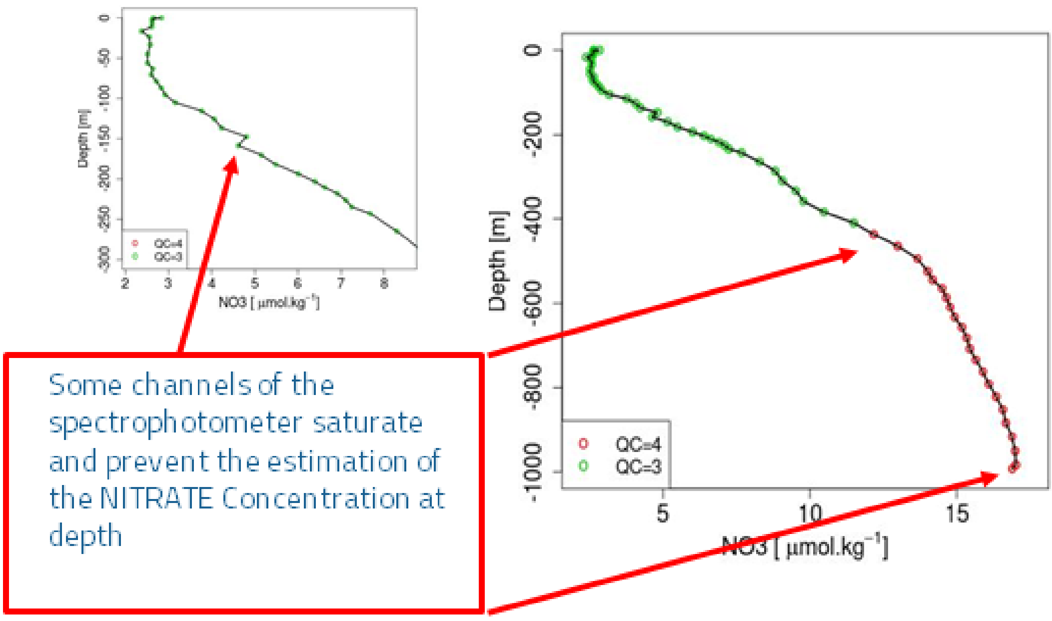

Figure 4: Illustration of some effects of the saturation of the spectrophotometer channels on the float 6901773

The RT QC for NITRATE is summarized on the flowchart presented on Figure 3, which is derived from Johnson et al., 2021 and Maurer et al., 2021. The details of the method are considered consolidated and will not be analysed in the framework of EA-Rise.

3 DM

3.1 R&D

3.1.1 General introduction

Spectrophotometers for NITRATE estimation present issues related to their manufacturer calibration. Tests on operational floats indicate that initial calibrations are often inaccurate. Moreover, sensors are also unstable in transport and in storage, presenting issues since the first profiles. Consequently, NITRATE estimations should be corrected after their deployment, in particular by correcting the OFFSET value, which could also drift over time. Procedures to correct NITRATE floats are presented in Johnson et al., (2017). The rationale of the correction is based on the hypothesis that the NITRATE concentration below 1000m could be considered stable in space and time. The measured NITRATE concentration from float at depth is compared to a reference value. The OFFSET value is then the difference between the reference and the float derived values. Additionally, the temporal evolution of this difference provides an evaluation of the DRIFT of this OFFSET value.

3.1.2 Scientific Rationale

The main challenge of the Delayed Mode QC for NITRATE is then to identify and use the correct reference value to estimate the OFFSET and the DRIFT. In the framework of EA-RISE, most of the activity for the NITRATE concentration parameter focused on the identification, use and testing of the reference value.

As a first attempt, the reference values are extracted from worldwide climatology like the World Ocean Atlas, (Garcia et al., 2019).

Another approach is represented by neural networks methods, which could provide alternatives to climatologies, at global (Sauzede et al., 2017, Bittig et al., 2018) and local (Fourrier et al., 2020, 2021) scales. These methods request the date, the location, the pressure, the salinity, the temperature and the dissolved oxygen concentration (DOXY). Among all the input parameters, the accuracy of the DOXY is particularly affecting the final NITRATE estimation.

Furthermore, identifying reference data in marginal seas could be challenging, because climatologies have too scarce resolution and neural networks methods are generally developed for global applications. A promising solution, and although local or regional climatologies exists, consists in the use of neural network methods locally adapted to regional sub-basins (i.e. CANYON - MED, Fourrier et al. 2020, 2021). In particular in the Mediterranean, where the number of european floats is high (see figure 5), such methods offer a suitable alternative to define reference value at depth.

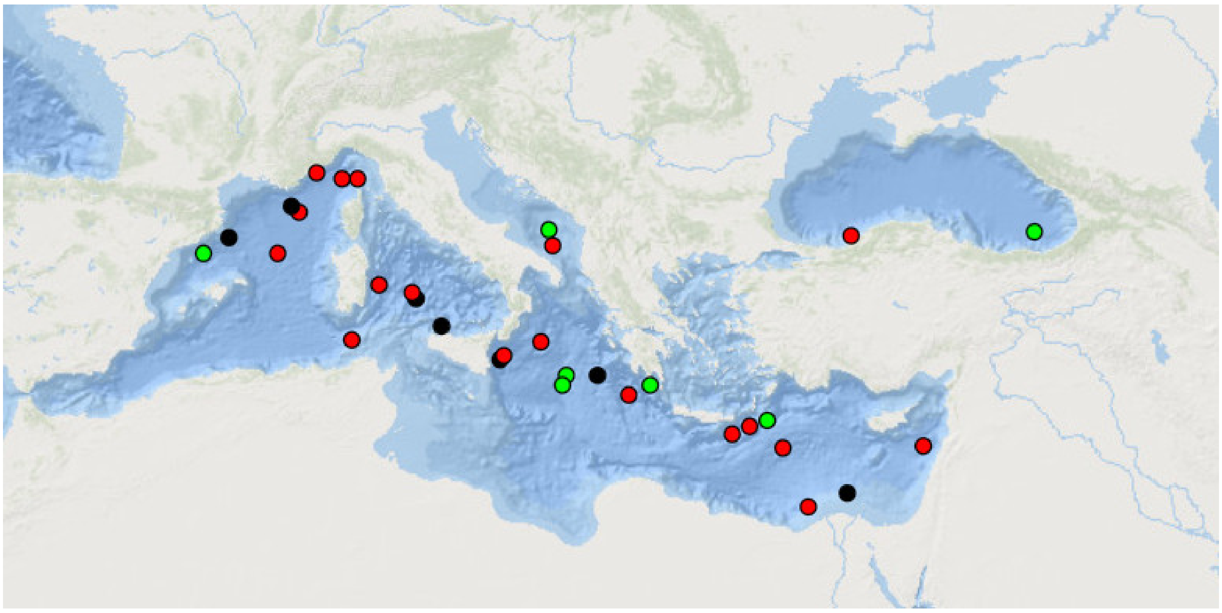

Figure 5: Location of 32 BGC-Argo-Floats equipped with NITRATE sensors deployed in the Mediterranean Sea and the Black sea.

The main question treated in EA-RISE was then to test the different ways to estimate the reference value, then to define the sequence of DM operations.

To estimate the reference value at depth (PRES_REF ranging from 900dbar to 1500dbar, depending on the programmation of the float), several approaches were tested in EA-RISE:

- The World Ocean Climatology (Garcia et al., 2019)
- Global Neural Network method (CANYON-B) (Bittig et al., 2018, Sauzede et al., 2017)
    - Accounting for DOXY inputs
    - Accounting for DOXY_ADJUSTED inputs
- Local Neural Network method (CANYON-MED) (Fourrier et al., 2020, 2021)
    - Accounting for DOXY inputs
    - Accounting for DOXY_ADJUSTED inputs

3.1.3 Implementation

For each NITRATE float profile:

- Extract LATITUDE, LONGITUDE of the float profile
- Extract DOXY(PRES_REF) and DOXY_ADJUSTED(PRES_REF) of the float profile (if available)
- Extract NITRATE=NITRATE(PRES_REF) of the float profile

To get WOA reference value:

- Extract WOA_NITRATE(PRES_REF) at the closest grid point in LATITUDE and LONGITUDE

To get CANYON reference value (CANYONB or CANYON-MED have the same inputs) :

- Compute reference value

  NITRATE_CANYON=CANYON(LATITUDE, LONGITUDE, PRES_REF, DOXY)

- Compute reference value (using DOXY_ADJUSTED)

  NITRATE_CANYON_ADJUSTED=CANYON(LATITUDE, LONGITUDE, PRES_REF, DOXY_ADJUSTED)

The different OFFSET values are then calculated as follow

NITRATE-NITRATE_WOA

NITRATE-NITRATE_CANYON

NITRATE-NITRATE_CANYON_ADJUSTED

Some examples of the OFFSET values are presented in the following figures.

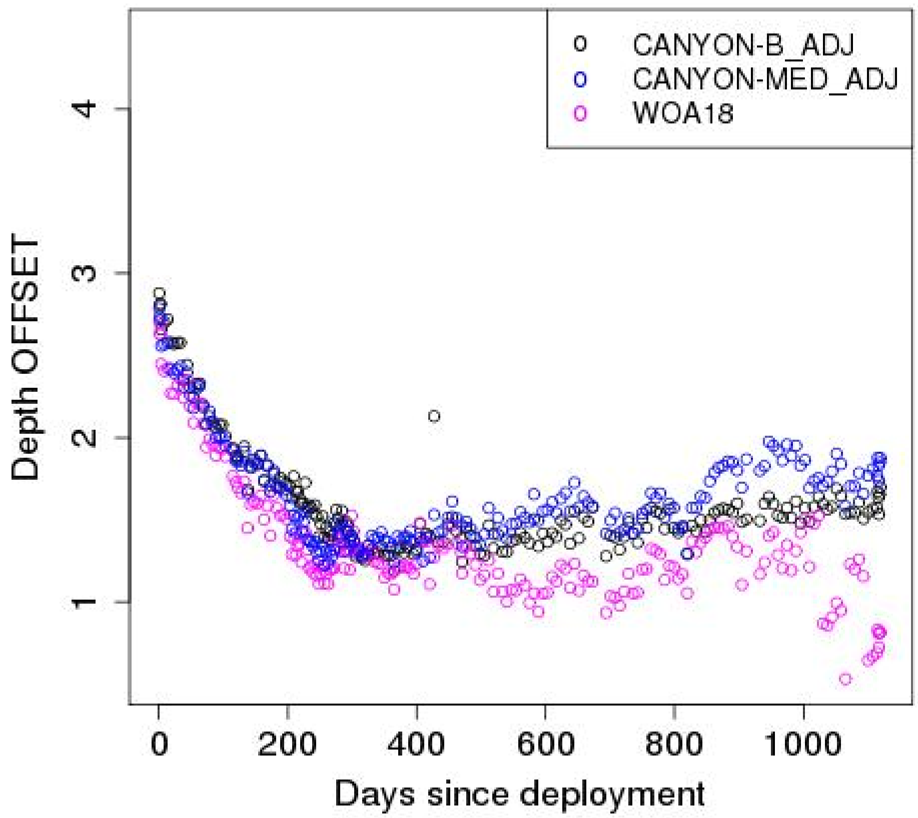

Figure 6: Comparison between different neural network methods with DOXY_ADJUSTED and WOA18 climatology for float **6901767**.

On Figure 6, we can notice that the WOA18 Depth OFFSET is patchier, particularly at the end of the float life than the ones retrieved with neural network methods. As a first recommendation, we can say that when possible (DOXY and DOXY_ADJUSTED of good quality), the priority should be given to the neural network methods.

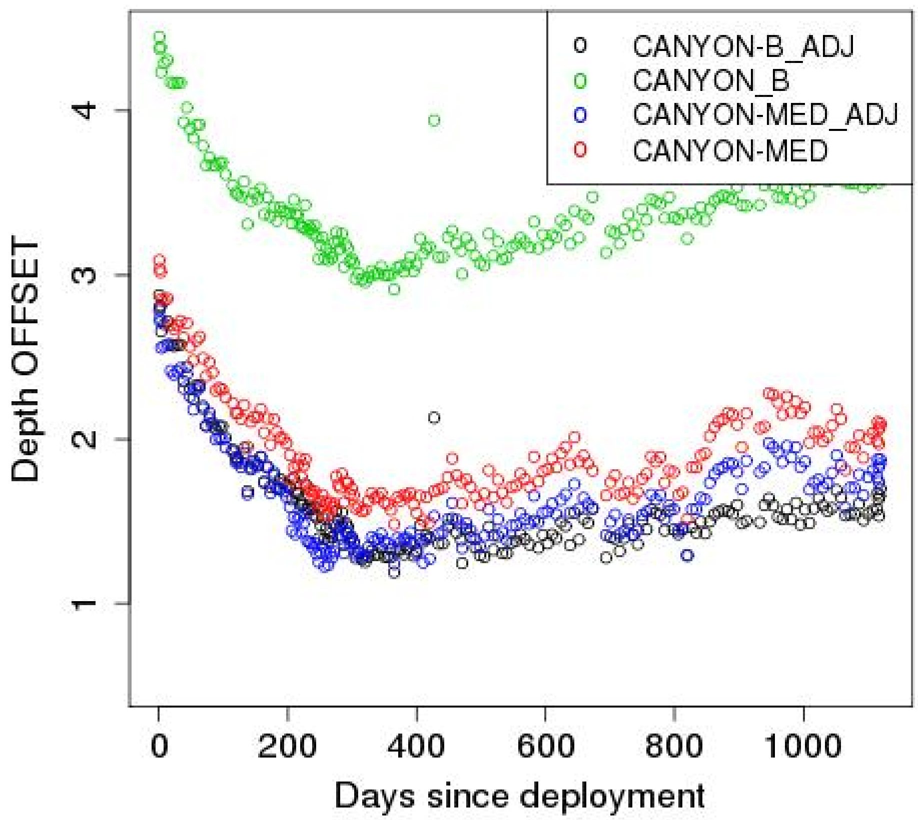

Figure 7: Comparison between different neural network methods to estimate the Offset at depth accounting or not the parameters DOXY_ADJUSTED for float **6901767**.

On Figure 7, we can notice a strong effect of DOXY adjustment on CANYON_B estimation of the value at depth (green compared to black), CANYON_MED seems to be less sensitive to DOXY adjustment (blue compared to red). CANYON and CANYON-MED are in good agreement once the DOXY_ADJUSTED is estimated (black compared to blue). As a conclusion, for marginal seas, local neural networks seems the correct way to estimate the correction of the calibration equation. First, it solved the issues of the poor representativeness of Global climatology in those areas. Second, it seems less sensitive to the delayed mode correction of the DOXY.

Once Figure 6 and 7 are performed, it is up to the DM operator to choose its reference dataset. The neural network approach is preferred if the DOXY/DOXY_ADJUSTED is correctly estimated. Here are some examples of some choices that can be made:

- Float with issue on DOXY(simple calibration, sensor out of service...) => WOA2018
- Float in the Mediterranean sea with a DOXY_ADJUSTED => CANYON-MED
- Float with DOXY_ADJUSTED (elsewhere) => CANYONB

Estimate the OFFSET trend: Linear trends vs broken lines

For nitrate sensors deployed on biogeochemical Argo profiling floats, it is not uncommon for jumps in the data series to occur due to dirty optics. It is recommended in the quality control manual to model the anomaly series through a segmented set of piecewise discontinuous linear fit, with each segment defined by a set of breakpoints.

In this section, we illustrate how we choose to adjust the measurements to the reference estimation. If we do not want to overfit the OFFSET, then we choose to apply a broken line scheme where the broken line RMS is at least twice lower than the RMS calculated with the linear trend.

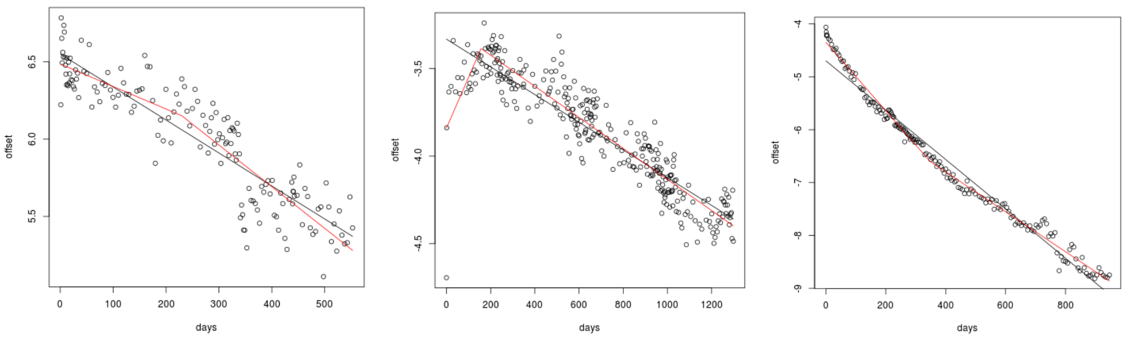

Figure 8: Different floats for which we consider that the linear fit is more relevant than the broken-lines method (**6901580**, **6901583**, **6901769**)

FLOAT	Broken lines RMS	Linear Fit RMS
6901580	0.161	0.168
6901583	0.118	0.142
6901769	0.116	0.209

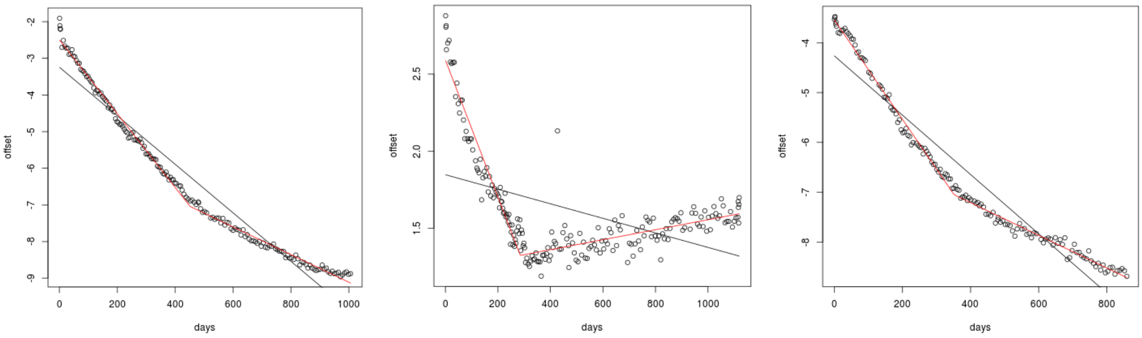

Figure 9: Different floats for which we consider that the broken lines method is more relevant than the linear fit (**6901764**, **6901767**, **6901770**)

FLOAT	Broken lines RMS	Linear Fit RMS
6901764	0.12	0.473
6901767	0.102	0.303
6901770	0.099	0.435

3.1.4 Application of the correction at the Coriolis DAC

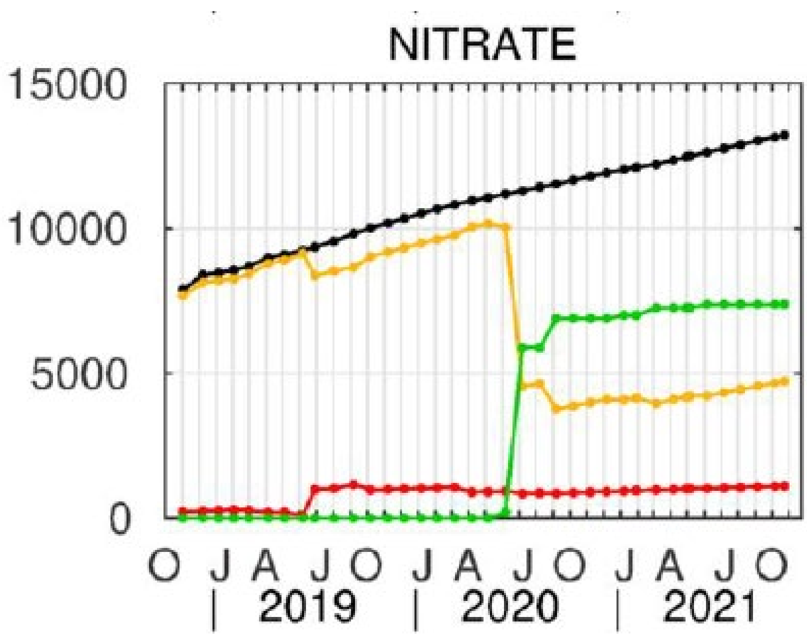

Figure 10: Status of the NITRATE PARAMETER at the Coriolis DAC (there are no NITRATE sensors at the BODC DAC). Black line: all the profiles, red line: PARAMETER_DATA_MODE="R", yellow line: PARAMETER_DATA_MODE="A", green line: PARAMETER_DATA_MODE="D"

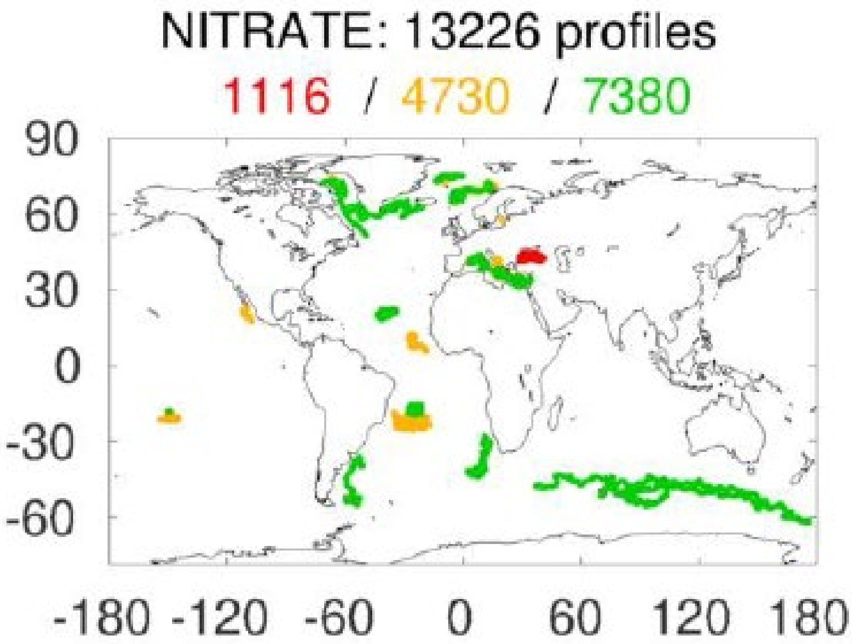

Figure 11: Location of the NITRATE profiles with respect to their PARAMETER_DATA_MODE. Red points : PARAMETER_DATA_MODE="R", yellow points : PARAMETER_DATA_MODE="A", green points : PARAMETER_DATA_MODE="D"

3.2 Operational

3.2.1 Visual control.

At this stage of the DM-QC, the initial step could be to set a QC=4, for profiles that obviously reported an issue. This way we can prevent their use in the estimation of the trend of the correction.

SCOOP-Argo (https://doi.org/10.17882/48531) is a tool developed at Coriolis for visual inspection of Argo profiles (Detoc et al., 2021), it allows to plot every station one by one or among the other profiles. This last option permits to highlight quite rapidly which profiles are outliers.

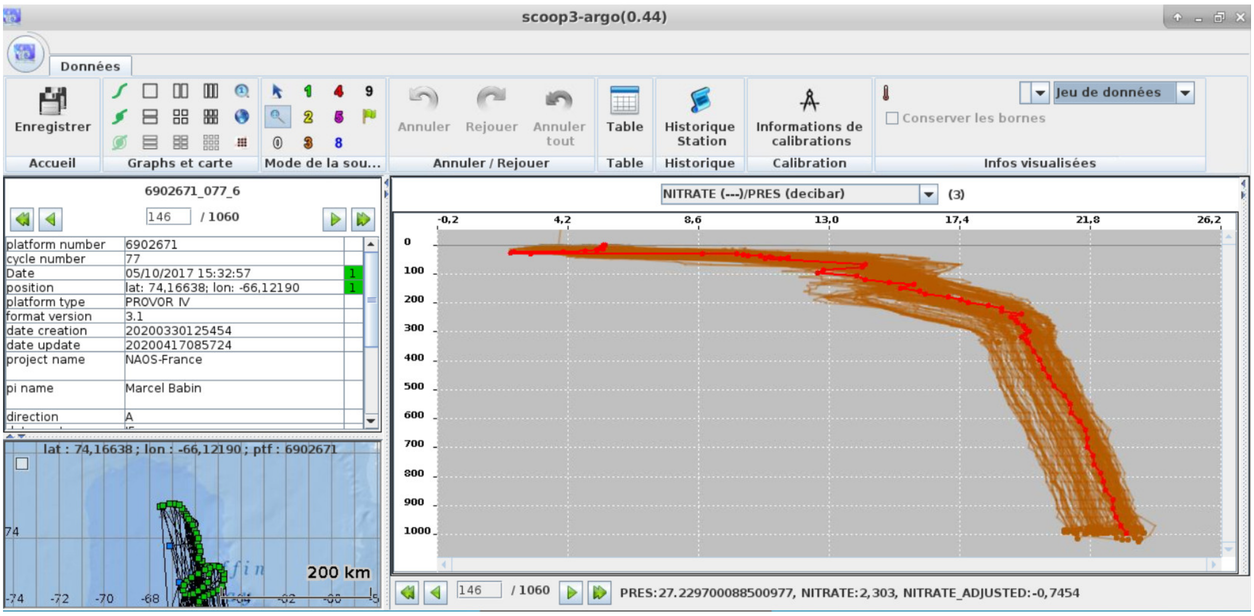

Figure 12 : Visual inspection for the float **6902671**, (NITRATE spiky profile, different from the other profiles => QC=4)

3.2.2 Estimation of the correction

For Matlab users, a complete Matlab code to accomplish this task is freely available at the following GitHub repository maintained by MBARI:

https://github.com/SOCCOM-BGCArgo/ARGO_PROCESSING/tree/master/MFILES/WOA

The sources of CANYONB and CANYONMED are available here :

https://github.com/MarineFou/CANYON-MED/

https://github.com/HCBScienceProducts/CANYON-B

Depending on the geographical area and on the programming language (Matlab for Sage, Matlab or R for CANYONB and CANYON-MED) one can choose to use one of these alternatives to estimate the OFFSET between the float NITRATE concentration and the computed reference NITRATE, but the principle of the estimation stays the same. We can plot it as a function of time and find the correct parametrisation of the fit, to characterise the adjustment through time:

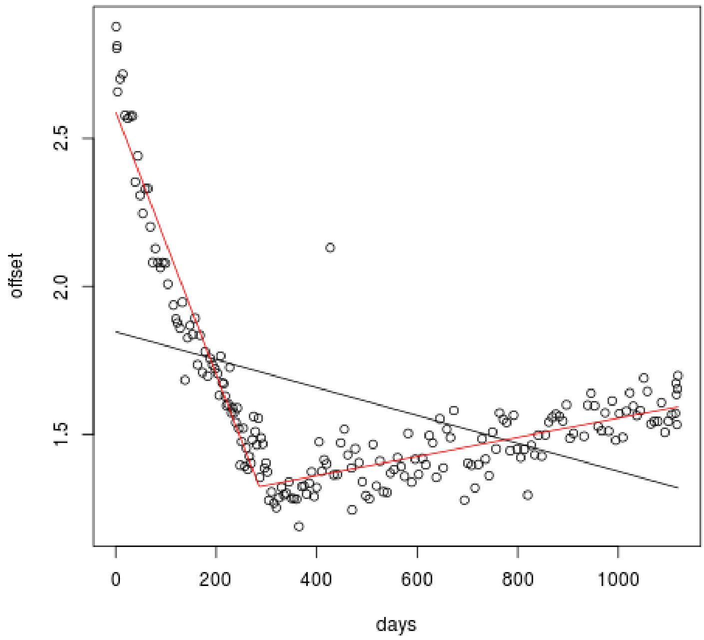

Figure 13: Comparison of the offset calculated with CANYONB with a DOXY_ADJUSTED (black dots) and the estimated correction with a single linear fit (black line) and a broken line (red line).

3.2.3 Evaluation of the correction

We present here several ways to evaluate the correction.

3.2.3.1 Evaluation of the correction by the comparison with neural network for the whole profile

As mentioned in the previous section, CANYON-B (Bittig et al., 2018) and/or CANYON-MED (Fourrier et al., 2020) are good candidates to compute (with DOXY_ADJUSTED as an input), the reference value at depth, while NITRATE is supposed to be quite stable at depth. However, CANYON-B or CANYON-MED could be applied to the whole DOXY_ADJUSTED profile to estimate a NITRATE profile (NITRATE_CANYON) which could be compared with the NITRATE_ADJUSTE from surface to depth. This is illustrated on Figure 14. One can also estimate for the whole float life the RMS between NITRATE_CANYON and NITRATE_ADJUSTED (Figure 15) and compare this value to the NITRATE_ADJUSTED_ERROR.

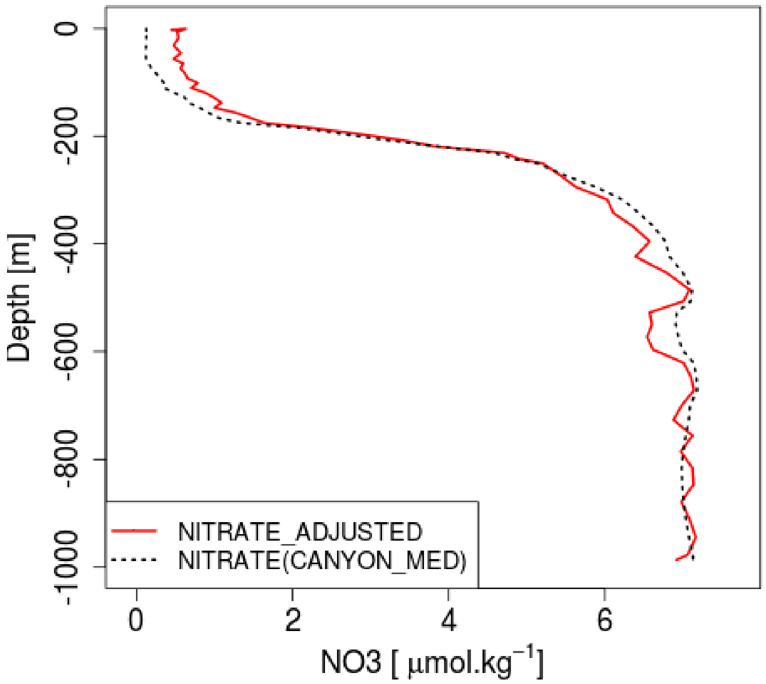

Figure 14 : comparison of a NITRATE_ADJUSTED profile and a CANYON-MED profile

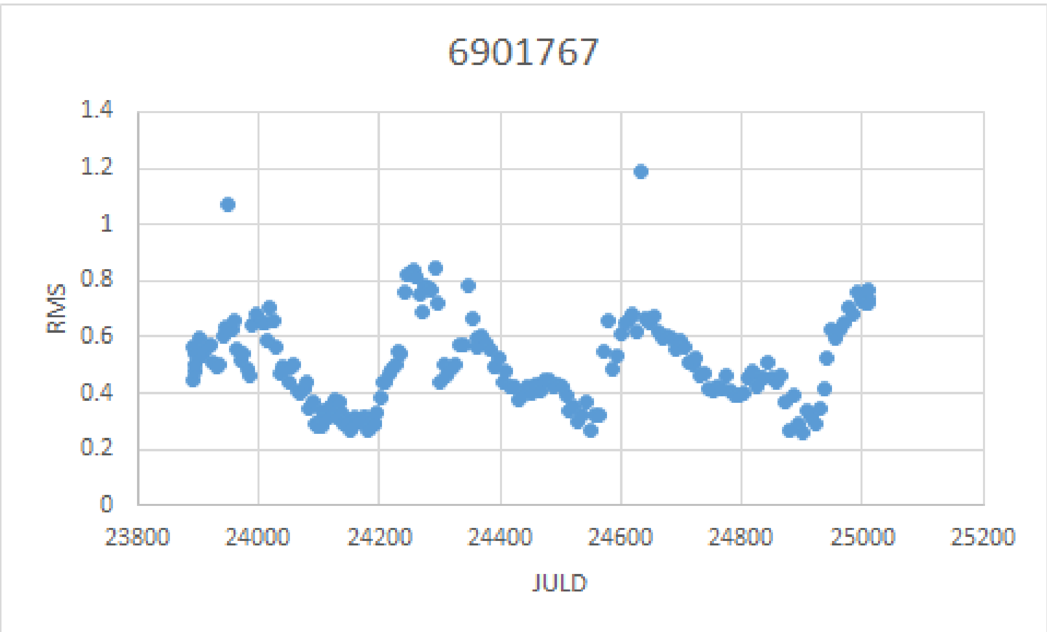

Figure 15 : Time series of the RMS between the NITRATE_ADJUSTED and the CANYON_MED profiles for the float **6901767**

3.2.3.2 Evaluation of the Offset correction with Bottle file (if available)

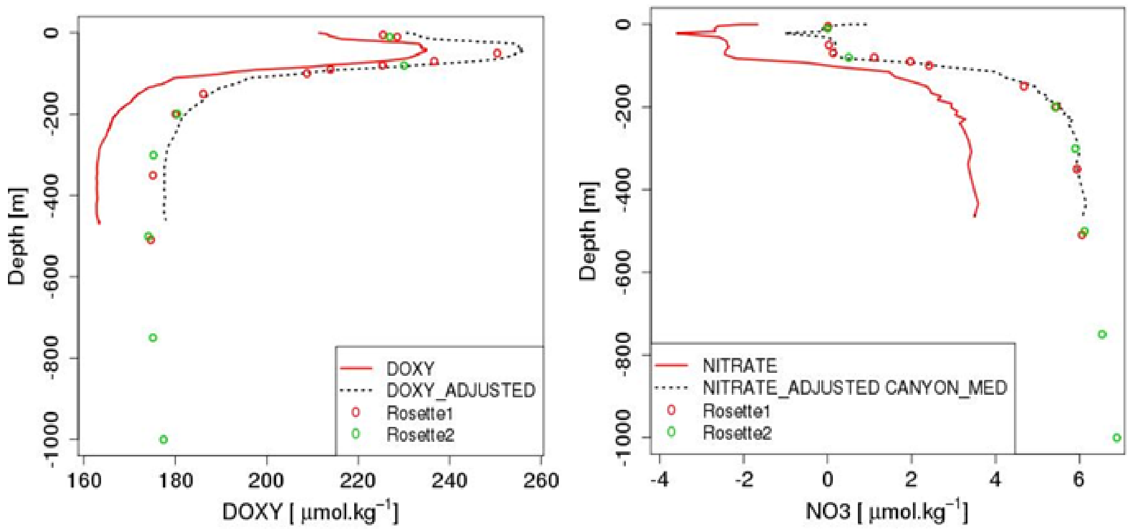

Figure 16 : On the left, comparison between DOXY and DOXY_ADJUSTED measured by the float **6901767** and by Winkler titration on the nearest rosettes, in time and space, to the deployment of the float. On the right, comparison between NITRATE and NITRATE_ADJUSTED (estimated with DOXY_ADJUSTED) measured by the float and by nitrate analysis on the nearest rosettes, in time and space, to the deployment of the float.

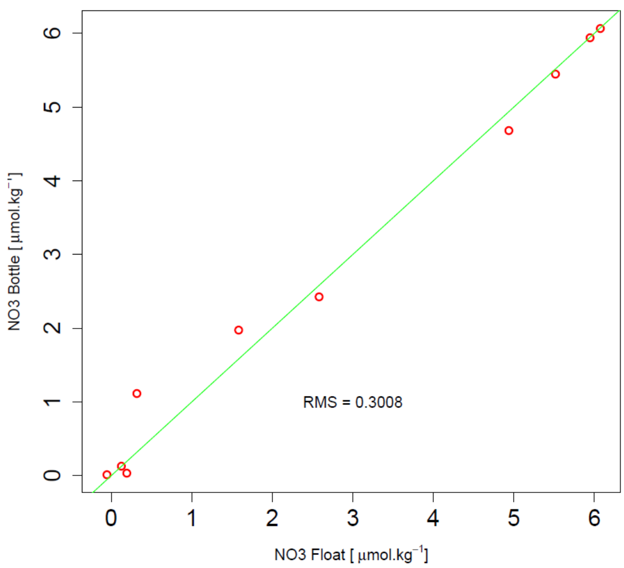

Figure 17 : Scatter plot of the Figure 16 for the NITRATE concentration

The RMS estimated between the bottle data at deployment and the NITRATE_ADJUSTED profile of the float is around 0.3, while the expected error should be within 2 umol/kg^{-1}.

3.2.3.3 Evaluation of the Drift correction with surface data

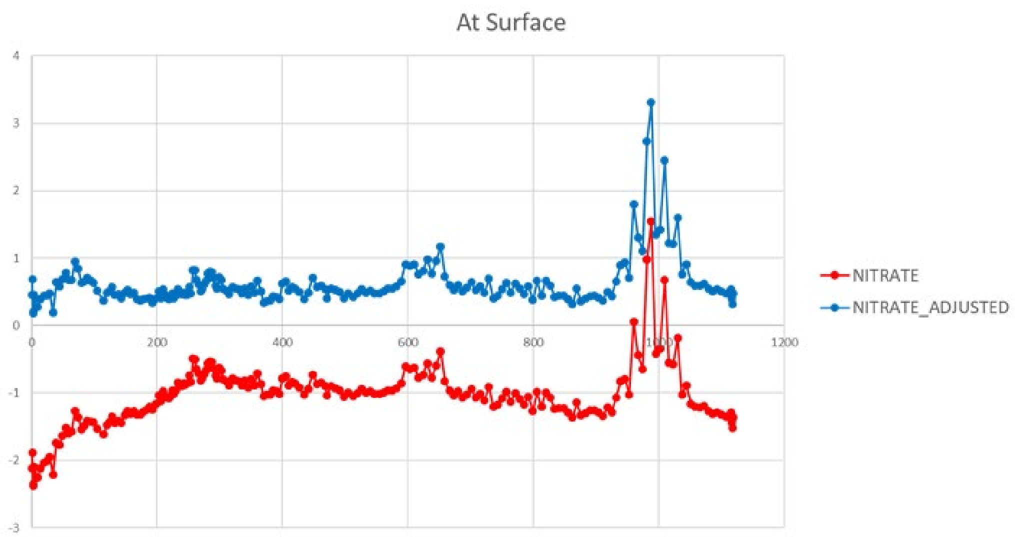

Figure 18: Comparison of the NITRATE_ADJUSTED concentration and the NITRATE concentration at the surface for the float **6901767**.

We can see on Figure 18, that the NITRATE exhibits an increasing gradient prior to day 300 and negative values at surface during most of the float lifetime. Once the OFFSET is estimated at depth (here with the broken lines of Figure 13 (red)) the early gradient and the negative values are corrected for NITRATE_ADJUSTED.

3.2.4 Fill the DM information and estimation of the ERROR

The last phase of the DM consists in the physical modification of the data file. For the parameter NITRATE, a standardization of the SCIENTIFIC_CALIB_xxx fields is an ongoing effort through the DACs (ref DOC QC). At the European level we currently fill these like presented for float 6901765, profile 140 (this will be revisited once agreed at the international level)

SCIENTIFIC_CALIB_EQUATION = “NITRATE_ADJUSTED=(NITRATE*SLOPE+OFFSET)+(DRIFT/100. *(profile_date_juld-launch_date_juld)/365.”

SCIENTIFIC_CALIB_COMMENT =

“Adjusted with CANYON_B (https://doi.org/10.3389/fmars.2018.00328) at depth”

SCIENTIFIC_CALIB_COEFFICIENT =

“OFFSET = -6.483617, SLOPE = 1, DRIFT=-172.1991, DRIFT_DAY_BEGIN=44”

NITRATE_ADJUSTED_ERROR estimation:

If the NITRATE adjustment is estimated using CANYON estimation with DOXY_ADJUSTED as an input:

NITRATE_ADJUSTED_ERROR = ERROR umol kg-1 + DOXY_ADJUSTED_ERROR/10

If the NITRATE adjustment is estimated without DOXY_ADJUSTED, as an input:

NITRATE_ADJUSTED_ERROR = ERROR umol kg-1 + 0.1*abs(NITRATE-NITRATE_ADJUSTED)

ERROR is currently 1 umol kg-1, but can be increased according to the Delayed mode operator.

3.4 Conclusion and perspectives

More than 7000 profiles have been corrected in delayed mode and the remaining profiles are at least adjusted in real time with the World Ocean Atlas as a reference data set but will soon be delayed moded as well.

Since summer 2021, it has been highlighted that some floats suffer from an Abrupt Salinity Drift (ASD). The salinity affects both the DOXY concentration and the NITRATE concentration calculations.

This issue will be addressed as a delayed mode procedure. Presently, there is an encouraging sensitivity study on the CMEMS product ARMOR3D (https://resources.marine.copernicus.eu/?option=com_csw&view=details &product_id=MULTIOBS_GLO_PHY_TSUV_3D_MYNRT_015_012).

This product will be used as a salinity input to perform the NITRATE and the DOXY_ADJUSTED concentration.

References:

Bittig, H., Steinhoff, T., Claustre, H., Fiedler, B., Williams, N.L., Sauzede, R. Körtzinger, A. and J.-P. Gattuso (2018). An alternative to static climatologies: Robust estimation of open ocean CO2 variables and nutrient concentrations from T, S and O2 data using Bayesian neural networks, 5 (328), Frontiers in Marine Science, 10.3389/fmars.2018.00328

Detoc Jerome, Garo Mickael, Carval Thierry, Thepault Baptiste, Mahoudo Pierre (2017). Scoop-Argo : visual quality control for Argo NetCDF data files. SEANOE. https://doi.org/10.17882/4853.

D'Ortenzio, F., S. Le Reste, H. Lavigne, F. Besson, H. Claustre, L. Coppola, A. Dufour, V. Dutreuil, A. Laës-Huon, E. Leymarie, D. Malardé, A. Mangin, C. Migon, P. Morin, A. Poteau, L. Prieur, P. Raimbault, P. Testor. 2012. Autonomously profiling the nitrate concentrations in the ocean: the PRONUTS project. Mercator Ocean Newsletter, #45, http://www.mercator-ocean.fr/content/download/1097/9483/version/2/file/lettre_45_en.pdf#page=8.

Fourrier, M., Coppola, L., Claustre, H., D'Ortenzio, F., Sauzède, R., and Gattuso, J.-P. (2020), A Regional Neural Network Approach to Estimate Water-Column Nutrient Concentrations and Carbonate System Variables in the Mediterranean Sea: CANYON-MED Front. Mar. Sci. 7:620. doi: 10.3389/fmars.2020.00620

Fourrier Marine, Coppola Laurent, Claustre Hervé, D'Ortenzio Fabrizio, Sauzède Raphaëlle, Gattuso Jean-Pierre (2021). Corrigendum: A Regional Neural Network Approach to Estimate Water-Column Nutrient Concentrations and Carbonate System Variables in the Mediterranean Sea: CANYON-MED, Front. Mar. Sci., 25 January 2021 | https://doi.org/10.3389/fmars.2021.650509.

Garcia H.E., T.P. Boyer, O.K. Baranova, R.A. Locarnini, A.V. Mishonov, A. Grodsky, C.R. Paver, K.W. Weathers, I.V. Smolyar, J.R. Reagan, D. Seidov, M.M. Zweng (2019). World Ocean Atlas 2018: Product Documentation. A. Mishonov, Technical Editor.

Johnson, K. S. and L. J. Coletti. 2002. In situ ultraviolet spectrophotometry for high resolution and long term monitoring of nitrate, bromide and bisulfide in the ocean. Deep-Sea Research I, 49, 1291-1305.

Johnson, K. S., S. C. Riser and D. M. Karl. 2010. Nitrate supply from deep to near-surface waters of the North Pacific subtropical gyre. Nature. 465, 1062-1065.

Johnson, Kenneth S., Luke J. Coletti, Hans W. Jannasch, Carole M. Sakamoto, Dana Swift, Stephen C. Riser. 2013. Long-term nitrate measurements in the ocean using the In Situ Ultraviolet Spectrophotometer: sensor integration into the Apex profiling float. Journal of Atmospheric and Oceanic Technology, 30, 1854-1866.

Johnson Kenneth, Maurer Tanya, Plant Joshua, Bittig Henry, Schallenberg Christina, Schmechtig Catherine (2021). BGC-Argo quality control manual for nitrate concentration. https://doi.org/10.13155/84370

Maurer, T. L., Plant, J. N., Johnson, K. S. (2021). Delayed-Mode Quality Control of Oxygen, Nitrate, and pH Data on SOCCOM Biogeochemical Profiling Floats. Frontiers in Marine Science 8. doi: 10.3389/fmars.2021.683207

Sauzede, R., Bittig, H., Claustre, H., Pasqueron de Fommervault, O., Gattuso, J., Legendre, L. and K.S. Johnson (2017). Estimates of water-column nutrients and carbonate system parameters in the global ocean: A novel approach based on neural networks. Frontier in Marine Science, 4:128. doi: 10.3389/fmars.2017.00128