Auxiliary material

1 The rationale of the PRONUTS processing

The processing of ISUS and SUNA sensor data obtained from PRONUTS floats follows the method described by *Johnson and Coletti* [2002a] and implemented in the software released with the sensor by the Satlantic[inc] manufacturer. Basically, processing is performed by using the measured spectrum (from 217 to 242 nm), corrected by an optical baseline (evaluated before deployment on NO_3-free water), and fitted with a regression algorithm, which evaluates bromide and chlorine absorbance [*Johnson and Coletti*, 2002a]. Afterwards, a new version of the algorithm was released [*Johnson et al.*, 2013; *Sakamoto et al.*, 2009], which better accounts for the bromide and chlorine influence on the measured spectrum and also for the temperature effects. At the time of the PRONUTS development, this version of the algorithm was not yet implemented on the commercialised instruments. Moreover, post-processing was not possible on the PRONUTS data, as the measured spectrum was not transmitted on land. Consequently, PRONUTS data were calibrated with a specific post-processing algorithm, which is mainly based on the *Johnson et al.* [2010] suggestions, although some variations were introduced to compensate for the impossibility to apply the *Sakamoto et al.* [2009] algorithm.

2 Temporal variable offset and correction

As shown by *Johnson et al.* [2010], temporal variations of the optical baseline (likely related to fouling) could induce an offset on the entire NO_3 profile. *Johnson et al*. [2010] removed the offset by assuming constant NO_3 at surface. For the PRONUTS data, both SUNA and ISUS sensors showed temporal variable offsets, which appear however constant throughout the water column (figure FS2). Note the different behaviours of the February and early March data. During these periods, NO_3 profiles are totally homogenous over the whole water column, confirming that the temporal variable offset is not dependent on depth. To remove the temporal variable offsets, the *Johnson et al.* [2010] approach was used, though we assumed constant NO_3 at 1000 m (instead of at surface). A correction term was computed for each profile as the difference between the mean NO_3 value reported by the sensors in the 800-1000m layer and the NO_3 colorimetric evaluation of samples collected at 1000m at the float deployment.

3 Temperature and salinity correction

Sakamoto et al. [2009] demonstrated that temperature and salinity variations could have an impact on the ISUS (and therefore also SUNA, which shares the same principles) NO_3 estimations. An improved algorithm, accounting for these effects, was then presented, which corrects the observed UV spectrum using concurrent temperature and salinity. On the software version of ISUS and SUNA sensors on the PRONUTS, the improved algorithm was not yet implemented. Consequently, to correct for temperature and salinity effects, a multi-regression algorithm was applied on the ISUS and SUNA PRONUTS NO_3 observations. Temperature, salinity, depth and NO_3 float data (as corrected for temporal offset) were regressed with a linear function to match the NO_3 colorimetric observations obtained at the deployment and (only for the ISUS) at the recovery. 21 water samples are collected (11 at the deployment, 10 at the recovery) and analysed with a colorimetric method [*Wood et al.*, 1967]. The SUNA and ISUS NO_3 values corrected with the multi-regression algorithm show a better agreement with colorimetric estimations (figure FS3 and FS4) than values with only the temporal variable offset correction.

4 Final adjustment

For some profiles, the temporal variable offset correction and the multi-regression algorithm generated negative NO_3 values (185 points over 17819). In these cases (occurring only between 0 and 30m depth), negative values are forced through zero. To maintain the shape of the profile as coherent as possible, a re-adjustment of the whole profile was then performed by linearly regressing the data over the deepest point and the re-adjusted negative value. Negative values, occurring in about 10% of points (131 on 9796 for the SUNA and 54 on 8023 for ISUS), were finally set to zero, and, in this case, a linear correction is applied to modify the calibration slope.

5 Practical application

1. The raw profiles of ISUS and SUNA sensors are calibrated at depth.

$$NO_{3offset\_corrected} = NO_{3raw} + Offset$$

$$Offset = Median[NO_{3raw}, 800\text{-}1000m] - 8.89$$

where 8.89 μMol is the NO_3 obtained from the 1000m water sample at the deployment via colorimetric method.

2. A linear equation (with coefficients calculated on the recover and deployment profiles) is applied to the corrected profiles, using temperature and salinity observations sampled by the floats at the same depths as the NO_3 measurements.

$$NO_{3ts\_corrected} = X0 + X1 * NO_{3offset\_corrected} + X2 * T + X3 * S + X4 * D$$

Where, T, S and D are respectively Temperature, Salinity and Depth corresponding to the NO_3 measurement.

3. If one negative value exists in the profile, it is forced through zero. If more than one value is presented, only the lowest is forced through zero. The rest of the profile is finally readjusted with a linear regression:

$$NO3_{readj} = \alpha * NO3_{ts\_corrected} + \beta$$

where α and β are obtained by solving the equation over the points:

$NO3^1_{readj} = 0$ $NO3^1_{ts\_corrected}$ negative

$NO3^2_{readj} = 8.89$ $NO3^2_{ts\_corrected}$ at 1000m

6 Statistical performances

The different steps of the PRONUTS processing are evaluated by comparison with NO_3 colorimetric evaluation (table TS01) at the deployment and recovery (only for the ISUS).

The temperature and salinity correction appears as the most performing algorithm for both sensors, reducing the RMS error on the colorimetric data by a factor of 2. The offset correction is, however, particularly important. The decrease of sensor performances (figure FS2) would prevent any exploitation of data, if no correction was performed.

Supplementary figure captions

Figure FS1. Trajectories of the two floats (PRONUTS-ISUS, left; PRONUTS-SUNA right). Colours indicate the sampling period. Black diamonds indicate the deployment points. The dotted line indicates the limits of the NW Mediterranean blooming region, as defined by *D'Ortenzio and Ribera* [2009]. The grey area indicates the deep convection mixed patch derived by the ocean colour image of the 22th of February 2012, following the method of *de Madron et al.* [2013].

Figure FS2. Time-series of the difference between the surface (10m) and the deep (800-1000m) raw NO_3 values for the SUNA (white circles) and for the ISUS (black circle).

Figure FS3. NO_3 concentration profiles at the deployment (SUNA left panel, ISUS central panel) and at the recover (ISUS, right panel). Black lines represent the raw data with the temporal variable offset correction. Red lines indicate the previous profiles after the temperature and salinity correction. Blue lines indicate the profile readjusted if at least one value was negative. Red circles indicate the NO_3 in situ estimations by colourimetric analysis, as derived by water samples collected simultaneously to the PRONUTS profiles (+/- 3 hours).

Figure FS4. Scatter plot of the PRONUTS versus in situ estimations for the different steps of the calibration (grey points indicate the raw data; black points, the raw data with the temporal variable offset correction; white points, the data with the salinity and temperature correction). Data at deployment (SUNA left panel, ISUS central panel) and recover (ISUS right panel) are plotted separately. Note that for the plot of the ISUS recovery, raw data values are not visible, being too high with respect to the selected axis scales.