Chemical reference-profiles from 20 years of Santander Standard Section

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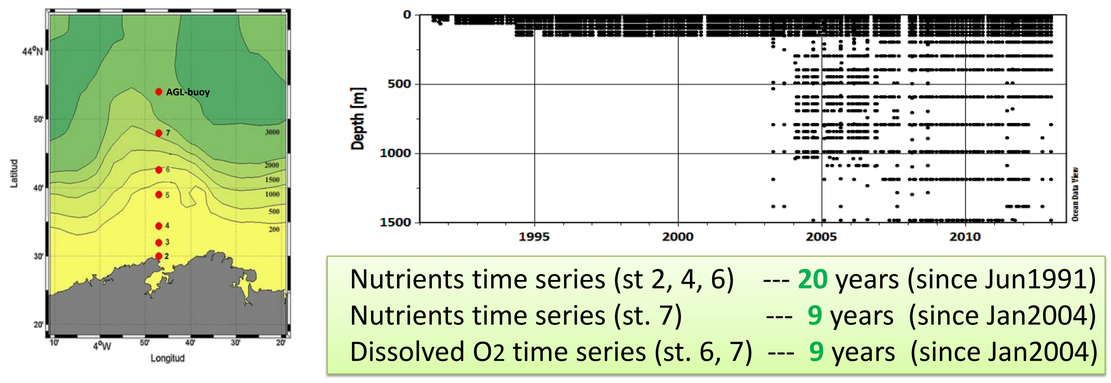
The Santander standard section is monthly sampled within the RADIALES time series monitoring program supported by the Spanish Institute of Oceanography (IEO). This monitoring began in June 1991, and in July 2007 it was strengthen with the ocean-meteorological Augusto Gonzalez de Linares (AGL) buoy. Therefore these is the longest dataset of multidisciplinary time series (physical, chemical and biological variables) in the area. In the framework of the European Marine Observation and Data Network (EMODnet) project, the chemical dataset have been subjected to strong quality control procedures, formatted and flagged according to internationally accepted criteria. This work gives added value to the original data, contributes to their reuse and provides reference profiles for future validations and variability studies.

Sampling and Sample Analysis

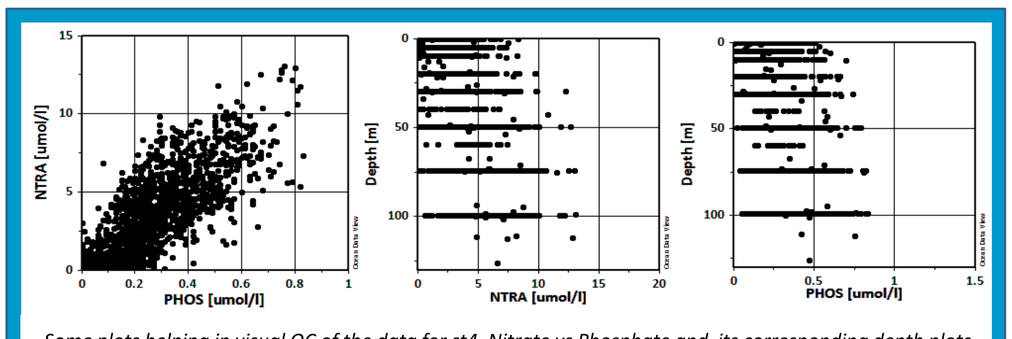
The Santander section include 7 stations from coast (st2, 25 m) to open ocean (AGL-buoy, 2500 m). Samples for nutrients analysis are taken in 5 of them (st2, st4, st5, st7 and AGL-buoy) and for dissolved oxygen determinations in 3 (st6, st7 and AGL-buoy). Samples for nutrients are frozen on board and later analyzed with a four-channel Technicon Autoanalyzer II. Samples for dissolved oxygen are determinate following Winkler method either on board or in the laboratory.



Map of the Santander section showing the position of the stations. And the sampling frequency for chemical variables.

Quality Control (QC)

The data are quality controlled following the recommendations of the International Oceanographic Data and Information Exchange (IODE) for chemical oceanographic data collections *(1)*. ***Automatic checks*** are performed by MATLAB scripts, including test for station headers (date, time, depth and position) as well as for variable data values (ranges, gradient and constant values). After that, the ***manual QC*** performed by visual inspection with ODV software *(2)* determinates the final data validity. This subjective check is carried out using various plots that help in the assignment of the QC-flag as property-property, depth, seasonal and time plots. As a result of these QC, each data is flagged following the SeaDataNet QC-flags scheme *(3)*.



Some plots helping in visual QC of the data for st4. Nitrate vs Phosphate and its corresponding depth plots.

Data Processing

For each station and parameter, a reference-profile was calculated by using a piece-wise linear least-square fit, except for AGL-buoy station because the sampling is performed only at 3m depth. To help in future assessments, range limits have been estimated based on 2 times standard deviation for coastal stations (st2 to st6) where the seasonal variability is greater, and just 1 time in the oceanic one (st7).
The mean and standard deviation was calculated at each sampling depth and also at the core of the water masses in the st7 (see table below). To calculate the value for Easter North Atlantic Central Water (ENACW) data between 200-400 m have been considered and for Mediterranean Water (MW) between 800-1000 m.

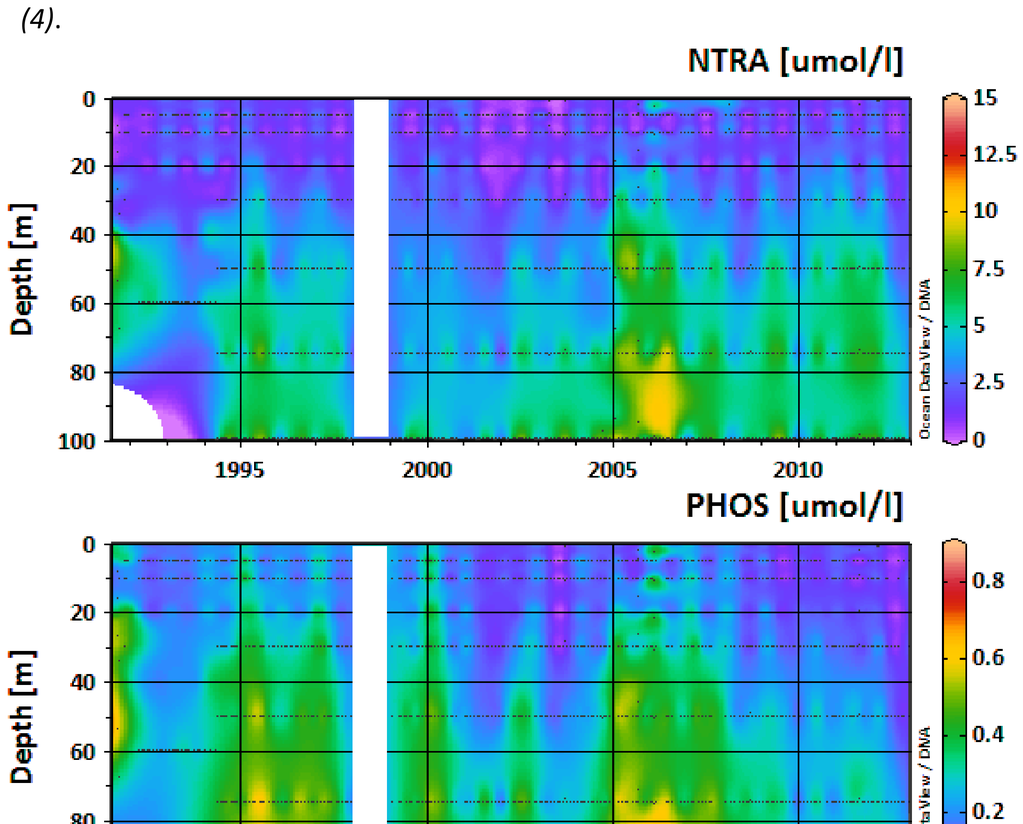
QC Results

A remarkable result of the QC is that all the data of 1998 were flagged as erroneous probably due to problems in the maintenance of samples under frozen conditions or contamination during the determinations.

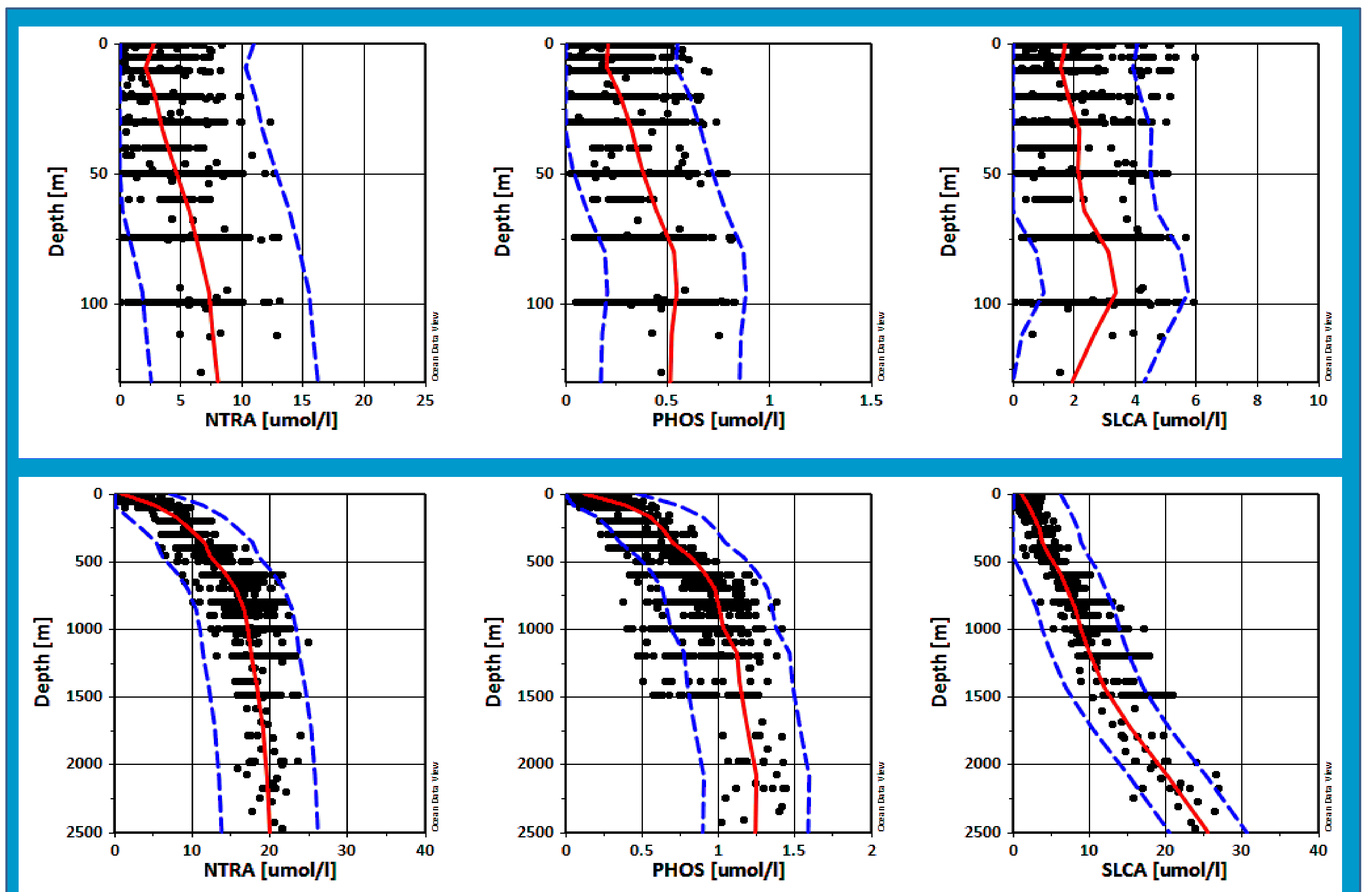
The graphics of reference profiles show how some valid determinations are out of the established limits, this is the reason of the necessity of visual checking in chemical data validation. And it remarks the importance of using different type of plots.

Time series

Time series of nutrients shows its seasonal variability mainly in upper layers, the increase due to the mixing caused by autumn-winter winds and the consequent run out when the stratification begins in spring. The highest values of the series of st4 was in 2006 winter probably resulting from the strong 2005 winter mixing *(4)*.



Time series of Nitrate and Phosphate in st4 (DIVA gridding).



Reference-profiles for Nitrate, Phosphate and Silicate for st4 (up) and st7 (down). All the data are shown (black points) with the mean (red line) and the range (dashed blue line).

Table . Mean ± standard deviation of nutrients on st7 for ENACW and MW.

Water masses	Nitrate (umol/l)	Phosphate (umol/l)	Silicate (umol/l)
ENACW	10.5± 1.8	0.5 ± 0.1	3.7 ± 0.9
MW	17.5 ± 2.1	0.9 ± 0.2	9.8 ± 2.0

Conclusions

- There is no simple way to assure independently the accuracy of nutrients and dissolved oxygen. Therefore, establishing local ranges is basic to improve objective QC checks and the whole time series assessment.
- Reference-profiles can be used in automatic checks, but manual QC by trained staff is required for their final validation, in order to keep extreme events or changes in environmental conditions.
- Maintaining the Santander Standard Section time series is of key importance for studying the climate variability along time and to determinate how the marine ecosystem responds to this variability.

References

(1) First IODE Workshop on Quality Control of Chemical Oceanographic Data Collections, IOC Project Office for IODE, Oostende, Belgium, 8-11 February 2010 Paris, UNESCO, 25 March 2010 (IOC Workshop Report No. 228)
(2) Schlitzer R. Ocean Data View, odv.awi.de, 2015.
(3) SeaDataNet Data Quality Control Procedures v2.0. May 2010
(4) Somavilla R., González-Pola C., Rodriguez C., Josey S.A., Sánchez R.F. and Lavín A. (2009). Large changes in the hydrographic structure of the Bay of Biscay after the extreme mixing of winter 2005. J. Geophys. Res., 114, C01001

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