

MOC²EQ 2010, biogeochemistry

Along the MOC²Equatorial 2010, several samples of water masses were taken from the whole water column. Samples of A_T, pH, O₂ and CO₃²⁻ were analysed on board, on the chemistry lab of the Spanish R/V Hespérides, while C_T samples were measured after in the CO₂ lab of Instituto de Investigaciones Mariñas (IIM-CSIC) in Vigo (Spain).

In the next table the number of measured samples per each variable is shown. In addition, the number of stations from the total of 109 where these samples were collected are also shown.

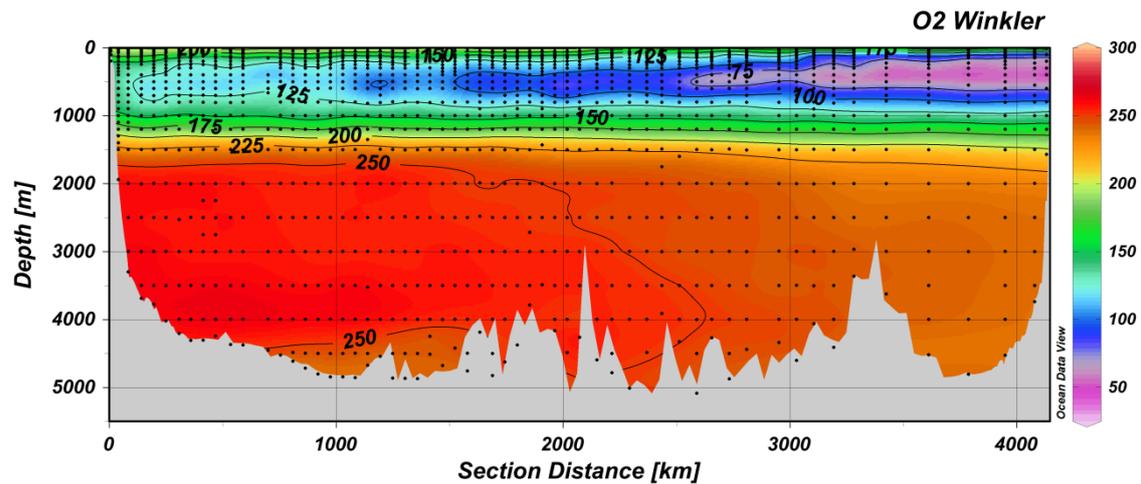
	O ₂	pH	CO ₃ ²⁻	A _T	C _T
Nº muestras	1614	1559	687	958	50
Estaciones	72	70	30	43	16

Winkler Oxygen (O₂)

With the main purpose of calibrating the O₂ sensor of CTD, samples of O₂ was taken in all the stations at twenty four levels of depth in the 7.5°N section of MOC²Equatorial 2010. The O₂ samples were analysed following the widely applied Winkler method (1888).

The O₂ samples were always the first in being taken from the Niskin bottles of the rosette. Samples were collected in calibrated flasks (~250 mL) with a PVC pipe avoiding the bubble formation. The sample fixation (precipitation) were done by adding 0.6 mL of manganous salt (MnCl₂ ·4H₂O) and 0.6 mL of alkali-iodide solution (NaOH + NaI). These samples have to be stored at darkness at least 24 hours before being measured. Then, 1 ml of sulphuric acid is added to dissolve the precipitate and to titrate the O₂ sample with thiosulfate 0.01N using a automatic 5ml burette "Titrande Metrohm". Taking into account the stoichiometry and the used volume of thiosulfate, the O₂ concentration is obtained in μmol kg⁻¹.

The O₂ concentration distribution of 7.5°N section is represented using the Ocean Data View program (ODV) (Schlitzer, R., 2011).



7.5°N O₂ distribution in the MOC²Equatorial cruise.

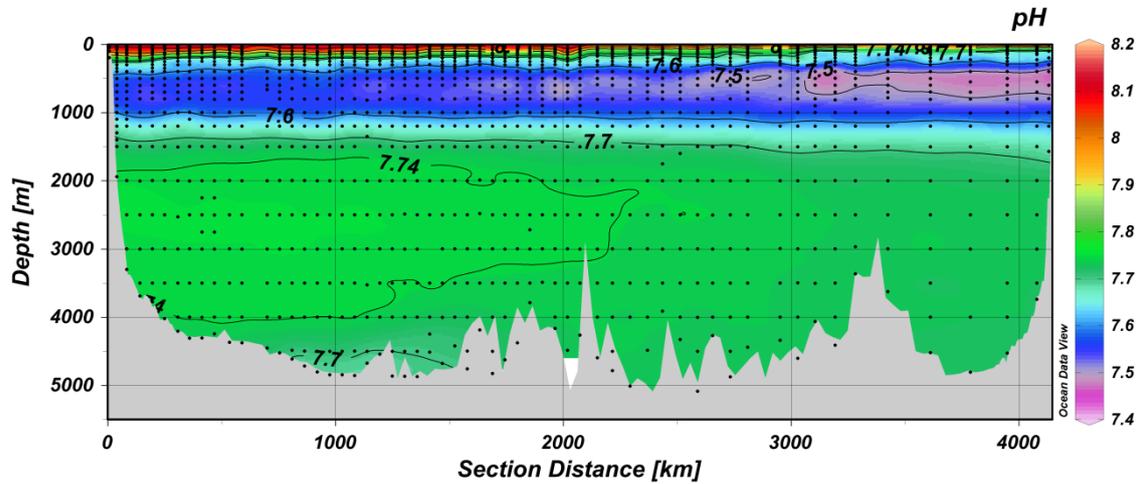
pH

Seawater pH samples were taken at twenty four levels of all stations along section 7.5°N of MOC² Equatorial cruise. The pH measurements were made using the spectrophotometric method described in Clayton and Byrne (1993). This method consists of adding 75 µl of m-cresol purple (mCP) to the seawater sample and measuring the absorbance of the sample at three wavelengths, i.e., $\lambda_{HI} = 434 \text{ nm}$, $\lambda_I = 578 \text{ nm}$ and $\lambda_{\text{non-abs}} = 730 \text{ nm}$. The reaction of interest at seawater pH is the second dissociation $HI_{(aq)}^- = H^+_{(aq)} + I^2_{(aq)}^-$ in which I is the indicator. Then the total hydrogen ion concentration can be determined by $\text{pH} = \text{p}K_2 + \log_{10}[I^2]/[HI]$.

pH samples were taken directly from the Niskin bottles into special optical glass spectrophotometric Hellma cells of 28 mL of volume and 100 mm of path length. These cells were carefully stored around one hour before the analysis in a thermostatic bath in which the temperature was controlled at 25.0°C. Absorbance measurements were performed with the Shimadzu UV 2401 PC spectrophotometer on board the R/V Hespérides. The pH values were given following the equations described in Dickson et al. (2007), who includes the correction due to the difference between seawater and the indicator acidity (ΔR). Apart from that, the effect of the impurities of the indicator described in Yao et al. (2007) was also applied, using the following equation to obtain the corrected pH data in seawater scale at 25°C:

$$pH_{SWS25} = pH_{\Delta R} - [0.0010 + 0.0008 \cdot (pH_{meas} - 7.2) + 0.0042 \cdot (pH_{meas} - 7.2)^2]$$

Taking into account these pH data, the complete pH profile of the 7.5°N section was plotted using ODV, as it is shown in the next graph.



7.5°N pH distribution in the MOC²Equatorial cruise.

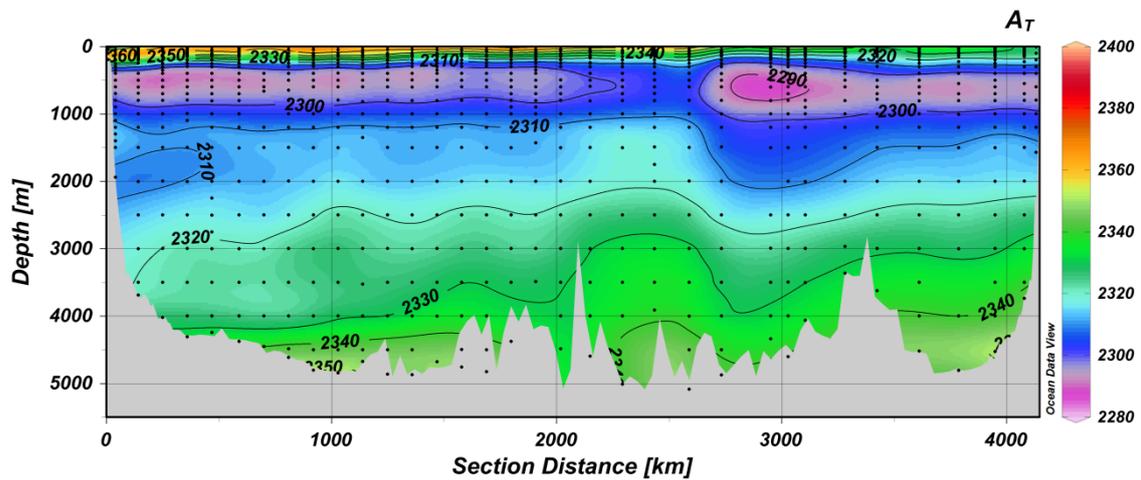
Alkalinity (A_T)

Samples of A_T were taken during MOC² in almost the half of the total stations. In order to analyse these A_T samples on board, the water was transferred directly from the Niskin bottle to 600 mL borosilicate glass bottles and stored for twenty-four hours before the analyses. Measurements of A_T were done by a one endpoint method using an automatic potentiometric titrator (Titrand 801 Metrohm) with a combined glass electrode (Perez and Fraga, 1987). A Knudsen pipette (~250 mL) was used to transfer the samples into an open Erlenmeyer flask in which the potentiometric titration was carried out with HCl (0.1 M). The final volume of titration was determined by means of two pH endpoints very close to one another, i.e., 4.45 and 4.42 (Mintrop et al., 2000). These AT measurements were done in 12 sets of analysis.

In order to estimate the accuracy of the A_T method, alkalinity measurements of certified reference material (CRM) of CO₂ from batch 99 provided by Dr. Andrew Dickson have been

analysed. And in addition, an extra calibration (substandard) was made by using a closed container of 50 L filled with open ocean surface water.

The distribution of A_T concentrations in $\mu\text{mol}\cdot\text{Kg}^{-1}$ of the 7.5°N section is shown in the next plot which was drawing using ODV.



7.5°N A_T distribution in the MOC²Equatorial cruise.

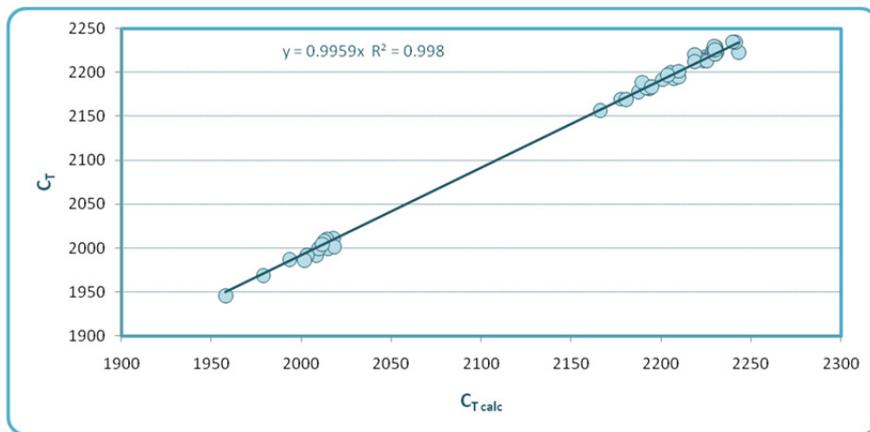
Total inorganic carbon (C_T)

Along MOC² 50 discrete samples of C_T were taken in the water column to be measured in the CO₂ lab of IIM in Vigo (Spain) using a SOMMA (Single-Operator Multiparameter Metabolic Analyzers) system connected to a model CM101_093 coulometer (UIC.INC, Joliet, ILLINOIS, USA). C_T samples were collected in 600 mL borosilicate glass bottles avoiding the formation of bubbles. To keep the samples free of fouling formation, 300 μL of de HgCl_2 (sat) were added into the bottles and conserving in darkness. The analysis consists on acidifying an aliquot of 20 mL with H_3PO_4 in a glass stripping chamber. Then, the resulting CO₂ gas is carried in the equipment by a free-CO₂ gas (N₂) into a coulometric cell, in which the coulometrical titration is performed (Johnson et al., 1993).

In order to estimate the accuracy of the A_T method, alkalinity measurements of certified reference material (CRM) of CO_2 from batch 99 provided by Dr. Andrew Dickson have been analysed. And in addition, an extra calibration (substandard) was made by using a closed container of 50 L filled with open ocean surface water.

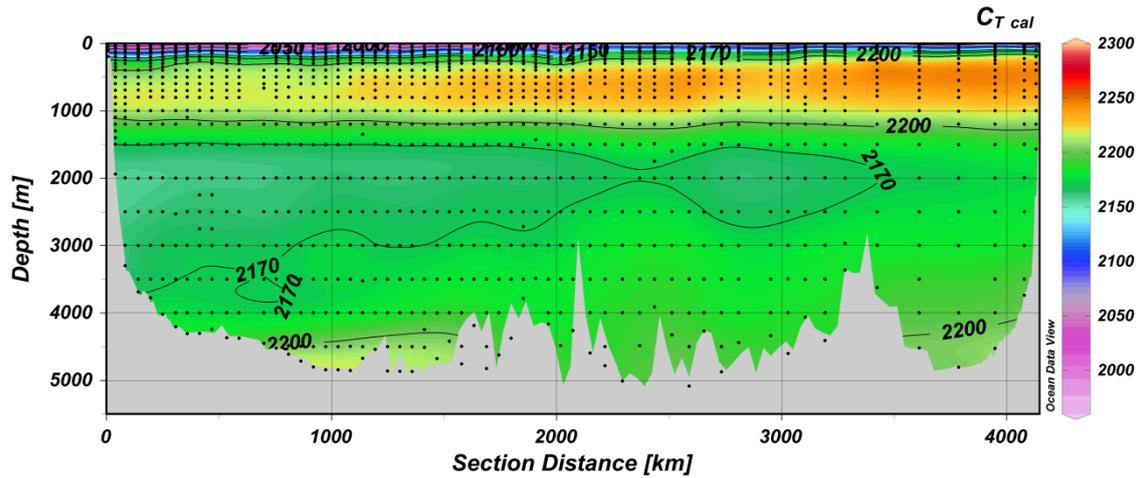
C_T measurements of certified reference material (CRM) of CO_2 from batch 100 provided by Dr. Andrew Dickson have been analysed in every C_T -analysis session in order to check the accuracy of the measurements.

The good agreement between these measured C_T and those calculated from A_T and pH using the inorganic carbon system thermodynamic equations and the acid constants from Mehrbach *et al.* (1973) fitted by Dickson & Millero (1987) is shown in the next graph, in which calculated C_T fits well with measured C_T ($R^2=0.998$).



Lineal adjustment between calculated and measured C_T .

Due to this high correlation, the calculated C_T profile is shown in the next graph for the 7.5°N section.



7.5°N calculated C_T distribution in the MOC²Equatorial cruise.

Ion Carbonate (CO_3^{2-})

Natural seawater samples of CO_3^{2-} were collected from the whole water column along thirty stations in MOC² at 24 levels of depth. These CO_3^{2-} samples were analysed on board the R/V Hespérides following the spectrophotometric method described in Byrne and Yao (2008). This method consists on the addition of 225 μL of stock solution of PbCl_2 (1.1 mM) to the seawater sample in order for this Pb^{+2} to react with the dissolved CO_3^{2-} of the sample obtaining the complex PbCO_3 . The $[\text{CO}_3^{2-}]$ is calculated in terms of UV absorbance ratios using the next equation (eq. 5 of Byrne and Yao, 2008).

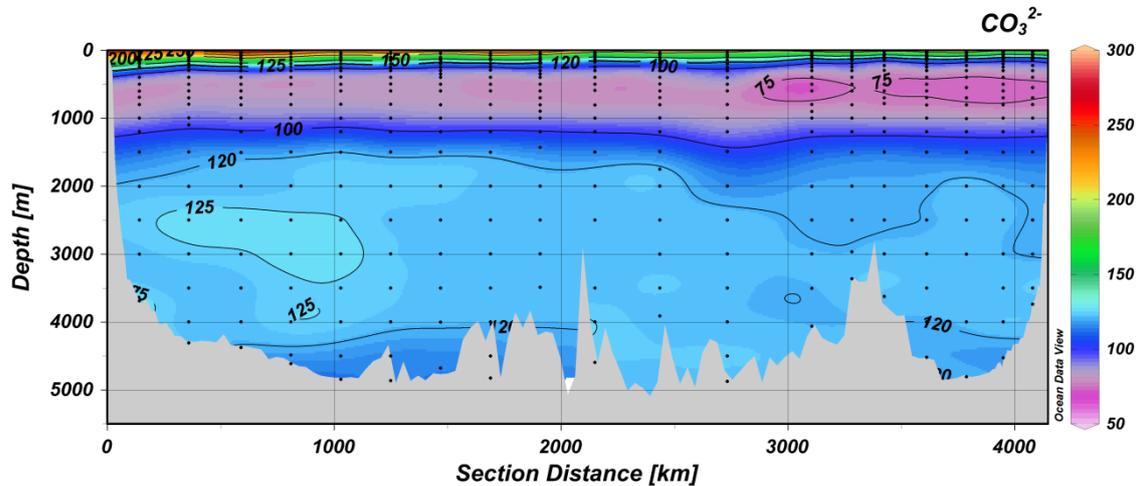
$$-\log[\text{CO}_3^{2-}]_T = \log_{\text{CO}_3} \beta_1 + \log\left(\frac{R-e_1}{e_2-R \cdot e_3}\right)$$

Where $R = \left(\frac{\lambda_2 - \lambda_3}{\lambda_1 - \lambda_3}\right)$, in which λ_1 (234 nm) is the UV absorbance wavelengths at the isobestic point of PbCO_3 , λ_2 (250 nm) is mean value of wavelengths presented high absorbance variation and λ_3 (350 nm) a non-absorbing wavelength to correct the sample manipulation.

Seawater was transferred directly from Niskin bottles into cylindrical quartz Perkin Elmer cells of 28 mL of volume and 100 mm of path length. These cells were carefully stored in a thermostatic bath at 25°C at least one hour before the analysis. Absorbance measurements

were performed with a Shimadzu UV 2401 PC spectrophotometer on board the R/V Hespérides.

The distribution of CO_3^{2-} along the 7.5°N is plotted in the next graph using the ODV program.



7.5°N CO_3^{2-} distribution in the MOC²Equatorial cruise.

References

- Byrne, R.H., Yao, W., 2008. Procedures for measurement of carbonate ion concentrations in seawater by direct spectrophotometric observations of Pb(II) complexation. *Marine Chemistry* 112, 128–135.
- Clayton, T.D., Byrne, R.H., 1993. Spectrophotometric seawater pH measurements: total hydrogen ion concentration scale calibration of m-cresol purple and at-sea results. *Deep-Sea Research* 40, 2115–2129.
- Dickson, A.G., Sabine, C.L., Christian, J.R., 2007. Guide to best practices for ocean CO_2 measurements. PICES Special Publication 3, 191 pp.
- Johnson, K.M., Wills, K.D., Butler, D.B., Johnson, W.K., Wong, C.S., 1993. Coulometric total carbon dioxide analysis for marine studies: maximizing the performance of an automated gas extraction system and coulometric detector. *Marine Chemistry* 44, 167–187.
- Mintrop, L., Pérez, F., González-Dávila, M., Santana-Casiano, J., Körtzinger, A., 2000. Alkalinity determination by potentiometry: Intercalibration using three different methods. *Ciencias Marinas* 26, 23–37.

- Perez, F.F., Fraga, F., 1987. A precise and rapid analytical procedure for alkalinity determination. *Marine Chemistry* 21, 169–182.
- Schlitzer, R., 2011. *Ocean Data View*.
- Winkler L. W., 1888. Die Bestimmung des im Wasser gelösten Sauerstoffes. *Berichte der deutschen chemischen Gesellschaft* 21, 2843–2854.
- Yao, W., Liu, X., Byrne, R.H., 2007. Impurities in indicators used for spectrophotometric seawater pH measurements: Assessment and remedies. *Marine Chemistry* 107, 167–172.