CRUISE REPORT: A06
(Updated DEC 2016)

Highlights

Cruise Summary Information

Section Designation	**A06**
alias	**MOC2EC2010, 75N**
Expedition designation (ExpoCodes)	**29HE20100405**
Chief Scientists	**Joseph L. Pelegrí / CSIC,c**
Dates	2010 APR 05 - 2010 MAY 16
Ship	*R/V HESPERIDES*
Ports of call	
Geographic Boundaries	10°N 52°W 10°W 0°N
Stations	109 (57 stations with bottle samples)
Floats and drifters deployed	0
Moorings deployed or recovered	0

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Links To Select Topics

Shaded sections are not relevant to this cruise or were not available when this report was compiled.

Cruise Summary Information	Hydrographic Measurements
Description of Scientific Program	CTD Data:
Geographic Boundaries	Acquisition
Cruise Track (Figure): CDIAC	Processing
Description of Stations	Calibration
Description of Parameters Sampled	Temperature Pressure
Bottle Depth Distributions (Figure)	Salinities Oxygens
Floats and Drifters Deployed	Bottle Data:
Moorings Deployed or Recovered	Salinity
	Oxygen
Principal Investigators	Nutrients
Cruise Participants	Carbon System Parameters
	CFCs
Problems and Goals Not Achieved	Helium / Tritium
Other Incidents of Note	Radiocarbon
Underway Data Information:	References
Navigation Bathymetry	
Acoustic Doppler Current Profiler (ADCP)	
Thermosalinograph	
XBT and/or XCTD	
Meteorological Observations	
Atmospheric Chemistry Data	
Lowered Acoustic Doppler Current Profiler (LADCP)	
Data Processing Notes	Acknowledgments

MOC²EQ 2010, biogeochemistry

Along the MOC²Equatorial 2010, several samples of water masses were taken from the whole water column. Samples of A_T, pH, O_2 and CO_3^{2-} were analysed on board, on the chemistry lab of the Spanish R/V Hespérides, while C_T samples were measured after in the CO_2 lab of Instituto de Investigacións 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.
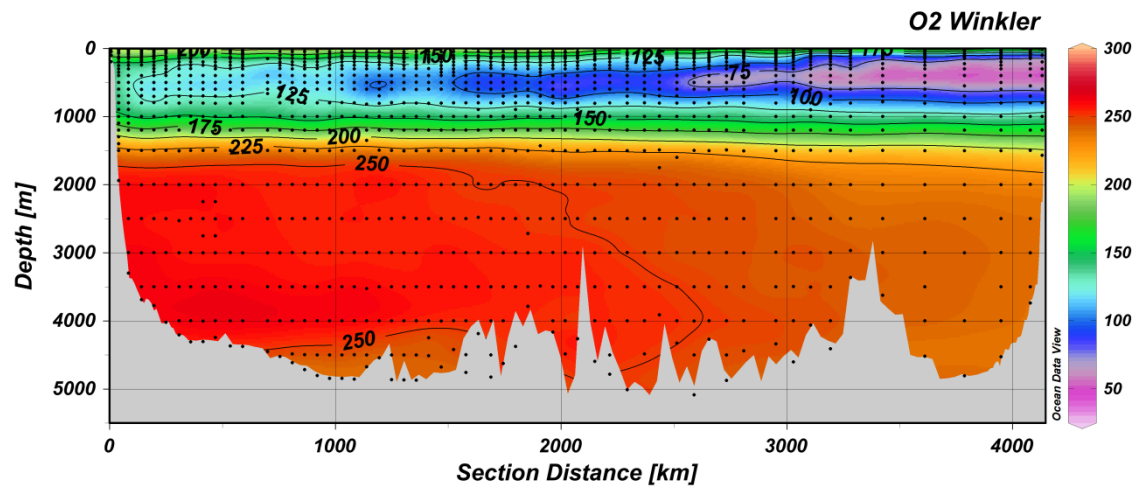
	O_2	pH	CO_3^{2-}	A_T	C_T
Nº muestras	1614	1559	687	958	50
Estaciones	72	70	30	43	16

Winkler Oxygen (O_2)

With the main purpose of calibrating the O_2 sensor of CTD, samples of O_2 was taken in all the stations at twenty four levels of depth in the 7.5ºN section of MOC²Equatorial 2010. The O_2 samples were analysed following the widely applied Winkler method (1888).

The O_2 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 ($MnCl_2$.$4H_2O$) 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 O_2 sample with thiosulfate 0.01N using a automatic 5ml burette "Titrando Metrohm". Taking into account the stoichiometry and the used volume of thiosulfate, the O_2 concentration is obtained in µmol kg^{-1}.

The O_2 concentration distribution of 7.5ºN section is represented using the Ocean Data View program (ODV) (Schlitzer, R., 2011).

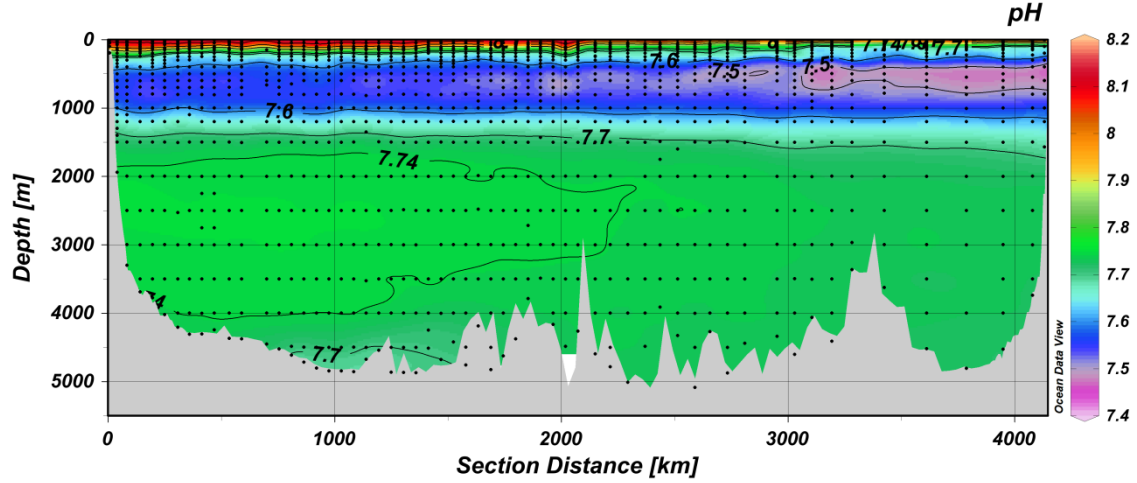7.5ºN O$_2$ distribution in the MOC^{2}Equatorial cruise.

pH

Seawater pH samples were taken at twenty four levels of all stations along section 7.5ºN of MOC^2 Equtorial 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., λ_{HI} = 434 nm λ_I = 578 nm and $\lambda_{non\text{-}abs}$ = 730 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 pH = pK_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 25.0ºC. 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 25ºC:

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

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

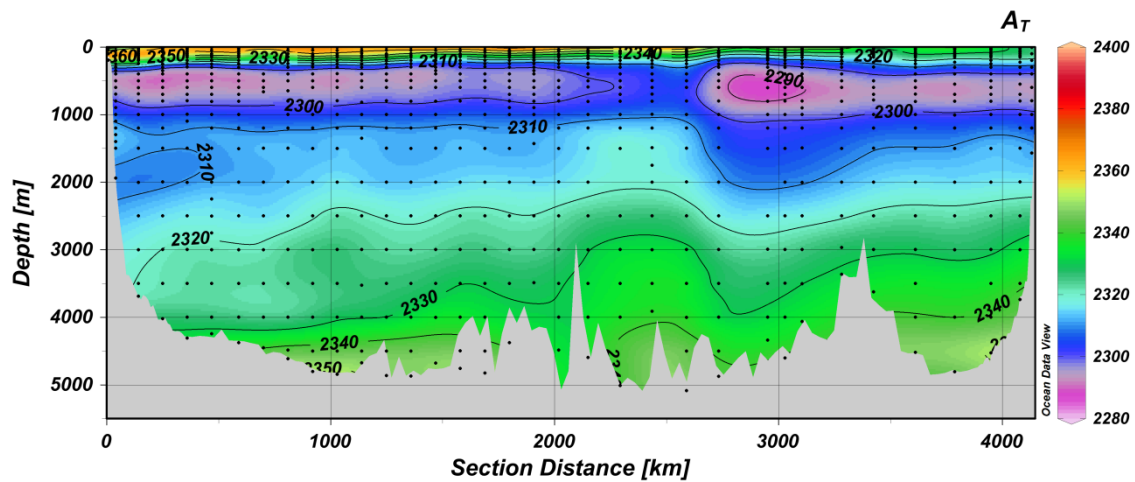7.5ºN pH distribution in the MOC[2] Equatorial cruise.

Alkalinity (A_T)

Samples of A_T were taken during MOC[2] 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 (Titrando 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 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.

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

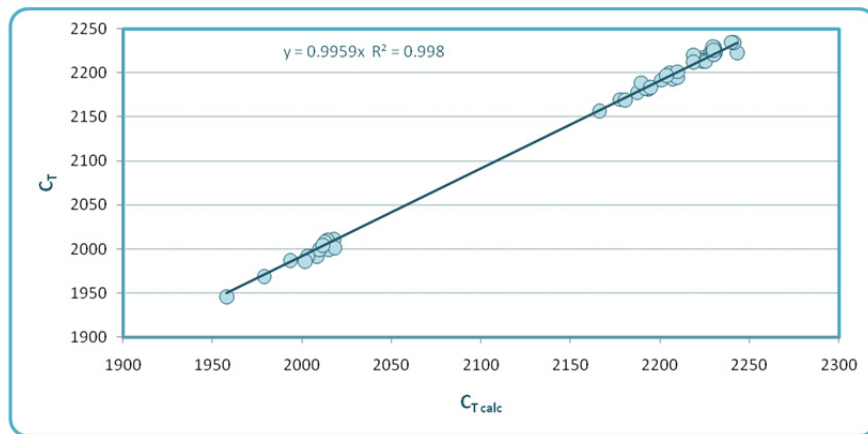

7.5ºN A_T distribution in the MOC[2] Equatorial cruise.

Total inorganic carbon (C_T)

Along MOC[2] 50 discrete samples of C_T were taken in the water column to be measured in the CO_2 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 CO_2 gas is carried in the equipment by a free-CO_2 gas (N_2) into a coulometric cell, in which the coulometrical tritation 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.
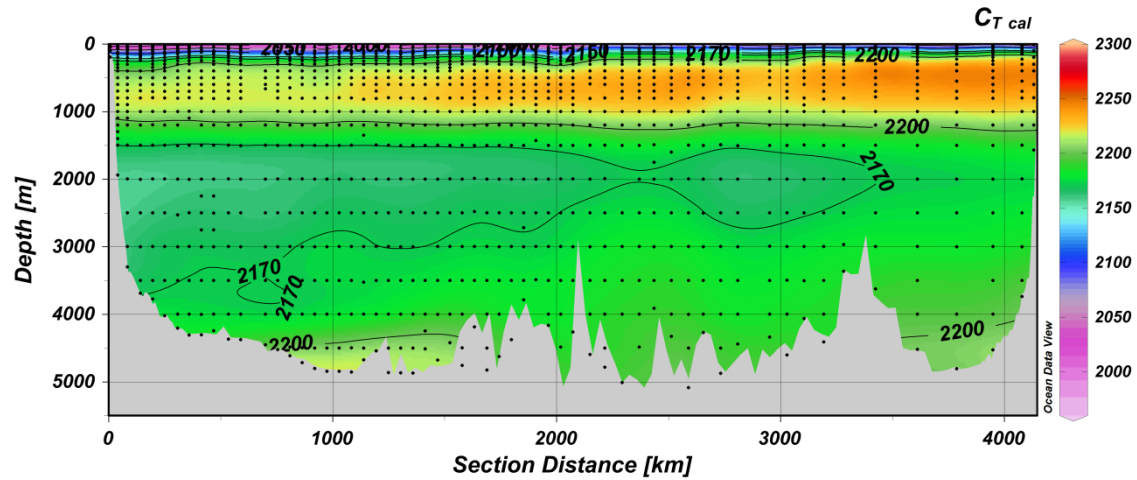
C_T measurements of certified reference material (CRM) of CO_2 from batch 100 provided by Dr. Andrew Dickson have been analysed in every C_T-analysis session in order to check the accuracy of the measurements.

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 7.5ºN section.

7.5ºN calculated C_T distribution in the MOC^2 Equatorial cruise.

Ion Carbonate (CO_3^{2-})

Natural seawater samples of CO_3^{2-} were collected from the whole water column along thirty stations in MOC^2 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 $[CO_3^{2-}]$ is calculated in terms of UV absorbance ratios using the next equation (eq. 5 of Byrne and Yao, 2008).
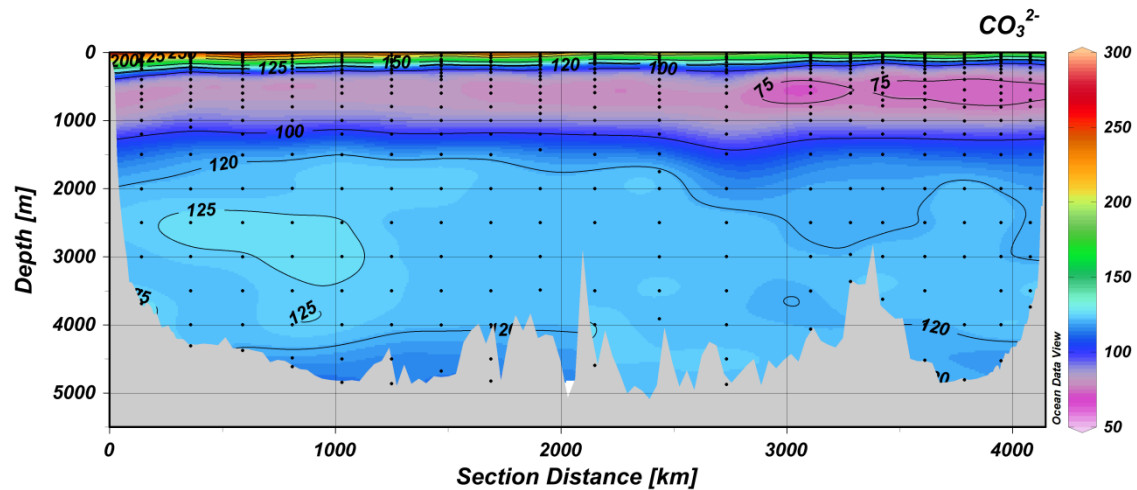
$$-\log[CO_3^{2-}]_T = \log_{CO3} \beta_1 + \log\left(\frac{R-e_1}{e_2-R\cdot e_3}\right)$$

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 25ºC 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 7.5ºN is plotted in the next graph using the ODV program.

7.5ºN CO_3^{2-} distribution in the MOC^{2}Equatorial 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.

CCHDO Data Processing Notes

- **Exchange and netCDF files online Rox**

Date: 2014-12-30
Data Type: BTL
Action: Website Update
Note:
```
=============================
29HE20100405 processing - BTL
=============================


2014-12-30

R Lee

.. contents:: :depth: 2

Submission
==========


==================== ============= ========================== =============== ====
filename             submitted by  date                       data type       id
==================== ============= ========================== =============== ====
29HE20100405.exc.csv Robert M. Key 2014-12-02 13:35:04.034075 data_suggestion 6325
==================== ============= ========================== =============== ====


Parameters
----------

29HE20100405.exc.csv
~~~~~~~~~~~~~~~~~~~~~

- CTDPRS
- CTDTMP
- CTDSAL [1]_
- OXYGEN [1]_
- SILCAT [1]_
- NITRAT [1]_
- PHSPHT [1]_
- CFC-11 [1]_
- CFC-12 [1]_
- TCARBN [1]_
- ALKALI [1]_
- PH_TOT [1]_
- PH_TMP
- HELIUM [1]_
- DELHE3 [1]_
- NEON [1]_ [3]_

.. [1] parameter has quality flag column
.. [3] not in WOCE bottle file

Process
```

```
=======


Changes
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29HE20100405.exc.csv
~~~~~~~~~~~~~~~~~~~~
- Changed empty CFC-11 and CFC-12 data values from flag 2 to flag 9


Conversion
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====================== =================== ======================
file                   converted from      software
====================== =================== ======================
29HE20100405_nc_hyd.zip 29HE20100405_hy1.csv hydro 0.8.2-40-g569f4c2
====================== =================== ======================

All converted files opened in JOA with no apparent problems.

Updated Files Manifest
======================
====================== ==================
file                   stamp
====================== ==================
29HE20100405_hy1.csv    20141230SIOCCHDRJL
29HE20100405_nc_hyd.zip 20141230SIOCCHDRJL
====================== ==================
```

- **File Submission** Andrew Barna

[29HE20100405.exc.csv (download)](#) #fb4cd
Date: 2014-12-02
Current Status: merged
Notes
```
Expocode: 29HE20100405
Ship: None
Woce Line: None
Note: None
```

- **File Submission** Robert Key

[29HE20100405.exc.csv (download)](#) #fb4cd
Date: 2014-12-02
Current Status: merged
Notes
```
Expocode: 29HE20100405
Ship: Hesperides
Woce Line: A06
Note: None
```

- **As Received** Andrew Barna

Date: 2014-12-02
Data Type:
Action: Data available
Note:
```
The following data are now available As Received, unprocessed by the CCHDO.

http://cchdo.ucsd.edu/cruise/29HE20100405
        29HE20100405.exc.csv
```

- **File Merge** cchdo_admin

[a06_29HE20100405_hy1.csv (download)](#) #4972e
Date: 2012-10-26
Current Status: merged
Notes
```
BTL
```

- **Exchange, NetCDF, WOCE files online** Carolina Berys

Date: 2012-10-26
Data Type: BTL
Action: Website Update
Note:
```
2012-10-26
A06 2010 ExpoCode 29HE20100405 processing notes - BTL
C Berys

SUBMISSION
29HE20100405.exc.csv submitted by Bob Key on 2012-10-12 containing bottle data

The file contains the following parameters (* with flag column):
  DEPTH
  CTDPRS
  CTDTMP
  CTDSAL*
  OXYGEN*
  SILCAT*
  NITRAT*
  PHSPHT*
  TCARBN*
  ALKALI*
  PH_SWS*
  PH_TMP
  THETA

The following changes were made to the submission file:
  none

FORMATTED FILE
* NetCDF bottle file converted using using hydro (M Shen)
* WOCE bottle file not created
* Exchange and NetCDF files opened in JOA with no apparent problems

FILE MANIFEST
a06_29HE20100405_hy1.csv
a06_29HE20100405_nc_hyd.zip

working directory
  /data/co2clivar/atlantic/a06_29HE20100405/original/2012.10.26_btl_cberys
```

- **Available under 'Files as received'** CCHDO Staff

Date: 2012-10-22
Data Type: BTL
Action: Website Update
Note:
```
The following files are now available online under 'Files as received', unprocessed
by the CCHDO.

Report MOC2EC2010.pdf
29HE20100405.exc.csv
```

- **File Submission** Robert M. Key

[a06_29HE20100405_hy1.csv (download)](download) #4972e
Date: 2012-10-12
Current Status: merged
Notes
```
Bottle data file
```

- **File Submission** Key, Robert M.

[a06_29HE20100405_hy1.csv (download)](download) #4972e
Date: 2012-10-12
Current Status: merged
Notes
```
Expocode: 29HE20100405
Ship: Hesperides
Woce Line: A06
Note: The attached report (chemistry) is all I've got for this one.
```

- **File Submission** Robert M. Key

[Report MOC2EC2010.pdf (download)](download) #68e7d
Date: 2012-10-12
Current Status: unprocessed
Notes
```
MOC2EQ Documentation
```

- **File Submission** Key, Robert M.

[Report MOC2EC2010.pdf (download)](download) #68e7d
Date: 2012-10-12
Current Status: unprocessed
Notes
```
Expocode: 29HE20100405
Ship: Hesperides
Woce Line: A06
Note: The attached report (chemistry) is all I've got for this one.
```

- **Exchange file to go online** Bob Key

Date: 2012-10-12
Data Type: BTL
Action: Submitted
Note:
```
The attached report (chemistry) is all I've got for this one.
```