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CALIBRATION OF CTD OXYGEN DATA COLLECTED IN THE CORAL SEA DURING THE 2012 BIFURCATION CRUISE

By C. Saout-Grit (1), A. Ganachaud (2), C. Maes (3), L. Finot (4), L. Jamet (4), F. Baurand(5) and J. Grelet (5)

Corresponding author: carole.saout@glazeo.net

[1] GLAZEO Nantes, France

[2] LEGOS IRD, UMR 5566-LEGOS,UPS (OMP-PCA) Toulouse, France

[3] LPO-IRD Brest, France

[4] US 191IRD LAMA, Nouméa

[5] US 191 IRD IMAGO Brest, France

Abstract

An updated procedure for a CTD-oxygen calibration along with new data processing was applied to recent hydrographic cruise data in the Coral Sea during the Cruise “BIFURCATION” in September 2012. After a brief introduction with the scientific context (section 1), we describe the contents and acquisition models of hydrological and chemical data that are used for the calibration (section 2), the post-cruise calibration method (section 3) and the calibration results (section 4).

Context

By its location within southwest Pacific Ocean, the Coral Sea is a key zone of connection between the South Pacific subtropical anticyclonic gyre and the equatorial regions. Because of its numerous reefs, islands and coral archipelagos, the Coral Sea is a place of formation of numerous, fine and intense oceanic jets, as the broad South Equatorial Current enters from its east.

Conducted in the context of the international program SPICE (Southwest PacIfic Ocean Circulation and Climate Experiment, Ganachaud et al. 2014), the BIFURCATION cruise had the main objective to complete the vision of the regional oceanic circulation in the Coral Sea, by documenting the fate of its main currents, the North Caledonian Jet as it flows over the Queensland Plateau off the Australian coast (Maes et al. cruise report, in preparation).

The cruise was led by the Institut de Recherche pour le Développement (IRD) aboard the oceanographic ship Alis between September 1st and September 15 2012, from Nouméa to Nouméa and produced forty hydrological profiles (**figure 1** ; stations 2-5 and 37-40 have been sampled at the same position).

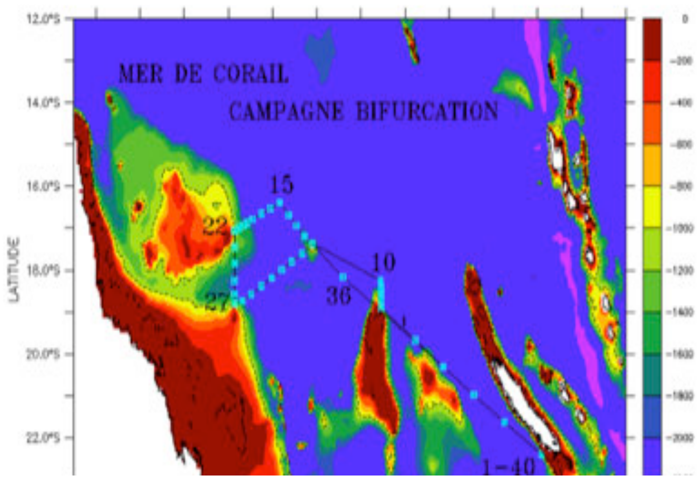


Figure 1: Route and Positions of 40 hydrological stations operated during the 2012 BIFURCATION Cruise

Post-cruise calibration procedure

At each station, two vertical CTD profiles are available. The first *downcast CTD profile* is obtained during the descent phase of the CTD rosette, from the surface to 2000 meters depth, with direct Seabird measurements of Pressure (dbar), Temperature (ITS-90, °C), Salinity (psu) and Dissolved-Oxygen concentration (O2). The second *upcast CTD profile* is obtained during the ascent phase of the CTD rosette, with again P/T/S/O2 Seabird direct measurements and in addition, water samples collected using a set of bottles mounted on the rosette. Those water samples provide chemical oxygen measurements through the Winkler procedure.

Hydrological Data

During the cruise, the CTD/O2 system which equipped the rosette was a real-time data acquisition system using a SBE911plusCTD type (http://www.seabird.com/sbe911plus-ctd) with two redundant measurement circuits for Conductivity/Temperature sensors, and a SBE-43 dissolved-oxygen sensor. The CTD/O2 system thus includes:

• one sensor for Pressure (P): range [0-6800] - resolution 0,068 - accuracy 1 dbar
• two sensors for Temperature (T1 and T2): range [-5-35] - resolution 0,0002 - accuracy 0,002 °C
• two sensors for Conductivity (C1 and C2): range [0-7] - resolution [4,1-5] - accuracy 0,0003 S/m
• two sensors for dissolved-oxygen concentration (DO1 and DO2): range [0-15] – resolution 0,01 - accuracy 0,01 ml/l

Each sensor has a serial number and was calibrated before the cruise, according to table 1. Post-calibration was made long after the cruise and was not used here.

Parameter	Calibration Date	Serial Number s/n
Pressure	05/11/2008	75674
Temperature T1	27/03/2012	2552
Temperature T2	27/03/2012	2551
Conductivity C1	14/03/2012	2343
Conductivity C2	14/03/2012	2340
Dissolved-Oxygen Concentration DO1	27/03/2012	0068
Dissolved-Oxygen Concentration DO2	14/03/2012	1337

Table 1: Serial numbers and calibration dates for primary and auxiliary circuits of SBE911plusCTD sensor used during the 2012-BIFURCATION cruise

The SBE43 dissolved-oxygen sensor allows the determination of the concentration of oxygen in the environment by counting the number of oxygen molecules per second (flux) that diffuse through a polarographic membrane. Knowledge of the flux of oxygen and the geometry of the diffusion path allows the determination of the concentration of oxygen. The permeability of the membrane to oxygen is a function of temperature and ambient pressure. The electronic interface provides voltages that proportional to membrane current (oxygen current) and membrane temperature (oxygen temperature).

Chemical Data

For twenty-one out of forty stations, water samples were collected during the ascent of the CTD rosette from 2000 meters to the surface, using eleven bottles mounted on the rosette (table 2). Chemical oxygen data (in umol/l) is obtained using the Winkler procedure (Langdon, 2010). For each bottle, the CTD pressure, temperature, salinity and oxygen are recorded. This gives the potential density needed for the post-cruise calibration procedure.

Station	7	8	9	12	13	14	16	17	18	19	21	23	25	26	28	29	31	32	33	34	40
Bottle ID																					
1	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
2	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
3	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
4	X	X	X	X	X	X	X	X		X	X	X	X	X	X	X	X	X	X	X	X
5	X		X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
6	X	X	X	X	X		X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
7	X	X	X	X	X		X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
8	X	X	X	X	X		X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
9	X	X		X	X		X			X	X	X		X		X	X	X	X	X	X
10	X	X			X		X			X	X	X		X		X		X		X	
11		X			X		X			X		X		X							

Table 2: Characteristics of chemical oxygen measurements with corresponding station and bottle identities.
X: measurement ok - Yellow: Oxygen dubious value – N1: Broken nylon- Light-green: leaking - Dark-green: no salinity

Data processing

In order to simplify the different treatments, maximize compatibility, reduce error possibilities, and ensure all necessary parameters are available and documented, the Seabird-formatted data from the CTD unit deck is converted to Netcdf Ocean Sites format using a Perl script that we have developed. From there, variables names are unique, correspond to an international format. The system also allows to conserved three versions of each parameter: raw, calibrated (as sensors return from calibration) and adjusted, along with quality control flags.

Calibration Procedure

Two issues arise when using SBE43 oxygen sensors. First, electrochemical sensors generally exhibit a sensor response time of several seconds, which describes how long it takes a sensor to equilibrate with its surroundings as oxygen diffuses across its membrane. SEABIRD suggests modelling this as the following function of pressure (P) and temperature (T):

$$\tau=\tau 20\times e^{[d1\times p+d2\times(t-20)]}$$

$\tau 20$ is the response time at 20°C and atmospheric pressure. $\tau 20$, d1 and d2 are coefficients given by Seabird after the laboratory calibration of the sensor.

Second, electrochemical oxygen sensors that experience the high pressures of full depth sampling (P>1000 dbar) exhibit a noticeable hysteresis, with oxygen sensors voltages during descent sometimes considerably higher than voltages at the same pressures during ascent.

The procedure of post-cruise CTD-O2 calibration based on chemical (Winkler) measurements follows Uchida et al (2010), from WOCE/GOSHIP (http://cchdo.ucsd.edu/manuals.html). Each step of the post-cruise calibration is graphically represented figure 2. The key step is an adjustement of the initial calibration coefficients provided by Seabird from either pre-cruise or post-cruise sensor calibration by minimizing the differences between SBE43 and Winkler data. We developed our own set of Matlab routines, based on an initial code developed by the PMEL (Pacific Marine Environmental Laboratory).

The process thus takes place in four successive stages:

Step 1: Merging chemical Winkler data with CTD

Simple in principle, this step may be long as we merge data of different nature – chemical data from a hand-filled excel sheet by the chemist with CTD data from automated procedure.This important step includes formatting and typo corrections.

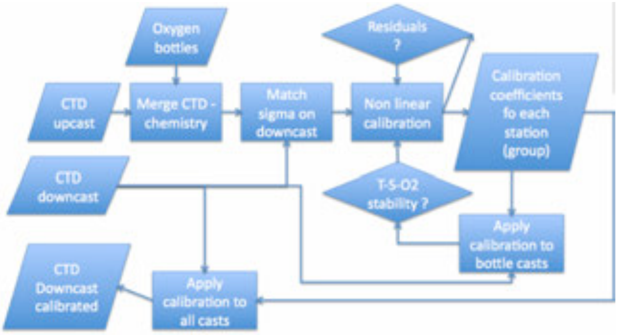


Figure 2: Calibration process for SBE-43 dissolved oxygen sensor for the BIFURCATION-2012 cruise

Step 2: Density adjustment

The CTD group at PMEL suggest to do the minimization only on the downcast profile to avoid hysteresis issues, and to correct for vertical motion of isopycnals due to internal waves between downcast and upcast by adjusting each up-cast bottle pressure so that its potential density matches the downcast potential density (Uchida et al, 2010). Down-cast O2-CTD values are adjusted to (up-cast) Winkler data using an hybrid equation from models of Owens-Millard (1985) and Murphy et al. (2008) to calculate and calibrate the SBE-43 sensor oxygen. The equation used for oxygen sensor calibration thus follows:

$$O_2 = (1+a\times istat)\times S_{oc}\times(V+V_{off}+\tau_{20} * e^{(d1\times p+d2\times t)}\times dVdt)\times Os\times e^{[tcor\times t]}\times e^{[pcor\times p/_{[273,15+t]}]}$$

- istat: station number
- A: linear dependency upon station number
- O_2: the calculated CTD oxygen
- O_s: the oxygen saturation, calculated from Garcia and Gordon (1992) formula.
- V: the oxygen voltage, and dVdt its temporal derivative
- p the pressure, and t the temperature
- d_1, d2, S_{oc} , V_{off}, τ20, tcor and pcor: initial values of pre-cruise sensor calibrations performed at SEABIRD (table 3), then adjusted by minimisation to bottles data during the calibration process.

	Calibration date	soc	voffset	E	T20	Tcor	D1	D2
s/n 68	27/03/2012	0.5198	-0.5092	3.6000e-002	1.42	-0.0019	1.92634e-004	-4.64803e-002
s/n 1337	14/03/2012	0.4291	-0.7091	3.6000e-002	1.37	-0.0019	1.92634e-004	-4.64803e-002

Table 3: Pre-calibration coefficients for the primary (s/n 68) and auxiliary (s/n 1337) circuits of SBE43 dissolved-oxygen sensor at their calibration dates – source: SEABIRD Electronics, Washington

Step 3: Iterative optimization of oxygen equation coefficients

Differences between data bottles and adjusted CTD data are minimized by groups of stations, using a non-linear non-forced optimization algorithm. After that, the residuals (ctd-bottles) are calculated, and those exceeding 2.8 standard deviation are tagged as outliers, removed (Millard, 1993) and the minimisation is iterated, until the entire removal of residuals exceeding 2.8 standard deviation.Several options are possible for this optimization. To remove an initial linear trend in the residuals due to the evolution of the sensor itself, we introduced a linear dependency of the station number. On some cruises, it is necessary to divide this optimization for subgroups of stations.

Step 4: Filtering of final data by vertical interpolation if necessary

The coefficients of the non-linear equation of calibration obtained at the end of step 3 are applied to the entire *downcast* CTD profile. A visual comparison with the corresponding *upcast* CTD profile and others surroundings profiles allows obvious error detection. Downcast oxygen profiles are finally cleaned up and quality flags are attributed for each data. Potential spikes visible in the descent profile, obviously linked to an electronic problem, are removed and the profile is vertically interpolated. Data which may have been interpolated on more than 2 dbar are flagged with Qc=6 ; Qc =2 is attributed for well-calibrated oxygen data (WHP flags).

At the end of the calibration procedure, calibrated and flagged CTD-O2 data are stored in a Matlab file before being converted to the OceanSites netCDF format (and flags). Graphic representations give, station by station the vertical variations of temperature, salinity and oxygen versus pressure.

Results

Chemical data

11 bottles samples at each station provide regular samples along the water column between 2000 meters and the surface (table 2). Duplicates bottles gives an estimate of the analytical error, which is 0.96 umol/kg (DOE) within GO-SHIP standards. Two technical problems occurred: the bottle 5 at station 8 with a broken nylon and oxygen dubious value; and the bottles 12 and 13 at station 23 were leaking as they arrived on deck.

Density adjustment

The pressure differences between the downcast-CTD and upcast-bottles sigma-matched pressures can reach 30m, with no particular dependency on depth or station number (figure 3, right panels). The associated shifts in oxygen are of order 5 umol/kg and are smaller than those at constant pressure (compare blue and red circles on **figure 3**, right panels).

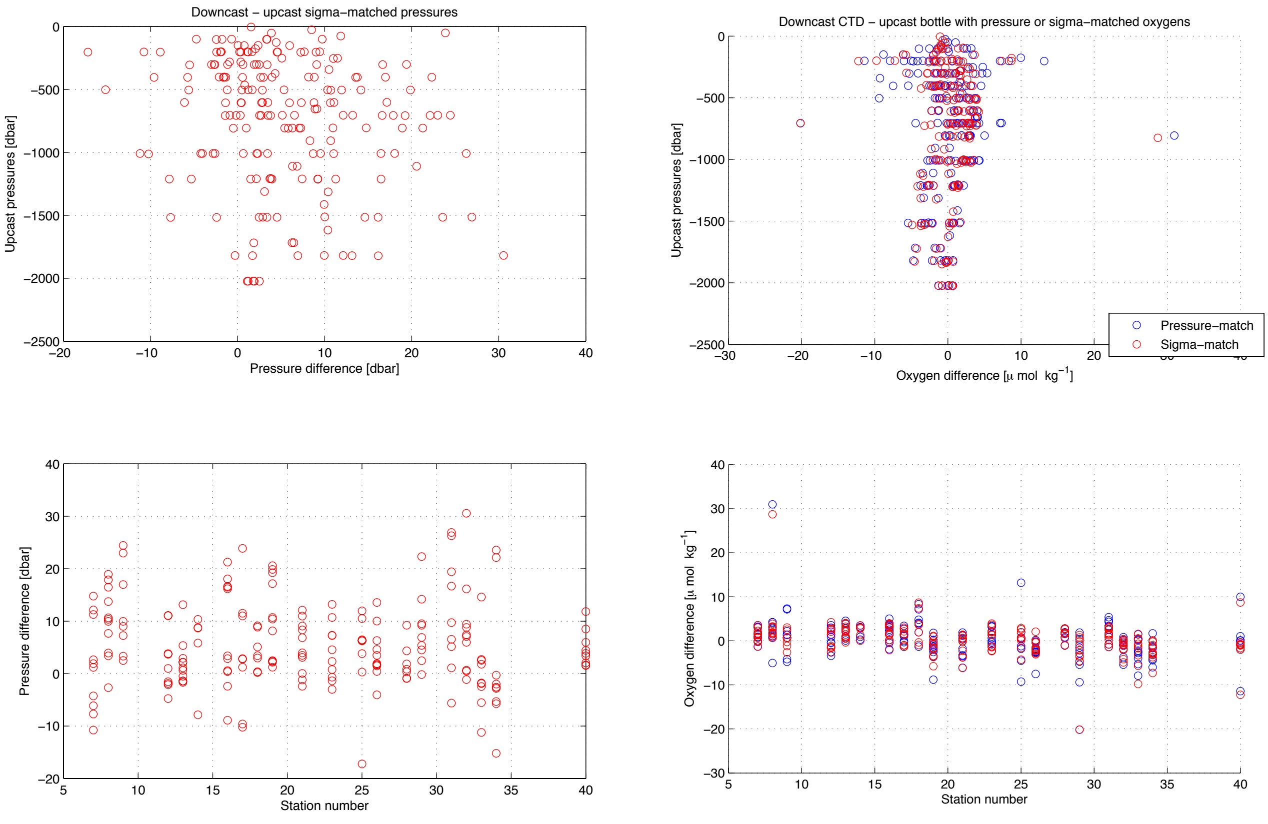


Figure 3: (left): Pressure differences (dbar) between downcast CTD-upcastBottle sigma-matched pressures, function of depth (top) and function of station number (bottom). (Right): Associated oxygen corrections (in umol/kg)

Minimizing the differences

To obtain the best fit, a linear dependency upon station number had to be introduced because a first trial indicated a trend in the residuals during the cruise. Figure 4 shows the residuals Oxygen (CTD-Winkler) after calibration: the total rms is close to 1.7 umol/kg. For this cruise, a global set of calibration coefficient was adapted without need for calibration by station subsets. Figure 5 shows a typical profile, with Winkler oxygen superimposed. The iterative procedure pointed to 6 outliers in the chemical data, which were flagged as such, out of a total of 195 samples.

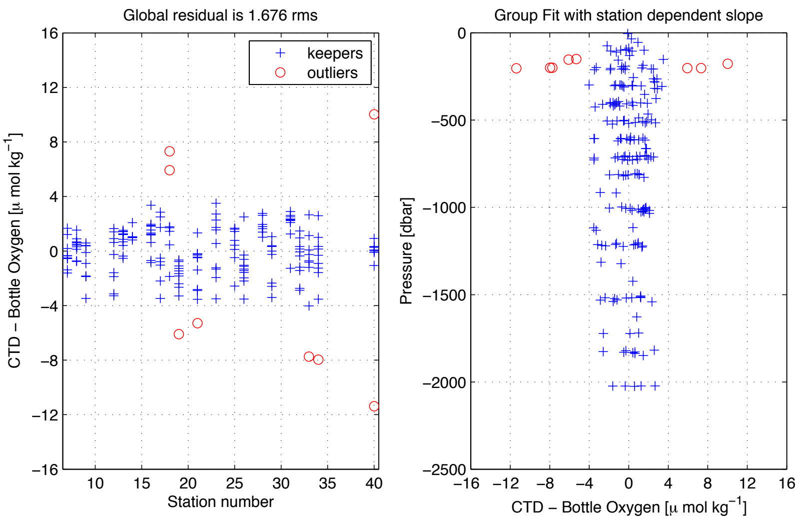
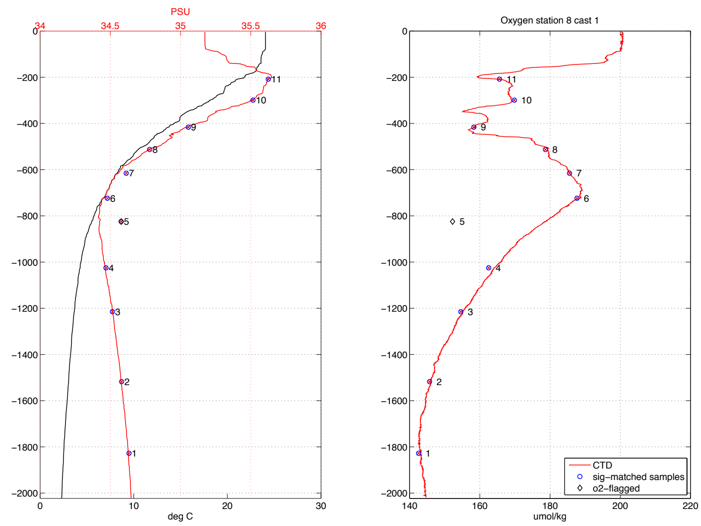


Figure 4: Oxygen residuals obtained at the end of the calibration procedure as a function of station number (left) or depth (right). Red circles indicate samples that were identified and flagged as outliers through the procedure (those are not used in the calibration).
Figure 5: (Left): Calibrated temperature/salinity with bottle salinities superimposed and (Right): Calibrated CTD Oxygen with Winkler Oxygen superimposed after density match, for station 8. The sampling bottle number is indicated.
For this station, bottle 5 as flagged in both oxygen and salinity.

Figure 5: (Left): Calibrated temperature/salinity with bottle salinities superimposed and (Right): Calibrated CTD Oxygen with Winkler Oxygen superimposed after density match, for station 8. The sampling bottle number is indicated.
For this station, bottle 5 as flagged in both oxygen and salinity.



Conclusion

CTD-O2 calibration from hydrographic data remains a technically difficult and time-consuming procedure. Our system allows an optimization of the procedure, making best use of the international formats. We evaluate the engineer time needed for calibration to about 1 month/100 profiles with an adequate technical and scientific expertise on oxygen data. The codes and documentation are available on request to the research community.

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While most Argo floats are deployed by research vessels, some are also deployed by the sailing community, through ship-based non-governmental organization or trans-oceanic races. It allows poorly sampled areas with no regular shipping to be sampled. Sailors got also involved in oceanographic science activities. An example of float deployment is given here (see Poffa et al., this issue) in the case of the 2015 Barcelona World Race where eight floats were successfully deployed in the Atlantic Ocean between 24° and 44° south.

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