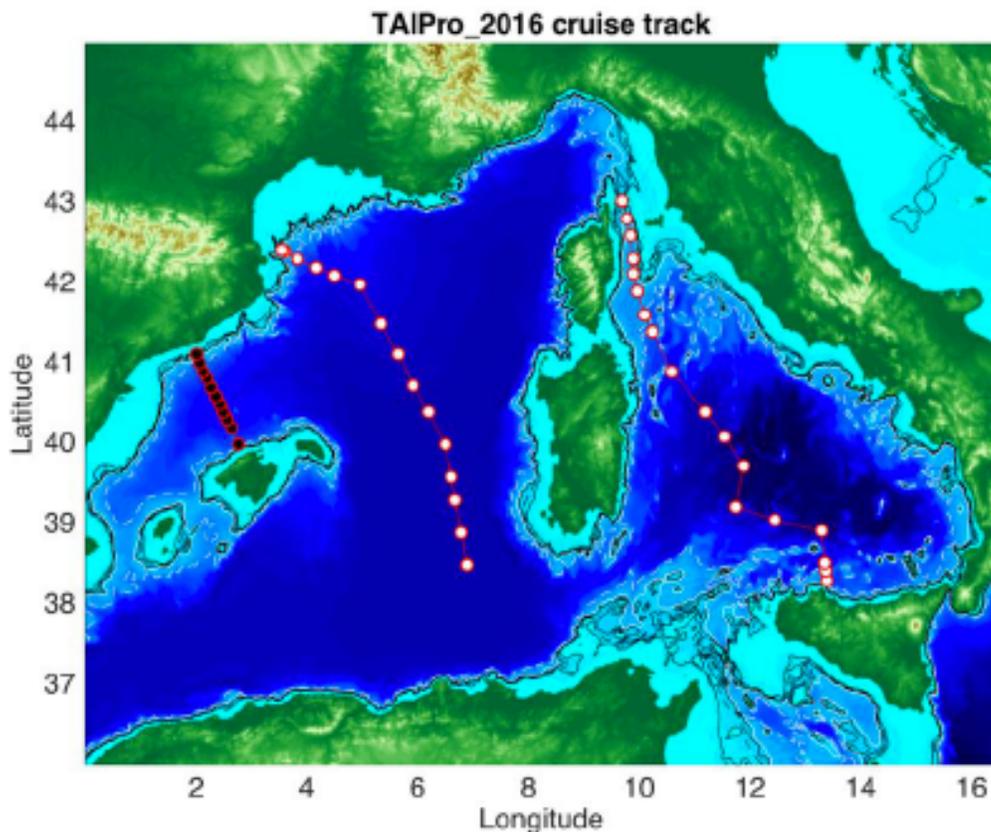


## CRUISE REPORT:

(Updated MAR 2020)



## Highlights

### Cruise Summary Information

Section Designation	<b>TAIPro-2016</b>		
Expedition designation (ExpoCodes)	<b>29AJ20160818</b>		
Chief Scientists	<b>Loïc Jullion / MIO</b>		
Dates	2016 AUG 18 - 2016 AUG 29		
Ship	RV Angeles Alvariño		
Ports of call	Palermo (Italy) – Barcelona (Spain)		
Geographic Boundaries	2.070000	43.050000	13.390000
		38.300000	
Stations	43		
Floats and drifters deployed	0		
Moorings deployed or recovered	0		

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EUROFLEETS2 Cruise Summary Report

**TAIPro-2016: A Tyrrhenian Sea & Alger-  
provençal component of the MedSHIP  
Programme**

RV Angeles Alvariño

18/08/16 – 29/08/16, Palermo (Italy) – Barcelona (Spain)

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**L. Jullion**

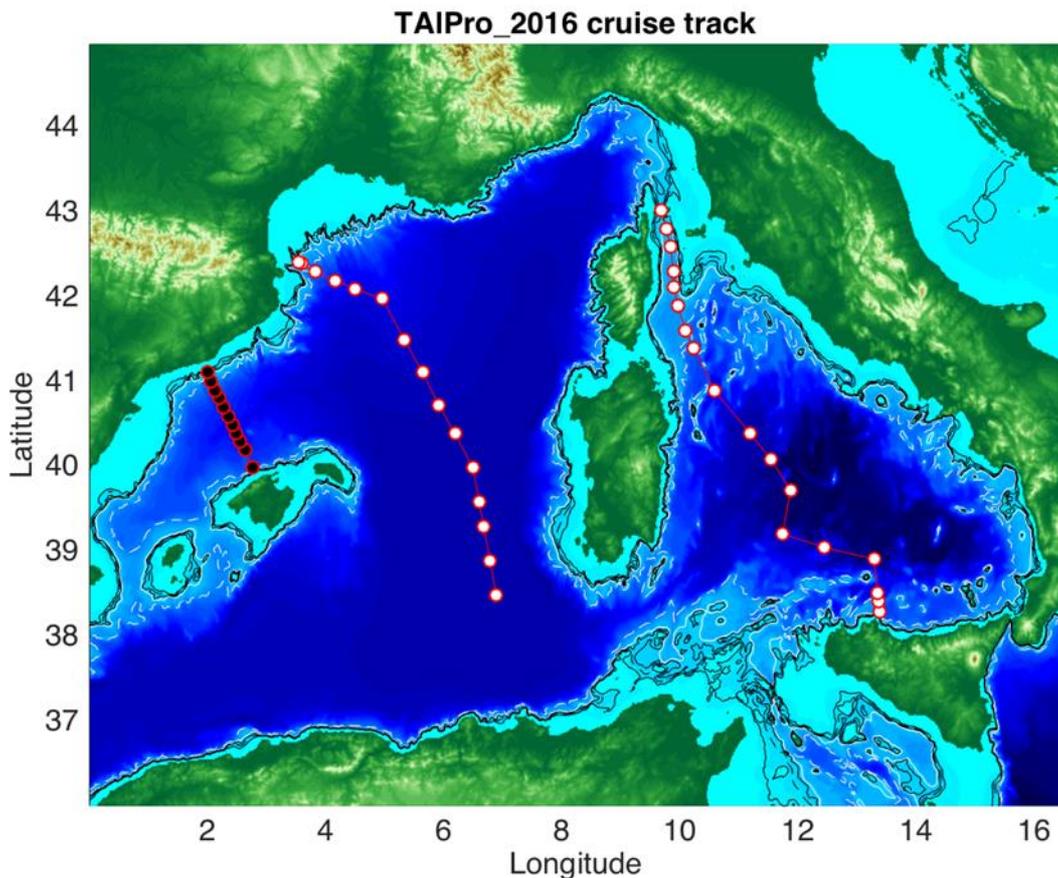
2016

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## 1 Summary

The TAIPro cruise (Palermo - Barcelona, RV Angeles Alvariño, 18/-8/2016 - 29/08/2-16) occupied three hydrographic transects across the Tyrrhenian Sea, the western Mediterranean Sea and the Catalan Basin (Fig. 1) as part of the MedSHIP programme (Mediterranean Ship-based Hydrographic Investigations Program). A total of 43 stations were occupied during which physical (temperature, salinity, pressure, velocity), biogeochemical (oxygen, nutrients, carbonate system, dissolved Barium, oxygen and nitrogen isotopes) and anthropic (CFCs, SF<sub>6</sub>) parameters were measured in order to monitor the physical and biogeochemical state of the Mediterranean Sea.



**Fig. 1:** Working area and cruise track of R/V Angeles Alvariño. Bathymetry from GEBCO

## 2 Research Programme/Objectives

The Mediterranean marine science community is committed to making regular surveys of the changing Mediterranean circulation. In the past, the Mediterranean has been sampled sporadically in time and space, mostly by national expeditions in regional waters. An outcome of the 43rd CIESM Workshop in 2012 was a recommendation for repeated oceanographic surveys of the Mediterranean in a programme called MedSHIP to observe the changing circulation in a manner similar to the international GOSHIP programme for the global ocean. The European Marine Board in its position paper "Navigating the Future IV" made creation of MedSHIP a priority for identifying climate change effects and aspects. Mediterranean marine

scientists have designed a plan involving 5 hydrographic sections (Figure 2) on which comprehensive physical and biogeochemical properties will be measured to highest international standards on a regular basis: there are 2 north-south sections in each of the eastern and western Mediterranean and a long, zonal section from the Strait of Gibraltar to the easternmost Mediterranean. There are 2 primary objectives for the MedSHIP repeat sampling:

First we want to observe the changes in physical and biogeochemical properties. The deep Mediterranean has low dissolved inorganic carbon to alkalinity ratio and low Revelle factor, being prone to accumulate more anthropogenic carbon than any other basin (Schneider et al., 2010, Álvarez et al., 2014), and we want to know how fast and where this carbon is being taken up. The salinity and temperature of the deep Mediterranean have been increasing with time, we want to document the changes and understand the processes that lead to the increasing salinity and temperature. Models suggest that stratification is increasing and oxygen concentrations are decreasing. We want to document these changes in the Mediterranean where the shorter turnover time scale suggest we can observe these climate changes more accurately over a shorter time scale than in the global ocean. Secondly we want to observe changes in the circulation. How often and how much deep water is formed. Are the currents changing in position and strength? In a broad sense the zonal section emphasises property changes while the north-south sections emphasise circulation changes, though in fact all sections contribute to both objectives. The overall plan is for the north-south sections to be done every 3 years and the zonal section to be done every 6 years. Tanhua et al. (2013) led the first zonal section through the Mediterranean. Last year in a proposal led by Schroeder, we proposed the entire MedSHIP programme in a single large proposal that was ultimately judged too ambitious to support. This year we are proposing to do the north-south sections in the eastern and western basins in 3 smaller proposals. As we stated at the outset, the Mediterranean marine science community is committed to regular, repeated MedSHIP sampling of the entire Mediterranean Sea.

TAIPro-2016 represents the Western Mediterranean basin component of the MedSHIP initiative (composed of three proposals submitted to the EUROFLEET call, CRELEV-2016 in the Eastern Mediterranean Sea led by Giuseppe Civitarese and Dimistris Velaoras and ESAW led by Miroslav Gacic and Giuseppe Civitarese). The cruise will occupy two meridional sections (Figure 3), one across the relatively flat and deep Algero-Provencal basin, and one across the deep and rugged Tyrrhenian Sea. The Algero-Provencal basin is the main site of Western Mediterranean Deep Water (WMDW) formation driven by intense air-sea heat loss in the northern part of the basin (Medoc Group, 1970). The Tyrrhenian Sea acts as a blender of various water masses originating from the Western and Eastern Basins (Roether and Lupton, 2011, Millot, 1999, Astraldi et al., 1996) and therefore plays an important role in the preconditioning of the water column leading to the formation of WMDW (Schroeder et al., 2010, Grignon et al., 2010). Fresh and warm Atlantic Water (AW) enters the Western Mediterranean Basin via Gibraltar as an eastward boundary current along the African coast referred to as the Algerian Current (Millot, 1985). This current, subject to strong mesoscale variability leading to the generation of long-lived anticyclonic eddies (Millot, 1999, Millot and Taupier-Letage, 2005), separates in a weak branch entering the Tyrrhenian Sea and a stronger branch

entering the Eastern Mediterranean basin through the Sicily Channel. The surface circulation along the northern slope of the Algero-Provencal basin is dominated by the Northern Current (Millot, 1999) characterized by a strong seasonal variability in its mesoscale activity. A return flow from the Eastern basin towards the Western one is made of warm and salty Levantine Intermediate Water (LIW). LIW crosses the Sicily Channel and is topographically constrained to veer north along the western coast of Sicily into the Tyrrhenian Sea.

### 3 Narrative of the Cruise

**Tuesday 16<sup>th</sup> August 2016.** Most of the science party arrived to Palermo, arriving from different European countries (France, Germany, Spain, Italy).

**Wednesday 17<sup>th</sup> August 2016.** Toste, Boie and Loïc met with the agent in charge of the logistics and the harbour master in order to clarify the authorisations needed by the ship in order to load and transport dangerous goods. The *RV Angeles Alvariño* did not have a certificate of carriage of dangerous goods and José the vessel manager, in collaboration with the agent, Antonello, had to work very hard to obtain a temporary certificate from Bureau Veritas. Finally, the harbour master authorised the loading of the lab container and of the boxes onto the ship. The rest of the science party joined us in Palermo.

**Thursday 18<sup>th</sup> August 2016.** Mobilisation day for the TAIPro cruise. Mireno, the Italian technician had to go and recover a profiling buoy that was cut loose east of Sicily. This is bad news since he was our only CTD technician. We hope he can join us later during the cruise. The different teams used this day to set up their equipment. The lab container and the boxes were finally loaded on the ship. The crew has to work hard to get the container ready to use. Some equipment seems to be missing in the oxygen boxes.

**Friday 19<sup>th</sup> August 2016.** Before departure, the second officer gave us a security briefing. The *RV Angeles Alvariño* set sail north around 10.00am local time. One hour later, we performed a trial station in order to practise CTD deployment/recovery and sampling. Contrary to most research vessels, the CTD operator is actually driving the winch (mainly in automatic mode). Warm weather and calm seas facilitated the work and gave some time for everybody to find their sea legs. First station arrived shortly after the test station. The oxygen team encountered some problems with the analysis.

**Saturday 20<sup>th</sup> August 2016.** Beautifully calm seas, warm weather. The CTD stations are now being occupied at a good pace and all the teams start to find their rhythm. The ship is sailing at 10-11 knots and we are ahead of schedule. The oxygen group is finally running some samples. At station 7, the alarm of the winch started ringing due to a problem with the break. This resulted in a 30 minutes stop at 617m in order to replace a component of the winch. Rest of the cast went smoothly. In the evening, the light of the ship attracted many squids that kept the crew busy trying to catch some of them (5 or 6 ended up on the aft deck thanks to Jaime, the bosun).

**Sunday 21<sup>th</sup> August 2016.** A severe wind storm is blowing over the gulf of lion and we are lucky to be shielded by Corsica and Sardinia. As we pass in front of the Bonifaccio strait around noon, we experience

the outer rim of the storm. On board instruments recorded wind gusts over 35 knots and the wave heights also increased significantly (about 2 meters). These conditions remained until the beginning of the evening. During station 11, the Seasave software used to record the CTD data froze during the upcast sound 400m while bottle 4 was fired. The reason remains unknown. The cast was aborted and since we are way ahead of schedule, we reoccupy the station.

**Monday 22<sup>th</sup> August 2016.** We finished the first leg of the cruise across the Tyrrhenian Sea around breakfast time and start the long (33h) steam toward the second leg. This break in the CTD allows the different teams to catch up on analysis and data QC. The transit around Cap Corse and the western Corsican coast offers some spectacular sceneries of the wild Corsican coast. The temperature in the chemistry lab where the salinometer had been set up is too high (33 degrees) for the analysis to give satisfactory results. The salinometer is moved to the transient tracer container on the aft deck. The air conditioning in the container maintains the temperature around 21 degrees.

**Tuesday 23<sup>rd</sup> August 2016.** Transit toward the second leg continued for most of the day. The first station of the second leg (no 19) was reached around 18h00 local time. The CTD data from the first leg are processed and the first sections of temperature and salinity produced. In the afternoon, Toste spotted a falcon circling around the ship. Wild life spotting has been scarce so far.

**Wednesday 24<sup>th</sup> August 2016.** The second leg continued. Due to the time gained during the first leg, two additional stations were added to the original plan. We now have a regular spacing of 20-25 miles between stations.

**Thursday 25<sup>th</sup> August 2016.** The end of the leg is approaching. Thanks to the automated winch, the nice weather and the absence of significant problems, the cruise is 24 ahead of schedule. An additional leg (6 stations in total) was added between Mallorca and Barcelona. During the afternoon, we sailed by the MeteoFrance weather buoy and several sperm whales, dolphins and one fin whale were spotted. The sea is remarkably calm. The final 4 stations of the leg were completed during the night.

**Friday 26<sup>th</sup> August 2016.** The last station of the 2nd leg was finished around 4.00am and the ship started its transit toward Mallorca (14h). We are going to sample the Northern Current at high resolution (6-7 nautical miles between stations). Most of the cast will be physics only with the exception of dissolved barium which will be sampled at every station and transient tracers which will be sampled at every other station.

**Saturday 26<sup>th</sup> August 2016.** CTD operations continued smoothly. The last station near Barcelona was finished around 19.00. An end-of-the-cruise barbecue on the aft deck was organised by the cook to celebrate a very successful cruise.

## **4 Conductivity-Temperature-Depth (CTD) measurements**

### *4.1 CTD setup, configuration and operations*

A total of 43 CTD casts were completed on this cruise, numbered by station (Section 7). The sensor configuration was as follows:

- Sea-Bird *9plus* underwater unit, s/n: 09P-0869
- Frequency 0 - Sea-Bird 3 Premium temperature sensor, s/n: 5604
- Frequency 1 - Sea-Bird 4 conductivity sensor, s/n: 4124
- Frequency 2 - Digiquartz temperature compensated pressure sensor, s/n: 1090
- Frequency 3 - Sea-Bird 3 Premium temperature sensor, s/n: 5573
- Frequency 4 - Sea-Bird 4 conductivity sensor, s/n: 4125
- V0 - Sea-Bird 43 dissolved oxygen sensor, s/n: 2285
- V2 - Benthos PSA-916T 7Hz altimeter, s/n: 56156
- V4 - WET Labs ECO-AFL/FL Fluorometer, s/n: FLNTURTD-2526
- V6 - WETLabs Light Scattering sensor, s/n: FLNTURTD-2526

Ancillary instruments & components were:-

- Sea-Bird *11plus* deck unit, s/n
- Sea-Bird 24-position Carousel
- RDI WorkHorse Monitor 300KHz ADCP (upward-looking)
- RDI WorkHorse Monitor 300KHz ADCP (downward-looking)
- 24 x Ocean Test Equipment ES-12L water samplers,

All sensors were calibrated in May 2016. The configuration file used for the cruise (1090\_BO-AA\_May\_2016\_OK.con) is shown in appendix. The rosette was equipped with 24 12l Niskin bottles. The spring were located outside the bottle. The CTD package was deployed on the starboard side of the ship. The winch during the downcast and the upcast is operated by the CTD operator. This step is mainly automatised. A target depth (wire length) is specified and once this depth has been reached, the CTD operator can take control of the winch to drive the CTD to the desired depth above the seafloor (10m). The rosette is equipped with a sonar altimeter which intercept the bottom 70-50 meters before getting to it. The altimeter is used just for safety, to avoid the rosette to touch the bottom, and for more precision in measuring depth. On the upcast, the winch is set in automatic mode and the CTD operator presses the stop button at each targeted depth. Near the surface, between bottle 2 and the surface, the winch is also operated in manual mode for security reason. During deployment and recovery the winch is controlled by the crew.



**Fig. 2:** *Rosette deployment*

#### 4.2 *CTD data processing*

The vertical profiles of all parameters were obtained by sampling the signals at 24 Hz, with the CTD/rosette going down at a speed of 1 m/s. The data were processed on board by using the SBE Data Processing software as follows: data conversion, alignment of CTD, cell thermal mass correction, computing of derived variables, low-pass filtering, bin averaging and splitting of downcast and upcast.

#### 4.3 *CTD data calibration*

Conductivity data from the CTD sensors will be calibrated after the cruise using the conductivity measurements obtained from water samples collected at each cast and analysed with a salinometer (see section 6.1). Oxygen data will be calibrated against water samples analysed on board (section 6.2).

### **5 Lowered Acoustic Doppler Current Profiler (LADCP)**

Two Lowered Acoustic Doppler Current Profilers (LADCP) are used to measure velocity and magnitude of the currents during the CTD cast. They are two RDI Workhorse 300 kHz ADCP, a master facing down and a slave facing up (Fig. 3). For data post-processing we used the LDEO LADCP (version 10.16) software.

The LADCPs were deployed for each cast. Apart from the first station during which the LADCPs did not record any data, no major problems were reported and 42 profiles were recorded.

**Fig. 3:** *Slave (upward looking) and master (downward looking) LADCP set up on the rosette*



## 6 Discrete Water Sample Analyses

### 6.1 *Salinometry*

Water samples were taken at each station in order to measure conductivity and to identify any bias or drift in the salinity sensors. Standard sample procedure was used. Conductivity was measured with a Guildline Autosol 8400B. Once collected the samples were brought in the room hosting the salinometer to give them time to adjust to the room temperature. Indeed, the room temperature is a critical part of the measurement. The temperature of the water in which the conductivity cell is bathed must be as close as possible from the room temperature and needs to be around 21 degrees for optimal results.

Originally, the salinometer was set up downstairs in the biology lab below the aft deck. However, boiling temperature (around 30 degrees) resulted in the inability to accurately standardise the instrument (using IAPSO standard sea water). It was decided to move the salinometer in the transient tracer container on the aft deck, the only part of the labs with a decent temperature control system. After about 24hours, the bath temperature was down to 22 degrees and the backlog of samples was analysed rapidly. The instrument is standardise at the beginning and the end of a set of measurements. For each sample, 3 readings of the conductivity ratio were taken (or as many samples as needed to obtain a sufficient stability).

### 6.2 *Dissolved Oxygen and Nutrients*

### 6.3 *Carbonate system parameters (Marta Álvarez, Mónica Castaño, Iraia Rodríguez)*

#### 6.3.1 *pH determination*

Spectrophotometric pH in seawater was measured following Clayton and Byrne (1993) at most of the stations and depths along the two main sections during the TalPro cruise and reported at 25°C and on the Total scale, hereinafter pH25T. No samples were taken at station 8 due to a lab collapse, see Table 4.

Sampling

pH was sampled after Dissolved Inorganic Carbon (DIC), which was also immediately taken after dissolved oxygen and the tracers, when sampled. Samples were collected in cylindrical optical glass 10-cm pathlength cells, which were filled to overflowing and immediately stoppered. After sampling the cells are immediately stabilised at 25°C.

Analytical method.

Seawater pH was measured using a double-wavelength spectrophotometric procedure (Byrne, 1987). The indicator was a solution of m-cresol purple (Sigma Aldrich) prepared in seawater (2 mM) and maintained at dark and with not air contact. All the absorbance measurements were obtained in the thermostatted (25±0.2 °C) cell compartment of a BECKAM COULTER DU-800 single beam spectrophotometer. The temperature was controlled with a JULABO F12 ED (12L) thermostatic bath.

After blanking with the sampled seawater without dye, 50 µl of the dye solution were added to each sample using an adjustable repeater pipette (Eppendorf Multipette plus). The absorbance was measured at three different fixed wavelengths (434, 487.6, 578 and 730 nm), pH, on the total hydrogen ion concentration scale, is calculated using the following formula (Clayton and Byrne, 1993):

$$\text{pH}_T = 1245.69/T + 3.8275 + (2.11 \cdot 10^{-3})(35-S) + \log((R-0.0069)/(2.222-R \cdot 0.133))$$

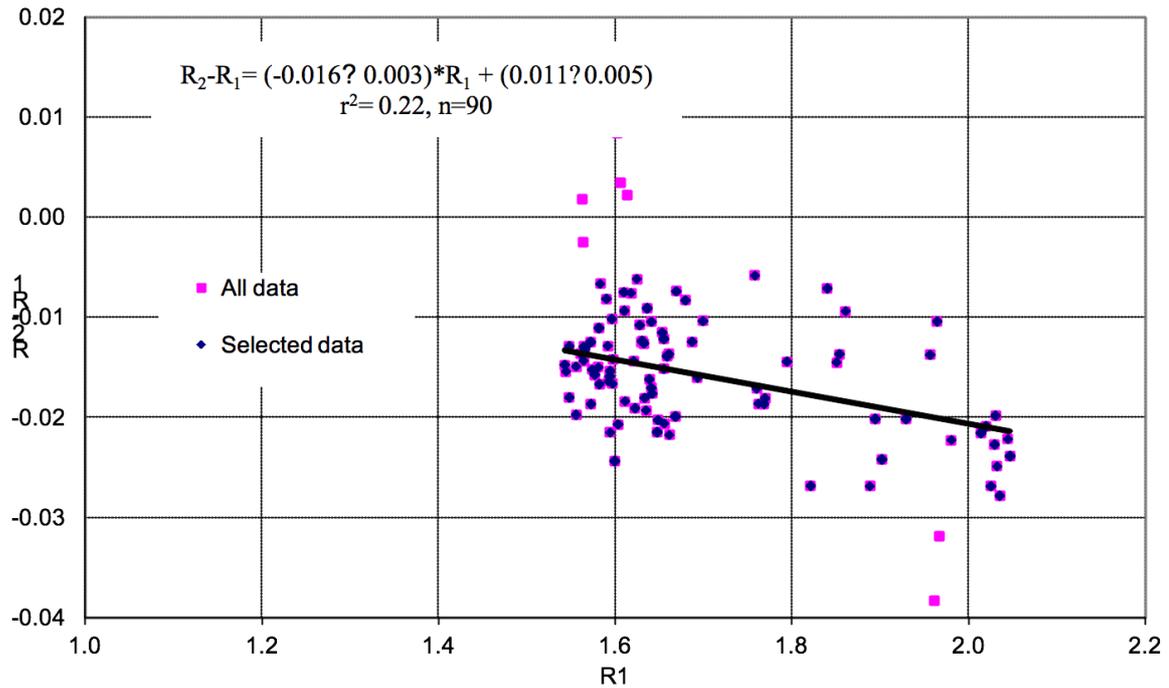
where R is the ratio of the absorbances (A) of the acidic and basic forms of the indicator corrected for baseline absorbance at 730 nm ( $R = (578A-730A) / (434A-730A)$ ), T is temperature in Kelvin scale and S is salinity.

As the injection of the indicator into the seawater perturbs the sample pH slightly, the absorbance ratios measured in the seawater samples ( $R_m$ ) should be corrected to the R values that would have been observed in an unperturbed analysis ( $R_{\text{real}}$ ). In order to do this, we obtain the correction in the absorbance ratio of every sample as a function of the absorbance ratio measured ( $R_m$ ). This linear function was calculated from second additions of the indicator over samples with a wide range of pH:

$$R_{\text{real}} = R_m - (-0.016 \pm 0.003 \cdot R_m + 0.011 \pm 0.005); \quad r^2 = 0.23, \quad n=90$$

This function also corrects for deviations in the linear relationship between absorbance and the indicator concentration; i.e., deviations from the Beer Law in the spectrophotometer. Figure 4 shows the relationship between the first addition ratio ( $R_1$ ) and the  $\Delta R$  ( $R_2 - R_1$ ) for the set of double additions over a range of R, equivalent to pH.

All the pH measurements are referred to 25°C and corrected for the addition of the indicator using the former formula. The magnitude of that correction over our range of pH is small ranging from 0.004 to 0.005 pH units, which are added to the uncorrected pH values.



**Figure 4.** Perturbation of sample pH induced by addition of indicator, expressed as DR ( $=R_2 - R_1$ ) as a function of  $R_1$ .  $R_1$  is the first addition and  $R_2$  the double addition. R is the ratio between absorbances ( $(578A - 730A)/(434A - 730A)$ ).

#### Accuracy.

In order to check the precision of the pH measurements, samples of CO<sub>2</sub> reference material (CRM, batch 147 distributed by A.G. Dickson from the Scripps Institution of Oceanography, SIO) were analyzed during the cruise. Just twice during the two weeks cruise, due to lack of time, ten to fifteen samples from a CRM bottle (batch 147, certified chemical characteristics for salinity, 33.427; silicate, 2.4  $\mu\text{mol kg}^{-1}$ ; nitrate, 0.36  $\mu\text{mol kg}^{-1}$ ; nitrite, 0.00  $\mu\text{mol kg}^{-1}$ ; phosphate, 0.33  $\mu\text{mol kg}^{-1}$ ; total alkalinity,  $2231.39 \pm 0.72 \mu\text{mol kg}^{-1}$ ; and total inorganic carbon,  $2014.52 \pm 0.57 \mu\text{mol kg}^{-1}$ ) were drawn carefully to avoid bubbles and analysed for pH using the spectrophotometric method. The corresponding theoretical pH<sub>25T</sub> value for this batch using the dissociation constants from Mehrbach *et al.* (1973) refitted by Dickson & Millero (1987) is 7.9195.

The two series of CRMs measurements analysed for pH are shown in Table 1. Our pH measurements are lower than the theoretical value and should be increased in  $0.0962 \pm 0.0012$  pH units without taking into account the 08/04 values. We will discuss this point at the end of this report.

Date	pH25T	STD	N	pH diff
23/08/2016	7.9165	0.0008	11	-0.0031
27/08/2016	7.9135	0.0018	12	-0.0060

**Table 1.** Mean and standard deviation (STD) values for the CRM batch 147 determinations on pH. N stands for the number of measurements and pH diff is the difference with the theoretical value using the Mehrbach et al. (1973) refitted by Dickson and Millero (1987) CO<sub>2</sub> constants.

### Reproducibility

Regarding the reproducibility of our measurements, just twice during the cruise due to time restrictions, we analysed several samples collected from the same Niskin bottle (Table 2). The mean of the STD is  $\pm 0.0015$  which could be considered as the reproducibility of pH measurements during the cruise.

Date	Station	Niskin	Pressure	Salinity	pH25T	STD	N
22/08/2016	18	2	450	38.675	7.8972	0.0012	5
26/08/2016	34	2	505	38.577	7.8761	0.0018	4

**Table 2.** Characteristics of the replicate samples taken along the cruise, the mean and standard deviation (STD) and number of cells collected from each bottle for the pH analysis.

### 6.3.2 Alkalinity determination

Total Alkalinity (TA) along the TalPro cruise was analysed following a double end point potentiometric technique by Pérez y Fraga (1987) further improved in Pérez et al. (2002). This technique is faster than the whole curve titration but comparable (Mintrop et al., 2000).

### Sampling.

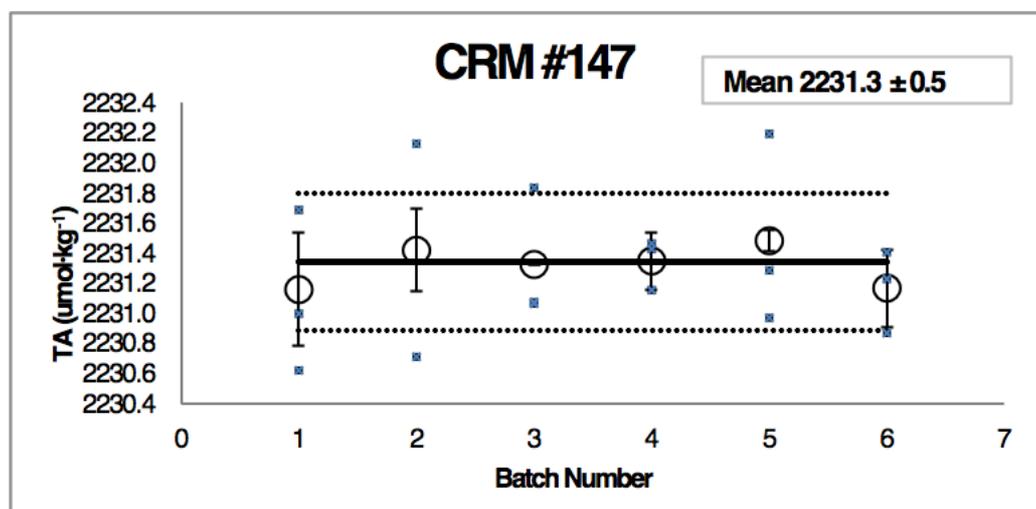
Seawater samples for TA were collected after pH samples, in 600 ml borosilicate bottles and stored in the laboratory until analysis, usually no later than 2 days. Samples were filled to overflowing and immediately stopped. Every other station was sampled for TA. No samples were taken at station 8 due to a lab collapse, see Table 4.

### Analytical Method

TA was measured using an automatic potentiometric titrator "Titrande 908 Metrohm", with a Metrohm Aquatrode Plus combination glass electrode and a Pt-1000 probe to check the temperature. The system is coupled with a 10 mL burette or exchangeable unit. Potentiometric titrations were carried out with hydrochloric acid ( $[HCl] = 0.1\text{ N}$ ) to a final pH of 4.40 (Pérez and Fraga, 1987). The electrodes were standardised using an ftatalate buffer of pH 4.41 made in  $CO_2$  free seawater (Pérez *et al.*, 2002). Concentrations are given in  $\mu\text{mol kg}^{-1}$ . Table 3 shows the value of the asymmetrical pH (pHas), which is the value of the electrode pH after its calibration. The 0.1 N hydrochloric acid was prepared mixing 0.5 mol (18.231 g) of commercially HCl supplied by Riedel-deHaën® (Fixanal 38285) with distilled water into a graduated 5-L beaker at controlled temperature conditions. The HCl normality is exactly refereed to 20°C. The variation of salinity after the titration is lower than 0.1 units, which is taken into account in the final TA calculation.

### Accuracy

CRM analyses were performed in order to control the accuracy of our TA measurements (Figure 5). Accordingly, the final pH of every batch of analyses was corrected to obtain the closest mean TA on the CRM analyses to the certified value. Table 3 shows the pH (DpH) correction applied to each batch and the mean value of the CRM determinations after applying the former correction.



**Figure 5:** Alkalinity ( $\mu\text{mol kg}^{-1}$ ) measurements on the CRM batch 147 during the cruise against batch number. The final mean and standard deviation (STD) for the 17 determinations was  $2231.3 \pm 0.5 \mu\text{mol kg}^{-1}$

Usually, each sample is analysed twice for alkalinity. Table 3 shows the average standard deviation of the replicates analysed during each batch of analysis. This difference was about  $1.0 \mu\text{mol kg}^{-1}$ . In order to check the precision of the TA measurements, atlantic surface seawater filtered and stabilized in our lab was used as a “quasi-steady” seawater substandard (SB). It consists in surface coastal seawater near IEO A Coruña filtered and stored in the dark into a large container (30 L) during 2 days before use.

This standard seawater was analyzed at the beginning and at the end of each batch of analyses to control the drift in the analyses for each batch. The estimated drift for each day was very low.

Batch	Aug 2016	Stations	N <sub>HCl</sub>	ΔpH	Fitted TA	Av. Dif.
1	20	2, 4, 6	0.099968307	0.012	2231.16±0.46(4)	0.75
2	21	7, 9	0.099968307	0.040	2231.42±1.00(2)	0.66
3	22	10 - 18	0.099968307	0.027	2231.33±0.44(3)	0.68
4	24	19,20,21,22,23	0.099968307	0.016	2231.35±0.17(3)	0.70
5	25	25, 26, 27, 28	0.099968307	0.029	2231.48±0.64(3)	0.53
6	26	29, 30, 31, 32, 33	0.100113611	0.060	2231.17±0.27(3)	0.57

**Table 3.** Alkalinity analysis supplementary information for each batch of analysis: N<sub>HCl</sub> is the normality referred to 20°C of the hydrochloric solution used; ΔpH is the pH correction applied to refer the TA determinations on the CRM to the corresponding nominal value (batch 147 with a certified TA of 2231.39±0.72 μmol kg<sup>-1</sup>). The mean value of the TA measurements on the CRM samples is also shown (Fitted TA±standard deviation (number of analysis)). The average of the difference (Av. Dif.) in the duplicate's analyses is shown.

### Reproducibility

Just once during the cruise we analysed several samples collected from the same Niskin bottle (Table 4). The STD is ±1 μmol kg<sup>-1</sup> which could be considered as the reproducibility of TA measurements during the cruise.

Date	Station	Niskin	Pressure (dbar)	Salinity	TA mmol kg <sup>-1</sup>	STD	N
22/08/2016	18	3	404	38.681	2602.6	1.04	9

**Table 4.** Characteristics of the replicate samples at station 18, the mean and standard deviation (STD) and number of analysis performed from each bottle for the TA analysis.

### 6.3.3 Carbonate ion concentration

The carbonate ion concentration (CO<sub>3</sub><sup>2-</sup>) was determined spectrophotometrically following the recent method first proposed by Patsavas et al. (2015), after the works by Yao and Byrne (2008) and and Easley et al. (2013).

#### Sampling.

CO<sub>3</sub><sup>2-</sup> was sampled after TA. Samples were collected in cylindrical optical quartz 10-cm pathlength cuvettes, which were filled to overflowing and immediately stoppered. After sampling the cells are immediately stabilised at 25°C. Using the same incubator as for the pH cells. The same sampling scheme was followed for TA, DIC and CO<sub>3</sub><sup>2-</sup> so as to have both an overdetermined CO<sub>2</sub> system and a good spatial (vertically and latitudinal) coverage, see Table 4..

#### Analytical method

The concentration of CO<sub>3</sub><sup>2-</sup> in seawater was measured using the method proposed by Patsavas et al. (2015). A solution of 0.022 M of the titrant Pb(ClO<sub>4</sub>)<sub>2</sub> (Fisher Scientific, 99.99% purity dissolved in distilled water) is added to the seawater sample, the complex PbCO<sub>3</sub> formed afterwards is detected spectrophotometrically in the UV spectra. All the absorbance measurements were obtained in the thermostatted (25±0.2°C) cell compartment of a BECKAM COULTER DU-800 single beam spectrophotometer. The temperature was controlled with a JULABO F12 ED (12L) thermostatic bath.

After blanking with the sampled seawater without the lead solution, 20 µl of the dye solution were added to each sample using an adjustable repeater pipette (Eppendorf Multipette plus). The absorbance was measured at three different three wavelengths (234, 250 and 350 nm), 234 nm is the isosbestic point, 250 nm is the mean value of the wavelengths presenting high absorbance variation and 350 nm is a non-absorbing wavelength..

Total carbonate ion concentration is given by:

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

where R is the ratio of the absorbances (A) ( $R = (250A-350A) / (234A-350A)$ ),  $\text{CO}_3\beta_1$  is the PbCO<sub>3</sub> formation constant, and  $e_i$  are the molar absorptivity ratios dependent on salinity. The fitting parameters are taken

from Patsavas et al. (2015). Small deviations from fitting temperature 25°C (maximum 1.5°C) are corrected using the equation from Fajar (2013) where T is temperature in °C:

$$[\text{CO}_3^{2-}]_T / [\text{CO}_3^{2-}]_{25} = -(0.033 \pm 0.001) \cdot (T-25) + (1.007 \pm 0.002)$$

As determined in Patsavas et al. (2015) the titrant-induced perturbation of the R term is given as follows:

$$\log(\text{Rp}-\text{Ri}) = -17.6664 \cdot \text{Rp}^2 + 19.8995 \cdot \text{Rp} - 7.7324$$

being Rp the perturbed (measured) absorbance ratio and Ri the initial one.

### Reproducibility

Regarding the reproducibility of our measurements, twice along the cruise when time was available, we analysed several samples collected from the same Niskin bottle (Table 3). The STD is  $\pm 6$  mmol/kg (2.3% precision) which could be considered as the reproducibility of  $\text{CO}_3^{2-}$  measurements during the cruise.

Station	Niskin	Pressure (dbar)	Salinity	$\text{CO}_3^{2-}$	STD	N
18	2	450	38.675	221.7	4.4	4
34	4	500	38.576	236.0	6.8	4

**Table 5.** Characteristics of the replicate samples taken, the mean and standard deviation (STD) and number of cells collected from each bottle for the  $\text{CO}_3^{2-}$  analysis, concentrations in  $\mu\text{mol/kg}$ .

#### 6.4.4 Dissolved Inorganic Carbon (DIC)

DIC samples were analysed with a VINDTA 3D system (www.MARIANDA.com), briefly seawater  $\text{CO}_2$  was extracted adding phosphoric acid, followed by coulometric detection (Johnson et al., 1993).

### Sampling

Seawater samples for DIC were collected after transient tracers and oxygen samples, in 500 ml borosilicate or 200 ml topaz bottles, on availability. Samples were rinsed and filled smoothly from the bottom, overflowing the water by at least a half bottle volume. A headspace of 1% of the bottle volume is left. Samples were left at room temperature in the dark until analysis, maximum 3 days after sampling. Table 6 shows the selected stations for the DIC samples. A total of 153 seawater samples for DIC were analysed on board (Table 6).

### Analytical method

Samples for DIC were analysed with a device called VINDTA 3D coupled to a UIC 5011 coulometer. The VINDTA 3D 075 was designed by the company Marianda. An exact volume, ~20 mL, of

the sample is acidified with H<sub>3</sub>PO<sub>4</sub> on a stripping chamber, the generated CO<sub>2</sub> is carried into a coulometer cell by a free-CO<sub>2</sub> gas, pure N<sub>2</sub>, where the coulometrical titration is performed (Johnson et al., 1993). In the coulometer cell, the acid (hydroxyethylcarbamic acid) formed from the reaction of CO<sub>2</sub> and ethanolamine is titrated coulometrically (electrolytic generation of OH<sup>-</sup>) with photometric endpoint detection. The product of the time and the current passed through the cell during the titration (charge in Coulombs) is related by Faraday's constant to the number of moles of OH<sup>-</sup> generated and thus to the moles of CO<sub>2</sub> which reacted with ethanolamine to form the acid.

#### Accuracy

No calibration unit is available for our VINDTA 3D. Therefore, no independent method to check the accuracy was available. Certified Reference Material (CRM) of CO<sub>2</sub> analyses were performed in order to control the accuracy of DIC measurements. In every DIC batch of analysis, CRM #147 provided by Dr. Andrew Dickson were analysed.

The ratio between the nominal value (2014.52±0.57 μmol/kg) and measured value of CRM was the calibration factor (CALFAC). The CALFAC was used to correct small drifts. The CALFAC was calculated for each newly born.

Station	DIC	pH25T	TA	CO32-
<b>1</b>				
<b>2</b>	12	12	12	11
<b>3</b>				
<b>4</b>		21	21	19
<b>5</b>		17		
<b>6</b>	20	20	20	19
<b>7</b>	7	21	21	
<b>8</b>				
<b>9</b>	11	19	19	19
<b>10</b>	8	16	9	8
<b>11</b>	9	12	5	6
<b>12</b>	5	10	5	5
<b>13</b>		11	6	
<b>14</b>	5	10	5	3
<b>15</b>		11	6	
<b>16</b>	5	10	5	4
<b>17</b>		10	5	
<b>18</b>	5	9	9	8
<b>19</b>	9	18	9	9
<b>20</b>		19	10	
<b>21</b>	10	18	9	9
<b>22</b>		16	9	
<b>23</b>	10	18	9	9
<b>24</b>		18	9	
<b>25</b>	8	17	9	9
<b>26</b>		18	9	
<b>27</b>	9	16	9	9
<b>28</b>		15	7	
<b>29</b>	8	16	8	8
<b>30</b>		12	7	
<b>31</b>	7	11	6	6
<b>32</b>		10	5	
<b>33</b>	5	10	5	5

**Table 6.** *Number of samples measured by station and variable.*

#### First quality control

A first visual inspection of the vertical distribution of ion carbonate (Table 7), pH25T (Table 8), DIC (Table 9) and TA (Table 10) data allowed us to identify some questionable data.

<b>Station</b>	<b>Niskin</b>	<b>Pressure (dbars)</b>
2	5	404.9
2	6	304
4	3	3044.6
4	4	2789.2
4	5	2535.1
4	6	2278.7
4	7	2025.9
4	8	1772.2
4	9	1517.8
4	10	1264.8
4	14	404
4	17	101.9
6	1	3208.4
6	3	2789.2
6	7	1771.1
6	9	1264.1
6	17	76.1
6	18	51.5
6	20	6.5
9	3	2535.4
10	7	757.8
10	9	404.4
10	13	81.3
11	6	303.3
11	7	211.3
11	9	72.6
12	1	665.4
12	3	404.7
12	5	200.2
12	7	77.8
12	9	25.1
16	3	405.6

16	9	25.1
18	3	404
18	9	23.8
19	3	2280
19	17	25
25	11	404
27	1	2496.7
27	17	5.4
29	13	75.7
29	15	25
31	3	500.5
31	11	5
33	1	760.3

**Table 7.** List of questionable data for ion carbonate.

Station	Niskin	Pressure
9	1	2946.5
19	3	2280
19	10	505.6
21	3	2281.1

**Table 8.** List of questionable data for pH25T.

Station	Niskin	Pressure
19	3	2280
23	11	408
21	3	2281.1

**Table 9.** List of questionable data for DIC.

Station	Niskin	Pressure
6	8	1517
7	21	3.6
19	3	2280
26	9	760

**Table 10.** List of questionable data for TA.

#### 6.4 CFCs & SF<sub>6</sub> (T.Tanhua, B. Bogner, J. Schrammer)

Measurements of the transient tracers CFC-12 and SF<sub>6</sub> are used to characterize ventilation in the Mediterranean, and particularly temporal changes in ventilation (e.g. Stöven and Tanhua, 2013; Schneider et al., 2014).

During the cruise, one GAS CHROMATOGRAPH / PURGE-AND-TRAP (GC/PT) systems were used for the measurements of the transient tracers CFC-12 and SF<sub>6</sub>. The systems are modified versions of the set-up normally used for the analysis of CFCs (Bullister and Weiss, 1988; Bullister and Wisegarver, 2008). Samples were collected in 250 ml ground glass syringes. An aliquot of about 200 ml of the samples was injected into the analytical systems. The analytes were stripped out of the water phase by a flow (120 ml/min) of ultra-clean N<sub>2</sub> during 5-6 minutes to the trap. The trap consist of 100 cm of 1/16" tubing packed with 70cm Heysep D and is kept at -60°C during the trapping phase. The trap was desorbed at 120°C and the analytes passed on to the gas chromatograph (GC). The GC was setup with a 1/8" main column packed with 180 cm Carbograph 1AC (60-80 mesh) and a 20 cm Molsieve 5A post-column, kept isothermal at 50°C. The pre-column was packed with 10 cm Porasil C and 20cm Molsieve 5A in a 1/8" stainless steel column, but had to be shortend to 15cm Porasil C and 20cm Molsieve 5A. Detection was performed on an Electron Capture Detector (ECD). This set-up allowed efficient analysis of SF<sub>6</sub> and CFC-12.

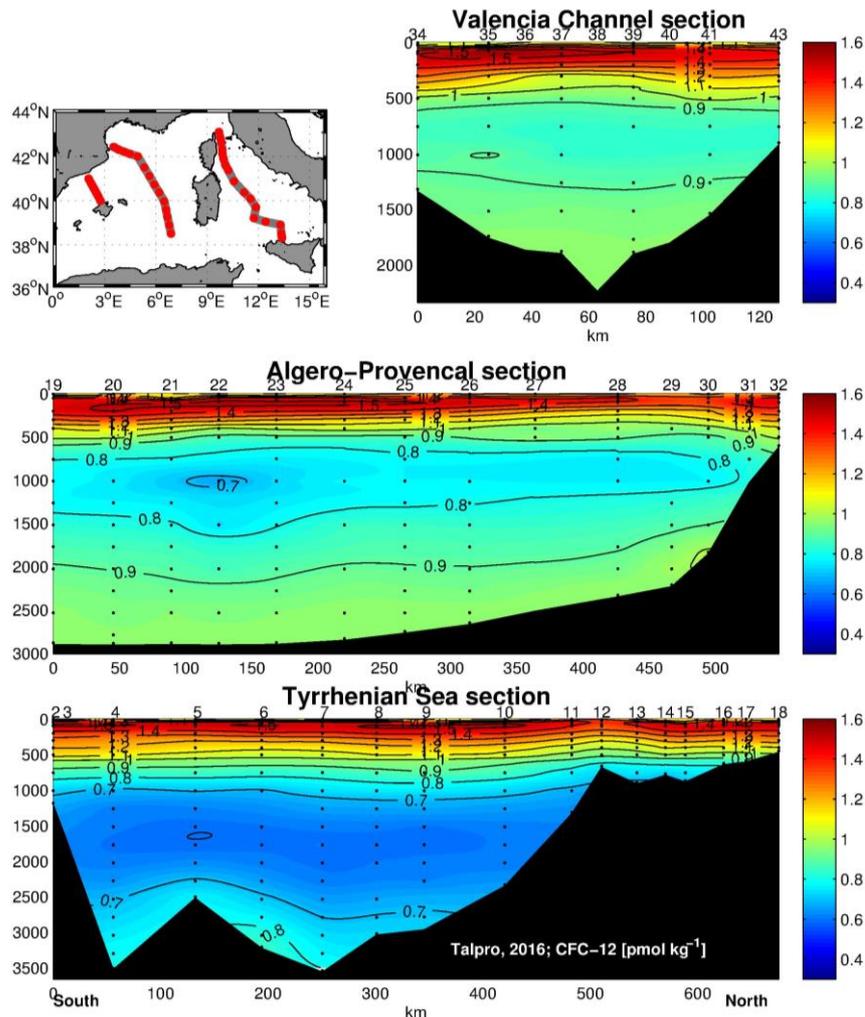
Standardization was performed by injecting small volumes of gaseous standard containing SF<sub>6</sub> and CFC-12. This working standard was prepared by the company Dueste-Steiniger (Germany). The concentrations in the standard have been calibrated vs. a reference standard obtained from R.F Weiss group at SIO, and the CFC-12 data are reported on the SIO98 scale. Another, final, calibration of the working standard will take place in the lab after the cruise. One calibration curve were measured to characterize the non-linearity of the system, and point calibrations were always performed between stations to determine the short term drift of the detector. Nineteen (19) replicate measurements were taken on eleven (11) stations; the determined values for precision and accuracy are listed in Table 11. In total 458 samples were measured for its transient tracer content.

Compound	Precision
SF <sub>6</sub>	2.8 %
CFC-12	1.0 %

**Table 11:** Precision of tracer measurements determined from replicate measurements and approximate limit of detection.

### Preliminary results:

The data show the well-known mid-depth tracer minimum zone at around 1000 meters depth on all three sections, Figure 6. It is interesting to see how the water at this level gets better ventilated towards the west. In the Tyrrhenian Sea one can clearly see increased values of CFC-12 in the bottom water, probably indicating inflow of newly ventilated Western Mediterranean Deep Water.



**Figure 6:** Sections of the concentration of CFC-12 ( $\text{pmol kg}^{-1}$ ) from the TalPro cruise. Data are preliminary and off-the-ship, but only small adjustments (if any) will be needed.

### 6.5 Nitrogen and Oxygen Isotopes (Francois Fripiat)

Seawater for nitrate  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  were collected unfiltered in a rinsed 60 ml high-density polyethylene bottle and immediately frozen at  $-20^\circ\text{C}$ . Prior to nitrate isotope analysis, nitrite will be removed or not with the sulfamic acid protocol of Granger and Sigman (2009) in order to have nitrate-only and nitrate+nitrite  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$ , respectively. The  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  will be measured using the ‘denitrifier method’ (Sigman et al., 2001; Casciotti et al., 2002). Briefly, 5-10 nmol of nitrate (or nitrate+nitrite) is quantitatively converted to  $\text{N}_2\text{O}$  gas by denitrifying bacteria that lack an active  $\text{N}_2\text{O}$  reductase. Both the N

and O isotopic composition is measured by gas chromatography/isotope ratio mass spectrometry (GC/IRMS) with on-line cryo-trapping.

#### 6.6 *Barium isotopes (Stéphanie Jacquet)*

Seawater was sampled with a CTD rosette equipped with xx x 12 liters bottles water-sampler. Then, 125 mL of unfiltered seawater were collected in HDPE bottles (rinsed three time with the same seawater sample), acidified with HCL (Optima grade) and kept at room temperature.

### 7 **Underway measurements**

#### 7.1 *Oceanlogger, Met. Data and Single-Beam Echosounder*

#### 7.2 *Vessel-Mounted ADCP*

The hydrographic data set has been integrated with direct current measurements. During the whole campaign a VM-ADCPs (RDI Ocean Surveyor, 150 KHz) works along the whole ship track. The depth range of the two current profilers is about 200m. Data acquisition is carried out using the RDI VMDAS software vers. 1.44. The ADCP data will be submitted to a post-processing with the CODAS3 Software System, which allows to extract data, assign coordinates, edit and correct velocity data. Data will be corrected in the value of sound velocity in water and in alignment of the instrument with respect to the axis of the ship.

### 8 **Data and Sample Storage / Availability**

The hydrographic data (CTD+Bottle) collected during the TAIPro cruise will be freely available on the Clivar and Carbon Hydrographic Data office (<https://cchdo.ucsd.edu/>). The Shipboard ADCP data will be archived at the Joint Archive for Shipboard ADCP (<http://ilikai.soest.hawaii.edu/sadcp/>)

## 9 Participants

No.	Name	Gender	Affiliation	On-board tasks
1	Loïc Jullion	M	MIO	PSO, CTD work
2	Katrin Schroeder	F	CNR	CTD/ LADCP work
3	Mireno Borghini	M	CNR	CTD/ LADCP work
4	Louise Rousselet, Student	F	MIO	CTD, Salinity
5	Toste Tanhua	M	GEOM	CFC/SF <sub>6</sub>
6	Boie Bogner	M	GEOM	CFC/SF <sub>6</sub>
7	Julia Schrandt, Student	F	GEOM	CFC/SF <sub>6</sub>
8	Marta Alvarez	F	IEO	Carbon
9	Monica Castaño Carrera	F	IEO	Carbon
10	Iraia Rodriguez Garcia, Student	F	IEO	Carbon
11	Melek Golbol	F	LOV	Nutrients, Oxygen
12	Coco Koedooder	F	LOV	Nutrients, Oxygen, Salinity
13	Marin Cornec, Student	M	LOV	Nutrients, Oxygen

MIO Mediterranean Institute of Oceanography, Marseille, France

CNR National Institute of Oceanography and Experimental Geophysics, Trieste, Italy

GEOM GEOMAR Helmholtz Centre for Ocean Research, Kiel, Germany

IEO Instituto Español de Oceanografía, A Coruña, Spain

LOV Laboratoire Océanographique de Villefranche, Villefranche, France

**10 Station List**

Station No.	Date	Time	Latitude	Longitude	Water		
					Depth	Gear	Remarks/Recovery
	2016	[UTC]	[°N]	[°W]	[m]		
1	19/08	11:44	38.3	13.4	460.0	ROS/CTD/LACDP	
2	19/08	13:07	38.4	13.4	1173.0	ROS/CTD/LACDP	
3	19/08	15:35	38.5	13.4	1614.0	ROS/CTD/LACDP	
4	19/08	19:05	38.9	13.3	3452.0	ROS/CTD/LACDP	
5	20/08	02:09	39.1	12.4	2463.0	ROS/CTD/LACDP	
6	20/08	07:17	39.2	11.8	3160.0	ROS/CTD/LACDP	
7	20/08	13:12	39.7	11.9	3484.0	ROS/CTD/LACDP	30 min stops@617m up
8	20/08	18:58	40.1	11.6	2975.0	ROS/CTD/LACDP	
9	20/08	23:40	40.4	11.2	2900.0	ROS/CTD/LACDP	Bottle 1: Leaking
10	21/08	06:07	40.9	10.6	2256.0	ROS/CTD/LACDP	
11	21/08	13:25	41.4	10.2	1300.0	ROS/CTD/LACDP	
12	21/08		41.6	10.1		ROS/CTD/LACDP	
13	21/08	19:22	41.9	10.0	885.0	ROS/CTD/LACDP	Bottle 1: Leaking
14	21/08	21:52	42.1	9.9	765.0	ROS/CTD/LACDP	Bottle 1: Leaking
15	21/08	23:49	42.3	9.9	857.0	ROS/CTD/LACDP	
16	22/08	02:46	42.6	9.8	616.0	ROS/CTD/LACDP	
17	22/08	04:39	42.8	9.8	580.0	ROS/CTD/LACDP	
18	22/08	07:19	43.0	9.7	450.0	ROS/CTD/LACDP	
19	23/08	16:20	38.5	6.9	2840.0	ROS/CTD/LACDP	Bottle 10: Leaking
20	23/08	21:12	38.9	6.8	2846.0	ROS/CTD/LACDP	
21	24/08	02:09	39.3	6.7	2855.0	ROS/CTD/LACDP	
22	24/08	06:15	39.6	6.6	2845.0	ROS/CTD/LACDP	
23	24/08	10:46	40.0	6.5	2850.0	ROS/CTD/LACDP	
24	24/08	15:58	40.4	6.2	2802.0	ROS/CTD/LACDP	
25	24/08	20:29	40.7	5.9	2710.0	ROS/CTD/LACDP	Bottle 8: Leaking
26	25/08	01:18	41.1	5.6	2559.0	ROS/CTD/LACDP	
27	25/08	06:05	41.5	5.3	2462.0	ROS/CTD/LACDP	Bottle 15: Pressure cap gone
28	25/08	11:30	42.0	5.0	2299.0	ROS/CTD/LACDP	Bottle 5: Misfired
29	25/08	17:17	42.1	4.5	2193.0	ROS/CTD/LACDP	
30	25/08	20:33	42.2	4.2	1810.0	ROS/CTD/LACDP	
31	25/08	23:49	42.3	3.8	1000.0	ROS/CTD/LACDP	
32	26/08	02:15	42.4	3.6	596.0	ROS/CTD/LACDP	
33	26/08	03:32	42.4	3.5	752.0	ROS/CTD/LACDP	
34	26/08	18:58	40.0	2.8	1293.0	ROS/CTD/LACDP	Bottle 10: Leaking
35	26/08	21:54	40.2	2.6	1723.0	ROS/CTD/LACDP	Bottle 7: Leaking
36	27/08	00:26	40.3	2.6	1828.0	ROS/CTD/LACDP	
37	27/08	02:57	40.4	2.5	1868.0	ROS/CTD/LACDP	Bottle 14: Leaking
38	27/08	05:15	40.5	2.4	2202.0	ROS/CTD/LACDP	
39	27/08	08:06	40.6	2.4	1864.0	ROS/CTD/LACDP	Bottle 1 & 5: Leaking
40	27/08	10:31	40.7	2.3	1765.0	ROS/CTD/LACDP	

## **11 Acknowledgements**

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## 12           References

Álvarez, M., Sanleón-Bartolomé, H., Tanhua, T., Mintrop, L., Luchetta, A., Cantoni, C., Schroeder, K., Civitarese, G. The CO<sub>2</sub> system in the Mediterranean Sea: a basin wide perspective. *Ocean Sci.*, 10, 69-92, doi:10.5194/os-10-69-2014, 2014.

Bullister, J. L., and Weiss, R. F.: Determination of CCl<sub>3</sub>F and CCl<sub>2</sub>F<sub>2</sub> in seawater and air, *Deep-Sea Res.*, 35, 839-853, 1988.

Bullister, J. L., and Wisegarver, D. P.: The shipboard analysis of trace levels of sulfur hexafluoride, chlorofluorocarbon-11 and chlorofluorocarbon-12 in seawater, *Deep-Sea Res. I*, 55, 1063-1074, 2008.

Byrne R. H. Standardization of standard buffers by visible spectrometry. *Analytical Chemistry*, 59, 1479-1481, 1987

Casciotti, K.L., D.M. Sigman, M. Galanter Hastings, J.K. Böhlke, and A. Hilkert (2002), Measurement of the oxygen isotopic composition of nitrate in seawater and freshwater using denitrifier method, *Anal. Chem.* 74, 4905-4912.

Clayton and Byrne, Spectrophotometric seawater pH measurements: total hydrogen ion concentration scale concentration scale calibration of m-cresol purple and at-sea results. *Deep-sea Research I*, Vol. 40, 10, 2115-2129, 1993

Dickson, A.G., Millero, F.J., A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media. *Deep-Sea Research* 34, 1733–1743, 1987

Granger, J., D.M. Sigman, Removal of nitrite with sulfamic acid for nitrate N and O isotope analysis with the denitrifier method, *Rapid Commun. Mass. Sp.* 23, 3753-3762, 2009

Grignon, L., Smeed, D.A., Bryden, H.L. and Schroeder, K., Importance of the variability of hydrographic preconditioning for deep convection in the Gulf of Lion, NW Mediterraneans, *Ocean Sci.*, Vol. 6 (2), pp. 573-586, Doi: 10.5194/os-6-573-2010, 2010.

Johnson, K.M., Wills, K.D., Butler, D.B., Johnson, W.K., Wong, C.S., Coulometric total carbon dioxide analysis for marine studies: maximizing the performance of an automated gas extraction system and coulometric detector. *Mar. Chemi.*, 44, 167-187, 1993

Johnson, KM, Dickson AG, Eiseid G, Goyet C, Guenther P, Key RM, Millero FJ, Purkerson D, Sabine CL, Schottle RG, Wallace DWR, Wilke RJ, Winn CD, Coulometric total carbon dioxide analysis for marine studies: assessment of the quality of total inorganic carbon measurements made during the US Indian Ocean CO<sub>2</sub> Survey 1994-1996. *Marine Chemistry*. 63, 21-37, 1998

MEDOC Group, Observation of formation of deep water in the Mediterranean Sea, 1969, *Nature*, 227, 1037–1040, 1970.

- Merzbach, C., Culberson, C.H., Hawley, J.E., Pytkowicz, R.M., Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure. *Limnology and Oceanography*, 18, 897–907, 1973
- Millot, C., Some features of the Algerian current. *J. Geophys. Res.* 90, 7169–7176, 1985
- Millot, C., Circulation in the western Mediterranean Sea. *J. Mar. Syst.* Vol. 20, pp. 423–442, 1999.
- Millot, C. and Taupier-Letage, I.: Circulation in the Mediterranean Sea, in: *The Mediterranean Sea, the Handbook of Environmental Chemistry*, Springer, Berlin/Heidelberg, 29–66, 2005.
- Mintrop, L., F. F. Pérez, M. González Dávila, A. Körtzinger and J.M. Santana Casiano, Alkalinity determination by potentiometry- intercalibration using three different methods. *Ciencias Marinas* , 26 , 23-37, 2000
- Patsavas MC, Byrne RB, Yang B, Easley RA, Wanninkhof R, Liu X., Procedures for direct spectrophotometric determination of carbonate ion concentrations: Measurements in US Gulf of Mexico and East Coast waters. *Marine Chemistry*, 168, 80-85, 2015
- Pérez, F.F. and F. Fraga, A precise and rapid analytical procedure for alkalinity determination. *Marine Chemistry*, 21, 169-182, 1987
- Pérez, F.F., A.F. Ríos, T. Rellán and M. Álvarez, Improvements in a fast potentiometric seawater alkalinity determination. *Ciencias Marinas*, 26, 463-478, 2000
- Roether, W. and Lupton, J.: Tracers confirm downward mixing of Tyrrhenian Sea upper waters associated with the Eastern Mediterranean Transient, *Ocean Sci.*, 7, 91–99, doi:10.5194/os-7-91- 2011, 2011.
- Sigman, D.M., K.L. Casciotti, M. Andreani, C. Barford, M. Galanter, and J.K. Böhlke, A bacterial method for the nitrogen isotopic analysis of nitrate in seawater and freshwater, *Anal Chem.* 73, 4145-4153, 2001
- Schneider, A., Tanhua, T., Roether, W., and Steinfeldt, R.: Changes in ventilation of the Mediterranean Sea during the past 25 year, *Ocean Sci.*, 10, 1-16, 10.5194/os-10-1-2014, 2014.
- Schroeder, K., Josey, S. A., Herrmann, M., Grignon, L., Gasparini, G. P., and Bryden, H. L.: Abrupt warming and salting of the Western Mediterranean Deep Water after 2005: Atmospheric forcings and lateral advection, *J. Geophys. Res.*, 115,C08029, doi:10.1029/2009JC005749, 2010.
- Stöven, T., and Tanhua, T.: Ventilation of the Mediterranean Sea constrained by multiple transient tracer measurements, *Ocean Sci. Discuss.*, 10, 1647-1705, 10.5194/osd-10-1647-2013, 2013.
- Tanhua T., D. Hainbucher, K. Schroeder, V. Cardin, M. Alvarez, and G. Civitarese, The Mediterranean Sea system: a review and an introduction to the special issue. *Ocean Sci.*, 9, 789– 803, 2013. doi:10.5194/os-9-789-2013,

## Appendix

```

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    <!-- 1 == SBE11plus Firmware Version < 5.0 -->
    <!-- 2 == SBE 17plus SEARAM -->
    <!-- 3 == None -->
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    <NmeaDepthDataAdded>0</NmeaDepthDataAdded>
    <NmeaTimeAdded>0</NmeaTimeAdded>
    <NmeaDeviceConnectedToPC>1</NmeaDeviceConnectedToPC>
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      <Sensor index="0" SensorID="55" >
        <TemperatureSensor SensorID="55" >
          <SerialNumber>5604</SerialNumber>
          <CalibrationDate>05-May-16</CalibrationDate>
          <UseG_J>1</UseG_J>
          <A>0.00000000e+000</A>
          <B>0.00000000e+000</B>
          <C>0.00000000e+000</C>
          <D>0.00000000e+000</D>
          <F0_Old>0.000</F0_Old>
          <G>4.30398343e-003</G>
          <H>6.24840983e-004</H>
          <I>1.92048856e-005</I>
          <J>1.59662161e-006</J>
          <F0>1000.000</F0>
          <Slope>1.00000000</Slope>
          <Offset>0.0000</Offset>
        </TemperatureSensor>
      </Sensor>
      <Sensor index="1" SensorID="3" >
        <ConductivitySensor SensorID="3" >
          <SerialNumber>4124</SerialNumber>
          <CalibrationDate>03-May-16</CalibrationDate>
          <UseG_J>1</UseG_J>
          <!-- Cell const and series R are applicable only for wide range sensors. -->
          <SeriesR>0.0000</SeriesR>
          <CellConst>2000.0000</CellConst>
          <ConductivityType>0</ConductivityType>
          <Coefficients equation="0" >
            <A>0.00000000e+000</A>
            <B>0.00000000e+000</B>
            <C>0.00000000e+000</C>
            <D>0.00000000e+000</D>
            <M>0.0</M>
          </Coefficients equation="0" >
        </ConductivitySensor>
      </Sensor>
    </SensorArray Size="15" >
  </Instrument Type="8" >
</SBE_InstrumentConfiguration SB_ConfigCTD_FileVersion="7.23.0.2" >

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    <CPcor>-9.57000000e-008</CPcor>
  </Coefficients>
  <Coefficients equation="1" >
    <G>-9.91717012e+000</G>
    <H>1.22225922e+000</H>
    <I>-2.41217980e-003</I>
    <J>2.35810579e-004</J>
    <CPcor>-9.57000000e-008</CPcor>
    <CTcor>3.2500e-006</CTcor>
    <!-- WBOTC not applicable unless ConductivityType = 1. -->
    <WBOTC>0.00000000e+000</WBOTC>
  </Coefficients>
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  <Offset>0.00000</Offset>
</ConductivitySensor>
</Sensor>
<Sensor index="2" SensorID="45" >
  <PressureSensor SensorID="45" >
    <SerialNumber>1090</SerialNumber>
    <CalibrationDate>09-May-16</CalibrationDate>
    <C1>-4.221482e+004</C1>
    <C2>4.483790e-002</C2>
    <C3>1.216550e-002</C3>
    <D1>3.555000e-002</D1>
    <D2>0.000000e+000</D2>
    <T1>3.018622e+001</T1>
    <T2>-2.528590e-004</T2>
    <T3>3.736680e-006</T3>
    <T4>4.041990e-009</T4>
    <Slope>1.00014140</Slope>
    <Offset>-0.36008</Offset>
    <T5>0.000000e+000</T5>
    <AD590M>1.282300e-002</AD590M>
    <AD590B>-8.821560e+000</AD590B>
  </PressureSensor>
</Sensor>
<Sensor index="3" SensorID="55" >
  <TemperatureSensor SensorID="55" >
    <SerialNumber>5573</SerialNumber>
    <CalibrationDate>05-May-16</CalibrationDate>
    <UseG_J>1</UseG_J>
    <A>0.00000000e+000</A>
    <B>0.00000000e+000</B>
    <C>0.00000000e+000</C>
    <D>0.00000000e+000</D>
    <F0_Old>0.000</F0_Old>
    <G>4.30867625e-003</G>
    <H>6.23443759e-004</H>
    <I>1.89574537e-005</I>
    <J>1.38904242e-006</J>
    <F0>1000.000</F0>
    <Slope>1.00000000</Slope>
    <Offset>0.0000</Offset>
  </TemperatureSensor>
</Sensor>
<Sensor index="4" SensorID="3" >

```

```

<ConductivitySensor SensorID="3" >
  <SerialNumber>4125</SerialNumber>
  <CalibrationDate>03-May-16</CalibrationDate>
  <UseG_J>1</UseG_J>
  <!-- Cell const and series R are applicable only for wide range sensors. -->
  <SeriesR>0.0000</SeriesR>
  <CellConst>2000.0000</CellConst>
  <ConductivityType>0</ConductivityType>
  <Coefficients equation="0" >
    <A>0.00000000e+000</A>
    <B>0.00000000e+000</B>
    <C>0.00000000e+000</C>
    <D>0.00000000e+000</D>
    <M>0.0</M>
    <CPcor>-9.57000000e-008</CPcor>
  </Coefficients>
  <Coefficients equation="1" >
    <G>-9.67145662e+000</G>
    <H>1.21180480e+000</H>
    <I>-2.34571857e-003</I>
    <J>2.31197448e-004</J>
    <CPcor>-9.57000000e-008</CPcor>
    <CTcor>3.2500e-006</CTcor>
    <!-- WBOTC not applicable unless ConductivityType = 1. -->
    <WBOTC>0.00000000e+000</WBOTC>
  </Coefficients>
  <Slope>1.00000000</Slope>
  <Offset>0.00000</Offset>
</ConductivitySensor>
</Sensor>
<Sensor index="5" SensorID="38" >
  <OxygenSensor SensorID="38" >
    <SerialNumber>2285</SerialNumber>
    <CalibrationDate>16-Mar-12</CalibrationDate>
    <Use2007Equation>1</Use2007Equation>
    <CalibrationCoefficients equation="0" >
      <!-- Coefficients for Owens-Millard equation. -->
      <Boc>0.0000</Boc>
      <Soc>0.0000e+000</Soc>
      <offset>0.0000</offset>
      <Pcor>0.00e+000</Pcor>
      <Tcor>0.0000</Tcor>
      <Tau>0.0</Tau>
    </CalibrationCoefficients>
    <CalibrationCoefficients equation="1" >
      <!-- Coefficients for Sea-Bird equation - SBE calibration in 2007 and later. -->
      <Soc>5.4368e-001</Soc>
      <offset>-0.5013</offset>
      <A>-3.1500e-003</A>
      <B> 9.8300e-005</B>
      <C>-1.5370e-006</C>
      <D0> 2.5826e+000</D0>
      <D1> 1.92634e-004</D1>
      <D2>-4.64803e-002</D2>
      <E> 3.6000e-002</E>
      <Tau20> 2.2300</Tau20>
    </CalibrationCoefficients>
  </OxygenSensor>
</Sensor>

```

```

    <H1>-3.3000e-002</H1>
    <H2> 5.0000e+003</H2>
    <H3> 1.4500e+003</H3>
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</OxygenSensor>
</Sensor>
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    <SerialNumber></SerialNumber>
    <CalibrationDate></CalibrationDate>
    <OutputType>2</OutputType>
    <Free>1</Free>
  </NotInUse>
</Sensor>
<Sensor index="7" SensorID="0" >
  <AltimeterSensor SensorID="0" >
    <SerialNumber>56156</SerialNumber>
    <CalibrationDate>22 Marzo 2012</CalibrationDate>
    <ScaleFactor>15.000</ScaleFactor>
    <Offset>0.000</Offset>
  </AltimeterSensor>
</Sensor>
<Sensor index="8" SensorID="27" >
  <NotInUse SensorID="27" >
    <SerialNumber></SerialNumber>
    <CalibrationDate></CalibrationDate>
    <OutputType>2</OutputType>
    <Free>1</Free>
  </NotInUse>
</Sensor>
<Sensor index="9" SensorID="20" >
  <FluoroWetlabECO_AFL_FL_Sensor SensorID="20" >
    <SerialNumber>FLNTURTD-2526</SerialNumber>
    <CalibrationDate>27-Dec-11</CalibrationDate>
    <ScaleFactor>1.00000000e+001</ScaleFactor>
    <!-- Dark output -->
    <Vblank>0.0760</Vblank>
  </FluoroWetlabECO_AFL_FL_Sensor>
</Sensor>
<Sensor index="10" SensorID="67" >
  <TurbidityMeter SensorID="67" >
    <SerialNumber>FLNTURTD-2526</SerialNumber>
    <CalibrationDate>27-Dec-11</CalibrationDate>
    <ScaleFactor>5.000000</ScaleFactor>
    <!-- Dark output -->
    <DarkVoltage>0.070000</DarkVoltage>
  </TurbidityMeter>
</Sensor>
<Sensor index="11" SensorID="27" >
  <NotInUse SensorID="27" >
    <SerialNumber></SerialNumber>
    <CalibrationDate></CalibrationDate>
    <OutputType>2</OutputType>
    <Free>1</Free>
  </NotInUse>
</Sensor>

```

```
<Sensor index="12" SensorID="27" >
  <NotInUse SensorID="27" >
    <SerialNumber></SerialNumber>
    <CalibrationDate></CalibrationDate>
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    <Free>1</Free>
  </NotInUse>
</Sensor>
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  <NotInUse SensorID="27" >
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    <CalibrationDate></CalibrationDate>
    <OutputType>0</OutputType>
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  </NotInUse>
</Sensor>
<Sensor index="14" SensorID="51" >
  <SPAR_Sensor SensorID="51" >
    <SerialNumber>QCR2200 sn 20415</SerialNumber>
    <CalibrationDate>7 March 2012</CalibrationDate>
    <ConversionFactor>9959300000000000.00000000</ConversionFactor>
    <RatioMultiplier>0.00000000</RatioMultiplier>
  </SPAR_Sensor>
</Sensor>
</SensorArray>
</Instrument>
</SBE_InstrumentConfiguration>
```

## CCHDO Data Processing Notes

- **File Merge CCHSIO**

[Talpro-2016\\_ctd.tab \(download\)](#) #3056f

**Date:** 2020-03-19

**Current Status:** merged

- **Reformat AWI formatted data into Exchange format CCHSIO**

**Date:** 2020-03-19

**Data Type:** CTD

**Action:** Website Update

**Note:**

2016 29AJ20160818 processing - CTD/merge -  
CTDPRS, CTDTMP, CTDSAL, CTDOXY, CTDFLUOR, CTDTREBDTY

2020-03-19

CCHSIO

Submission

filename	submitted by	date	id
Talpro-2016_ctd.tab	Carolina for Toste Tanhua	2019-10-17	14671

Changes

Talpro-2016\_ctd.tab

- Reformatted AWI file into EXCHANGE format files.
- Added units and cruise information as comments.
- Checked CTD and Bottle data: date/time/lat/lon/depth are same.
- Removed leading 0s from STNNBR.
- Removed two test sample depths from event/station 004,

dTalpro\_Stn04\_test\_1db.

- Changed CTDSAL units from 'Practical' to PSS-78.
- CASTNO: not supplied by originator - CCHDO assigned all CASTNO=1 or CASTNO=2 for stations 11, 29.
- CTDSAL: changed units from Practical to PSS-78. Data values remain unchanged.
- Added flags=2 for all parameters, as T.Tanhua notes all params are calibrated and CTDOXY calibrated with bottle samples.
- CTDTMP: Used first occurrence of primary temperature sensor in original data file.
- CTDSAL: Used first occurrence of primary salinity sensor in original data file.
- Converted CTDOXY from ML/L to UMOL/KG.

- CTDFLUOR: changed units from UG/L to MG/M3 as they are they are equivalent.  
 - Changed date/time of station 29 to match Cruise Report: 2016-08-25T17:17:00

Conversion

```
-----
file                converted from      software
-----
29AJ20160818_nc_ctd.zip 29AJ20160818_ct1.zip hydro 0.8.2-57-g8aa7d7a
```

Updated Files Manifest

```
-----
file                stamp
-----
29AJ20160818_ct1.zip 20200319CCHSIO
29AJ20160818_nc_ctd.zip 20200319CCHSIO
```

:Updated parameters: CTDPRS,CTDTMP,CTDSAL,CTDOXY,CTDFLUOR,CTDTRBDTY

opened in JOA 5.2.1 with no apparent problems:

```
29AJ20160818_ct1.zip
29AJ20160818_nc_ctd.zip
```

opened in ODV with no apparent problems:

```
29AJ20160818_ct1.zip
```

- **File Online Carolina Berys**

[Talpro-2016 hydrochem.tab \(download\)](#) #a741a

**Date:** 2019-10-17

**Current Status:** unprocessed

- **File Online Carolina Berys**

[Talpro-2016\\_ctd.tab \(download\)](#) #3056f

**Date:** 2019-10-17

**Current Status:** merged

- **File Submission Carolina for Toste Tanhua**

[Talpro-2016\\_hydrochem.tab \(download\)](#) #a741a

**Date:** 2019-10-17

**Current Status:** unprocessed

**Notes**

Hydrochemistry from <https://doi.pangaea.de/10.1594/PANGAEA.902293> and  
CTD data from <https://doi.pangaea.de/10.1594/PANGAEA.902330> on 2019-10-17

- **File Submission Carolina for Toste Tanhua**

[Talpro-2016\\_ctd.tab \(download\)](#) #3056f

**Date:** 2019-10-17

**Current Status:** merged

**Notes**

Hydrochemistry from <https://doi.pangaea.de/10.1594/PANGAEA.902293> and  
CTD data from <https://doi.pangaea.de/10.1594/PANGAEA.902330> on 2019-10-17