FICARAM-XVII Cruise Plan
11 March – 31 April 2019
BIO HESPERIDES

General Objective- The FICARAM-XVII will be the seventeenth repeat of section conducted in 1994. This section is part of the international program GOSHIP (http://www.go-ship.org/CruisePlans.html) to develop a globally coordinated network of sustained hydrographic sections as part of the global ocean/climate observing system.

The general objective of the FICARAM-17 cruise is to assess the climate change monitoring the keys variables. Firstly, we will investigated the temporal evolution of the anthropogenic carbon storage and the ocean acidification, and evaluate the CO_2 absorption capacity in the South Atlantic region and the Atlantic Equatorial zone. Secondly, the changes in the surface and in the main thermocline of thermohaline properties and circulation. Thirty, the changes in the biological and biogeochemical mechanisms that hinder total dissolved organic carbon (DOC) remineralisation in marine systems, taking a multidisciplinary perspective and applying many different approaches.

This cruise is planned in the frame of the European Project AtlantOs (https://www.atlantos-h2020.eu/) funded by H2020. In addition, three foreign University are involved. Robert Key of the Princeton University will deploy several biogeochemical floats and conduct sampling for carbon isotopes. Dean Roemmich of University of California, San Diego, will deploy several deep-argo floats ((http://www-argo.ucsd.edu). Toste Tanhua of GEOMAR (Helmholtz-Zentrum für Ozeanforschung Kiel) will be performed the chlorofluorocarbons analysis on board for water mass dating. Finally, Mercedes de la Paz, principal investigator of the project "Investigación de las fuentes y sumideros de N_2O y CH_4 en sistemas marinos de afloramiento" (CTM2015-74510-JIN) of Instituto

Figure 1.- Planned stations along the FICARAM-XVII section

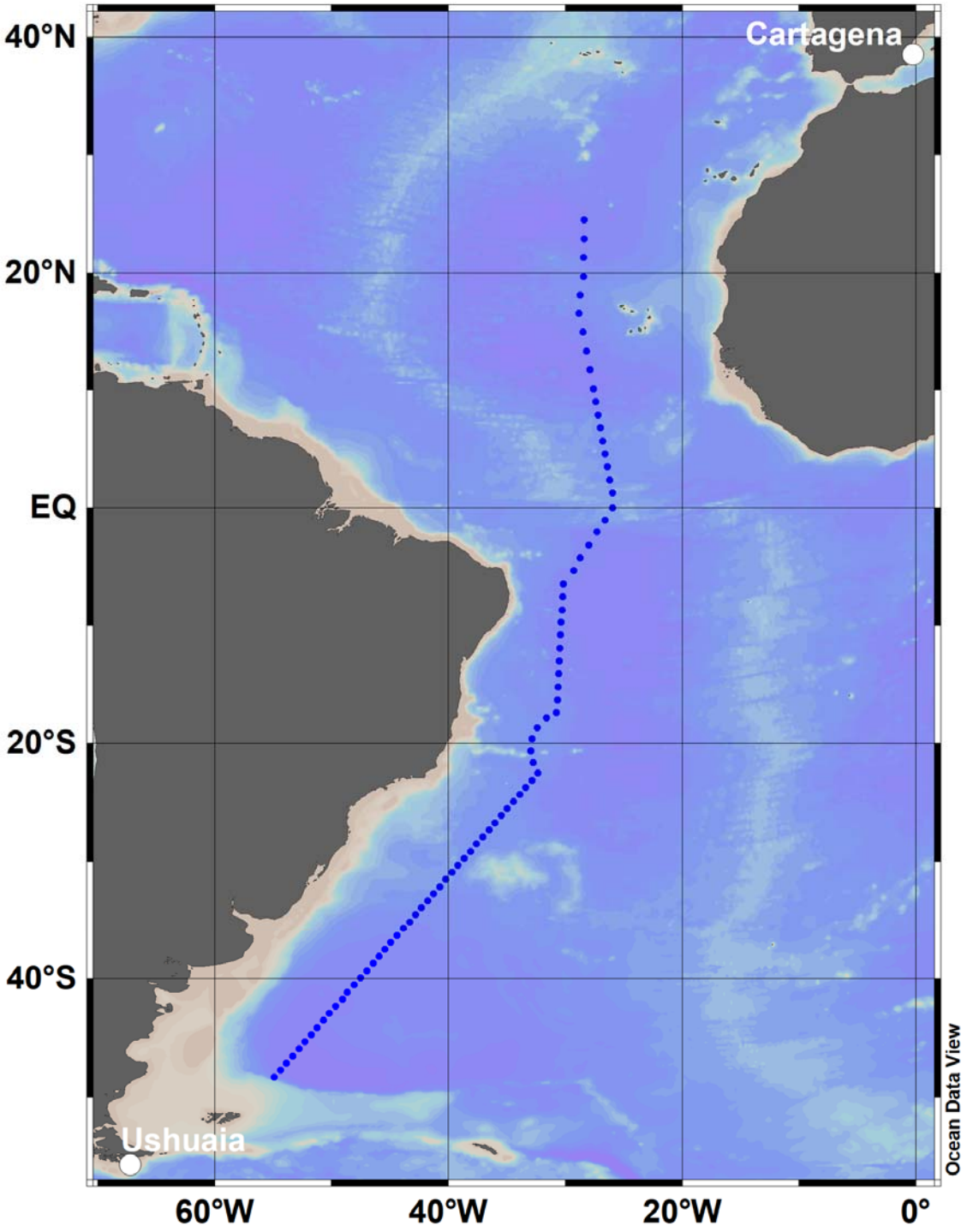

Table 1.- Station data

Station	LATITUDE	LONGITUDE	BOTTOM DEPTH (m)
1	-48.3054	-54.9226	4944
2	-47.7050	-54.3820	5928
3	-47.1050	-53.8640	6166
4	-46.5060	-53.3340	6176
5	-45.9050	-52.8120	6150
6	-45.3050	-52.2870	6012
7	-44.7050	-51.7650	5878
8	-44.1020	-51.2430	5651
9	-43.5060	-50.7160	5389
10	-42.9070	-50.1980	5574
11	-42.3060	-49.6660	5807
12	-41.7290	-49.0910	5666
13	-41.1040	-48.6600	5525
14	-40.4850	-48.0970	5309
15	-39.8970	-47.5540	5265
16	-39.3010	-47.0150	5213
17	-38.6820	-46.4440	5180
18	-38.0790	-45.9770	5148
19	-37.4870	-45.4620	5098
20	-36.9030	-44.9560	5056
21	-36.2980	-44.4030	4951
22	-35.6820	-43.8970	4911
23	-35.1160	-43.3510	4834
24	-34.4890	-42.8410	4679
25	-33.9030	-42.3290	4529
26	-33.3090	-41.8050	4578
27	-32.7020	-41.2850	4488
28	-32.1040	-40.7600	4183
29	-31.5050	-40.2360	3671
30	-30.8820	-39.7130	4376
31	-30.3200	-39.1930	4178
32	-29.7070	-38.6690	4294
33	-29.1260	-38.1460	4360
34	-28.4940	-37.6040	4439
35	-27.9050	-37.0890	4676
36	-27.3210	-36.5600	4610
37	-26.7150	-36.0360	4533
38	-26.1000	-35.5120	4233
39	-25.5060	-34.9960	4334
40	-24.9080	-34.4680	4572
41	-24.3010	-33.9340	4612
42	-23.7050	-33.4130	4597

Station	LATITUDE	LONGITUDE	BOTTOM DEPTH (m)
43	-23.1080	-32.8900	4767
44	-22.5050	-32.3730	4536
45	-21.6180	-32.7830	4407
46	-20.6180	-32.9930	4264
47	-19.5840	-32.8600	4100
48	-18.6350	-32.4000	4279
49	-17.8320	-31.6340	4676
50	-17.4020	-30.7690	4877
51	-16.2870	-30.7090	4924
52	-15.2030	-30.6430	4849
53	-14.1000	-30.5840	4928
54	-13.0000	-30.5350	5185
55	-11.9030	-30.4730	5441
56	-10.8050	-30.4270	5336
57	-9.7020	-30.3670	4289
58	-8.6070	-30.3160	5372
59	-7.5050	-30.2600	5412
60	-6.4050	-30.2010	5070
61	-5.3080	-29.3010	5299
62	-4.1980	-28.7530	5214
63	-3.1050	-28.0360	5086
64	-2.0060	-27.3160	5111
65	-1.0050	-26.6000	3511
66	0.0000	-26.0000	3683
67	1.2940	-26.0000	3278
68	2.4020	-26.2030	4137
69	3.4970	-26.4040	4030
70	4.5970	-26.6060	4321
71	5.6950	-26.8070	3311
72	6.7950	-27.0090	4412
73	7.9000	-27.2110	5055
74	8.9950	-27.4120	5102
75	10.0930	-27.6130	5286
76	11.6960	-27.9070	5806
77	13.2970	-28.2010	5466
78	14.9000	-28.4950	5177
79	16.5020	-28.8410	4893
80	18.0980	-28.7330	4324
81	19.7040	-28.4570	4881
82	21.2960	-28.4470	5104
83	22.8960	-28.4290	5598
84	24.5000	-28.4190	5631

Table 2.- Participants (provisional)

Nom	Sex	Organism	Task
Fiz Fernández Pérez	M	CSIC-IIM	Chief Scientist
Celia Marrasé Peña	F	CSIC-ICM	FDOM/DOC
Jose Luis Pelegrí		CSIC-ICM	Physical measurements/CTD
Fernando Alonso Pérez	M	CSIC-IIM	Responsible of Nutrients
Mercedes de la Paz Arándiga	F	CSIC-IIM	Responsible of N_2O/CH_4
Xosé Antonio Padín Alvarez	M	CSIC-IIM	Responsible pH and underway pCO_2
Antón Velo Lanchas	M	CSIC-IIM	Responsible Oxygen and Alkalinity
Marcos Morente Fontela	M	CSIC-IIM	Alkalinity, TCO2 and pH
Jesus Rey	M	CSIC-IIM	Alkalinity, pH and pCO2
Robert Key		Princeton Uni	14C/13C and BGC Floats
Dean Roemmich		University of California	Deep Argo Buoy
Toste Tanhua		GEOMAR	CFC/SF_6
To be nominated		CSIC-UTM	Chief Technician Informatics
To be nominated		CSIC-UTM	Technician CTD-physical
To be nominated		CSIC-UTM	Technician CTD-physical
To be nominated		CSIC-UTM	Technician CTD-physical
To be nominated		CSIC-UTM	Technician CTD-physical
To be nominated		CSIC-UTM	Technician Chemical support

Mail list
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Celia Marrase: celia@cmima.csic.es (biological oceanography)
Dean Roemmich: droemmich@ucsd.edu (Deep Argo floats program)
Robert Key: key@Princeton.EDU (14C/13C; SOCCOMM floats)
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Toste Tanhua: ttanhua@geomar.de (CFC/SF6)
Bernadettes Sloyan (GO-SHIP) : Bernadette.Sloyan@csiro.au

1. HYDROGRAPHIC STATIONS CTD

To achieve the general objective of the cruise, 84 full depth CTD casts are planned from the Ushuaia to Cartagena (Figure 1). For practical reasons ZEE waters have been avoided. A SBE911plus (Sea-Bird Electronics) CTD probe will be used for the station-based profiling of the water column (from surface to a distance of ~15 meters from the bottom). The CTD unit is equipped with dual temperature and conductivity sensors, a Digiquartz with TC pressure sensor, a SBE-43 oxygen probe, a SeaPoint fluorometer, a SeaPoint turbidimeter and an altimeter. The rosette is also equipped with 24 Niskin bottles (12 L). At each station, the cable will be placed during the downcast at a speed of 1 meter per second (0.45 m/s or less for the ~100 m surface). During the upcast, the winch was stopped at 24 depth levels for Niskin bottle sampling.

2. CHEMICAL ANALYSIS

2.1. Seawater sampling

It is planned to samples seawater to preform on board the analysis of CFC/SF6, oxygen, pH, alkalinity, nutrients, FDOM (fluorescence of dissolved organic matter) and salinity. Additional sampling of N_2O/CH_4, DIC, DOC, $^{14}C/^{13}C$ will be taken to do the analysis on land-based labs.

2.2. Oxygen

With the main purpose of calibrating the O_2 sensor of CTD, samples of O_2 will be taken in all the stations at 24 depths in the FICARAM-XVII section. The O_2 samples will be analysed following the widely applied Winkler method. The O_2 samples will be always the firsts taken from the Niskin bottles of the rosette or after N2O/CH4 samples when they will be sampled. Samples will be collected in calibrated flasks (~113 mL) with a silicone pipe avoiding bubble formation. Sample fixation (precipitation) will be done by adding 0.6 mL of manganous salt ($MnCl_2 \cdot 4H_2O$) and 0.6 mL of alkali-iodide solution (NaOH + NaI). These samples will be stored in darkness at least 24 hours before being measured. Then, 0.8 mL of sulphuric acid will be added to dissolve the precipitate and to titrate the O_2 sample with thiosulfate using an

automatic 5 mL burette “Titrando Metrohm”. Concentration of thiosulfate solution will be periodically controlled by standardization with potassium iodate 0.02N for each session. Blanks will be also measured periodically during the cruise. O_2 concentration is obtained in μmol kg^{-1} by recording sampling temperature and thus having the mass of pickled sea water.

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2.3. Dissolved N_2O/CH_4

Discrete samples from the water column will be in several station to be decided. For each water depth, two replicates will be taken from the Niskin bottles after arrival on deck. Samples will be taken in 120 mL vials for the simultaneous analysis of N_2O and CH_4. Vials will be filled using a silicon tube squeezing air bubbles to assure air bubble free sampling. The silicon tube will be placed on the bottom of the vial, and then left for seawater overflow for at least 2 times the vial volume, and finally the vials will be closed vial with a rubber plug under running water. Close attention will be paid when closing the vials in order to avoid trapping air bubbles in the sample. When all samples for one station will be collected, the vials will be close with an aluminum capsule using a crimping tool. The samples will be conserved right after sampling one station using saturated $HgCl_2$. The N_2O and CH_4 concentration will be determined by gas chromatography in the laboratories of the IIM-CSIC. Gas trace samples can be stored up to 10 months without an effect on the N_2O and CH_4 concentration if stored properly. Samples will be analyzed with a static equilibration method: a headspace of 20 mL with a secondary standard will be added to the sample vial and left to equilibrate with the liquid phase for at least 2 h. Afterwards subsamples will be taken from the headspace and injected automatically into the gas chromatographic system. N_2O and CH_4 will be determined simultaneously by ECD and FID detectors, respectively.

2.4. pH

Seawater pH samples will be taken at 24 levels in all the stations along the FICARAM-XVII section. pH measurements will be 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 its absorbance at 3 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 will be taken directly from the Niskin bottles into special optical glass spectrophotometric cells of 28 mL of volume and 100 mm of path length. These cells will be carefully stored in a thermostatic bath at 25.0ºC around one hour before the analysis. Absorbance measurements will be performed with a Perkin Elmer Lambda 850 UV-VIS spectrophotometer on board the R/V Hespérides. pH values will be given following the equations described in Dickson *et al*. (2007), who includes a correction due to the difference between seawater and the acidity indicator (ΔR).

2.5 Alkalinity

Samples of A_T will be taken during the FICARAM section every each station, almost half of the total stations. In order to analyze these A_T samples on board, the water will be transferred directly from the Niskin bottle to 600 mL borosilicate glass bottles and stored for 24 hours before the analyses. Measurements of A_T will be done by a one endpoint method using an automatic potentiometric titrator (Dosino 800 Metrohm) with a combined glass electrode (Perez and Fraga, 1987). A Knudsen pipette (~195 mL) will be 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 will be determined by means of one pH endpoint (Mintrop *et al*., 2000). In order to estimate the accuracy of the A_T method, A_T measurements of certified reference material (CRM) for CO_2 from batch 100 provided by Dr. Andrew Dickson will be analyzed. In addition, an extra calibration (substandard) will be made by using a closed container of 75 L filled with open ocean surface water.

2.6. Nutrients

Dissolved nutrients will be sampled in all stations and all depths after tracer gases, dissolved oxygen, total inorganic carbon, pH and alkalinity. Samples will be withdrawn to 30 mL solid-polyethylene containers after rinsing twice with the same water. Samples will be preserved in the dark at 4ºC when analyses started more than one hour after collection, and they will be analysed no more than 24 hours after collection. Nutrient analyses will be performed by using a SKALAR segmented flow auto-analyzer. Nitrate+nitrite, phosphate and silicate were simultaneously determined. Determination procedure will be settled as a pumping cycle of 120 seconds sucking the sample and 80 seconds sucking from a milli Q water reservoir. Every

analysis spent ~8 mL of sample. Determinations of nitrate, phosphate and silicate will be carried out following methods described by Hansen and Grassoff (1983) with some improvements (Mouriño and Fraga, 1985). GO-SHIP nutrients standards will be used to test the quality of the calibrations. Primary standards for nitrate+nitrite, phosphate and silicate will be performed from nutrient salt materials (KNO_3, KH_2PO_4 and Na_2SiF_6, respectively) dried 24 hours over silica gel prior to weigh. Primary solutions will be performed with milli Q in calibrated volumetric flasks. A stock standard solution will be prepared by mixing the three primary standards and preserved in the dark at 4 ºC. Daily working standard solutions will be produced dissolving different volumes of stock standard solution in low nutrient seawater (LNSW), filtered through 0.2 µm. These solutions will be prepared every two days and preserved in the dark at 4 ºC. Several LNSW sets will be used in the cruise. At station 14, water deeper than 5000 meters, corresponding to Antarctic Bottom Water (AABW) will be collected and filtered through 0.2 µm in order to have a high nutrient standard. AABW standard will be measured every day of analysis. Certificate Reference Material for nutrients will also be used on board for checking the results.

2.9. Salinity

Salinity samples will be collected in all stations at selected depths to calibrate the conductivity sensor installed in the CTD bathysonde and in the underway thermosalinograph. Samples will be stored during 24 hours in the laboratory under controlled temperature (22ºC) before analysis. During the first leg of the cruise, salinity samples will be collected in all stations at 3 selected depths (two in deep water and one in surface) and will be analyzed using PORTASAL Guildline and calibrated with one only existing IAPSO standard seawater. A container of 50 liters will be filled with seawater collected at 2500 meters depth at station 5. This water will be used during the cruise as a substandard during the cruise and will be analyzed at the beginning and at the end of each series of analysis to check the drift of the PORTASAL

3.- Floats deployments

3.1- Deep Argo (Dean Roemmich)

At present, Argo is extending its 0-2000 m profiling into the deep ocean, with pilot arrays of Deep Argo (0 – 6000 m) floats. A Deep Argo pilot array is planned for the Argentine Basin of the South Atlantic Ocean. The Argentine Basin is known to have a substantial warming signal in its deepest layers, and is of high interest for improved understanding of ocean-climate changes. The proposed GO-SHIP A-17 line would provide a valuable deployment opportunity for Deep Argo floats as well as the high-quality reference data that is essential for quality assessment of Deep Argo temperature/salinity profile data. The proposed 2019 FICARAM-XVII cruise, and in particular the GO-SHIP A-17 line, has my strongest endorsement for its high scientific value and its importance in the international collaboration for sustained global ocean observations.

3.2 Biogeochemical Argo (Robert Key)

The SOCCOM group (Princeton University) will conduct a program of deployment biogeochemical ARGO floats during the cruise. A CTD profiles and inorganic system measurement will ne also include to calibrate the float sensors.