CSIC contribution to harmonization and quality control of N_2O and CH_4 measurements in the ocean

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CSIC contribution to Ingos:

TASKs in WP6:

Task 6.1: Set up of OA-ICOS/Equilibrator to measure dissolved N_2O and CH_4 in seawater – *lead by IFM-GEOMAR , contributor: UEA*

Task 6.2: ***Inter comparison exercise of gas chromatographic*** *(GC) versus OA-ICOS methods - Lead by GEOMAR, Contributors: UEA, CSIC, UiB*

Task 6.3: *Establish* ***N_2O and CH_4 measurements at open ocean*** *and coastal time series stations - Lead by GEOMAR ; Contributor: CSIC*

Task 6.5: Establish N_2O and CH_4 measurements at **repeated hydrographic section**- Lead by CSIC (Emma Huertas)

Task 6.6: Archive data (including data quality check in MEMENTO-led by IFM-GEOMAR. Contributors: UEA, CSIC

Task 6.2: Intercomparison exercise

Analytical System used by CSIC (developed by Mercedes de la Paz)

- Dissolved N_2O and CH_4 are measured simultaneously by single-phase equilibration gas chromatography, with ECD detector for N_2O and FID for CH_4
- GC set-up in the CSIC-IIM, using a home-made automated equilibration system

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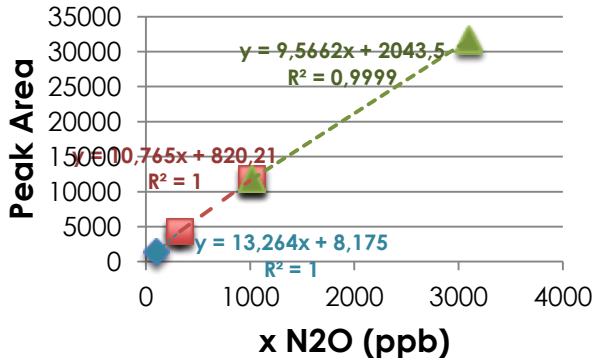
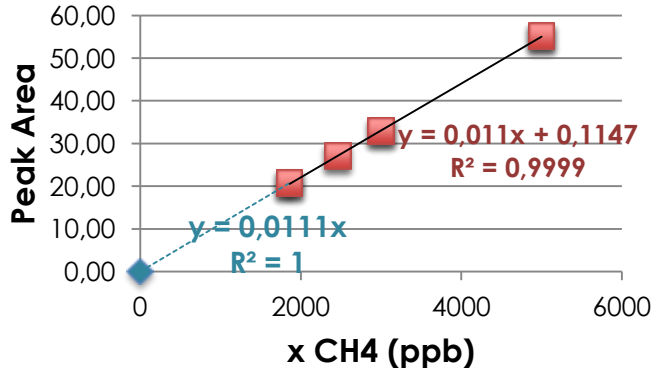
Task 6.2: Intercomparison exercise: second round

Participants: GEOMAR, Germany and CSIC, Spain

Samples were collected the 5th of November 2013 in the Boknis Eck
Six replicates of 20 mL were collected at six different depth levels (1, 5, 10,15,20,25 m)

Standard	N_2O ppb	CH_4 ppb	Uncertainty (%) N2O	Uncertainty (%) CH4
STD 0	100,52	2464		
STD 1	1020	3000	10	6
STD 3	324,97	1863,38	0,5%	0,2
STD 2	3100	5000	10	5





Depth (m)	CTD sal	CTD temp	CH4 nmol/L	SD CH4 nmol/L	pCH4 in situ (ppb)	SD pCH4 in situ	N2O nmol/L	SD N2O nmol/L	pN2O ppb	SD pN2O nmol/L
25	17.61	11.48	213.7	0.2	145815.3	157.5	10.22	0.02	341.3	0.6
20	17.63	11.48	230.5	0.4	156772.1	266.6	10.19	0.01	339.7	0.2
15	17.95	11.53	251.6	0.6	165340.2	408.2	10.24	0.05	330.6	1.6
10	19.13	11.99	69.5	1.3	44858.1	824.3	10.33	0.02	326.3	0.6
5	23.71	12.16	15.8	0.2	10191.9	104.4	10.39	0.04	328.4	1.2
1	24.33	12.12	14.5	0.3	9332.9	189.0	10.38	0.01	326.9	0.2

D 6.2 Report on inter comparison exercise

Task 6.2: Intercomparison exercise

Member of the **SCOR WG 143** *Dissolved N_2O and CH_4 Measurements: Working Towards a Global Network of Ocean Time Series Measurements of N_2O and CH_4 ,* that was approved in November 2013. Funding period is from 1st January 2014 to 31st December 2017.

Activities: An intercalibration exercise amongst WG members. Publication on recommendations and protocols for calibration, quantification, and data reporting. Review of existing and near-future methods for quantifying N_2O and CH_4 in seawater including spectroscopy measurements.

Meeting #1: Honolulu, Hawaii USA on Friday 21 February 2014.

Attendants: Damian Arevalo-Martinez (GEOMAR), Herman Bange (GEOMAR), John Bullister (NOAA PMEL), David Capelle (UBC), Bonnie Chang (UW), Mercedes de la Paz (CSIC), Laura Farias (U Concepcion), Sarah Ferron (UH), Annette Kock (GEOMAR), Gregor Rehder (IOW), Alyson Santoro (U Maryland, Horn Point), Philippe Tortell (UBC), Sam Wilson (UH), Guiling Zhang (Ocean U China)

1st Report was submitted in June 2014. **//portal.geomar.de/web/scor-wg-143**

Task 6.2: Intercomparison exercise

Participation in the 1st International Intercalibration Exercise

Table 1. Timetable of WG activity relating to the intercalibration of dissolved N_2O and CH_4.

Activity	Dates of activity						
Analysis of seawater samples from Stn ALOHA	Nov 2013	May 2014					
Production of gas standards		May 2014	Sept 2014				
Comparison of calibration procedures				Oct 2014	Nov 2014		
2nd analysis of ALOHA seawater					Nov 2014	May 2015	
Report writing							June 2015

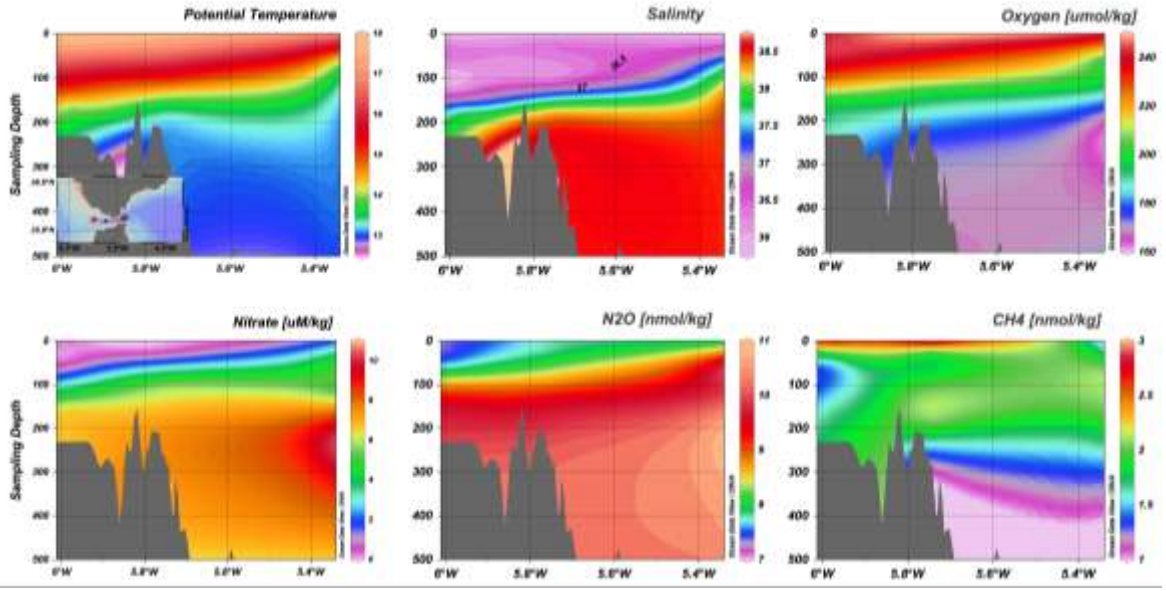
The WG is currently halfway through its first intercalibration exercise analyzing seawater samples collected from the Hawaii Ocean Time-series (HOT) program long term monitoring Station ALOHA in the North Pacific. Samples were collected at different locations in the water-column to ensure a range of N_2O and CH_4 concentrations would be analyzed. Datasets from the participating laboratories are being currently compiled. CSIC data were sent on January 2014.

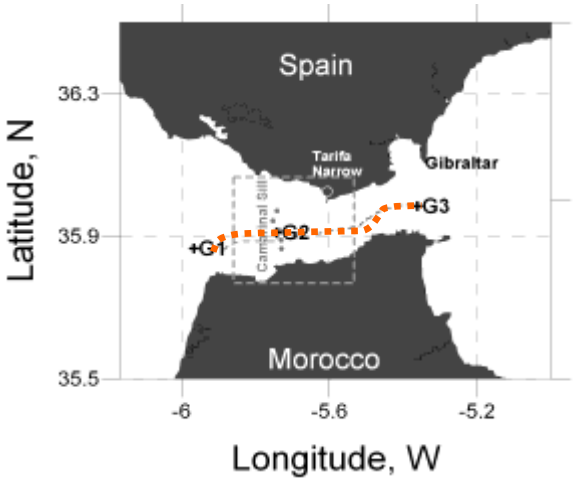
Task 6.3: N_2O and CH_4 measurements at time series stations

Distribution of nitrous oxide and methane in Atlantic and Mediterranean waters through the Strait of Gibraltar

Gibraltar Fixed Time Series

Campaign	Date	Ship
GIFT 0611	26 July 2011	RV *García del Cid*
GIFT 0811	4-5 August 2011	RV *Cornide de Saavedra*
GIFT 1111	10 November 2011	RV *García del Cid*
GIFT 0212	27-28 February 2012	RV *García del Cid*
GIFT 0513-Ficaram XV	23 May 2013	RV *Hespérides*

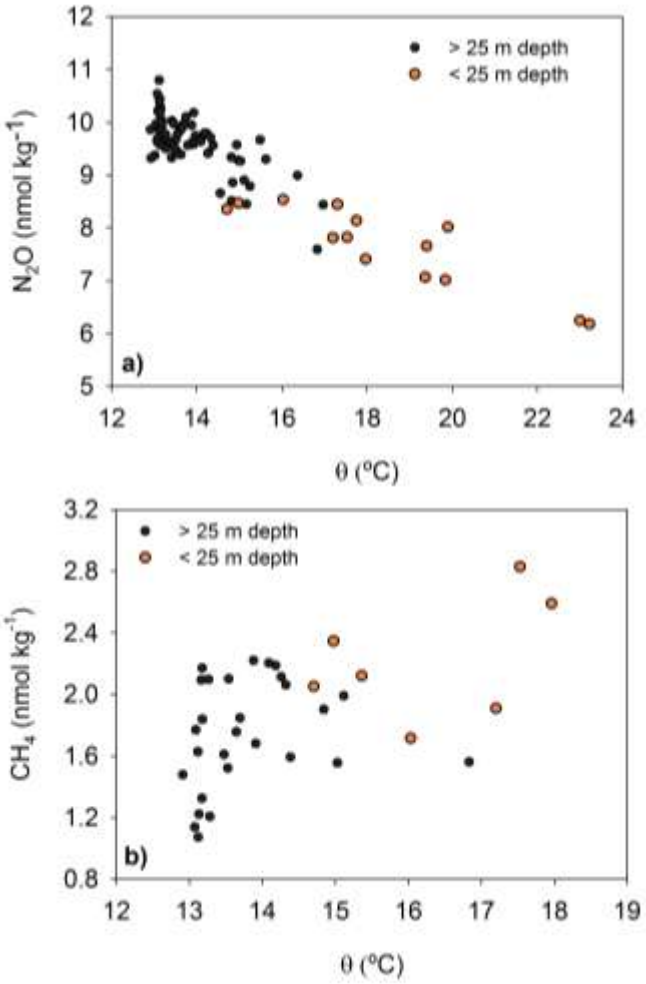




de la Paz et al (2014) Marine Chemistry (submitted)

Task 6.3: N_2O and CH_4 measurements at time series stations

D 6.3 Report on time series data Ready for submission



month	Temperature	N_2O (nmol kg^{-1})	CH_4(nmol kg^{-1})	Sat N_2O (%)	Sat CH_4 (%)	Windspeed (m s^{-1})	Air-sea Flux N_2O (µmol m^{-2} d^{-1})	Air-sea Flux CH_4µmol m^{-2} d^{-1})
Feb	15.02	8.41±0.08	2.17± 0.07	100.1± 1.7	91	3.7	0.01± 0.12	-0.19± 0.13
May	17.75	7.62±0.29	2.71±0.11	100± 3	122	5.4	0.08± 0.37	0.85± 0.26
Jul	22.04	6.81±1.04	--	105± 9	--	2.2	0.13± 0.24	--
Aug	20.20	7.90±0.34	--	108.23± 0.13	--	5.4	1.09± 0.03	--
Nov	18.96	7.04±0.04	--	100.0± 0.7	--	4.9	0.00± 0.07	--

*N_2O distribution follows the two layers scheme circulation in the Strait of Gibraltar

*Mediterranean deep waters are highly undersaturated in CH_4

* Nitrification acts as the main N_2O source in the Mediterranean overflow water

* Temperature controls the seasonal variability of N_2O in the upper layer

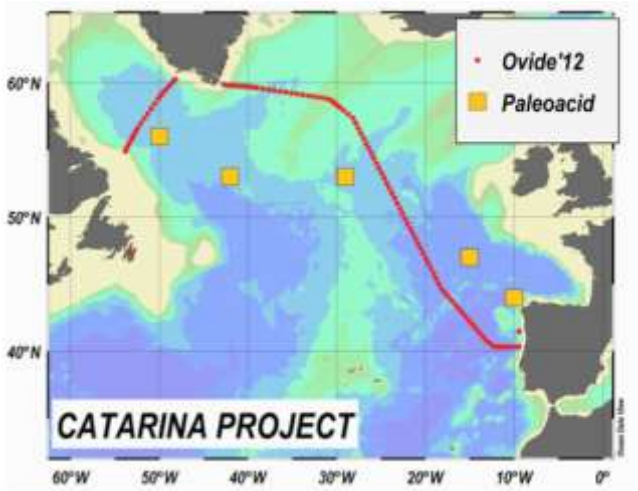
Task 6.5: N2O and CH4 measurements at repeated hydrographic section

OVIDE-Repeated hidrographic Section connects Lisbon with Greenland

Sampled from 2002 every other year

- Project CATARINA: Ovide cruise in June/July 2012

CArbon Transport and Acidification Rates In the North Atlantic



A total of 103 stations:
95 stations in the Atlantic Ovide section+
8 stations in the Labrador Sea

643 samples for N_2O and CH_4 in
100 mL bottles, triplicates

Atmospheric air samples trough TNA Ingos service

- Isotopic composition of CO and H_2, and potentially N_2O. Aprox 1 sample per day: 25 were filled with atmospheric air. Analysis in the Institute for Marine and atmospheric Research Utrechtt. Results not yet

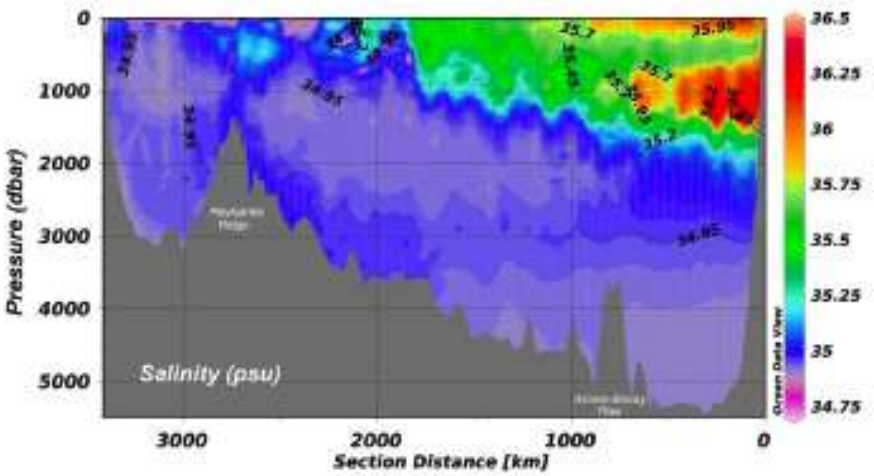
- Isotopic composition of CH_4 concentration and $\delta^{13}C$ analysis. Gas bag for air sampling at atmospheric pressure. Analyzed in University of London (Rebeca Fisher). Presented last meeting

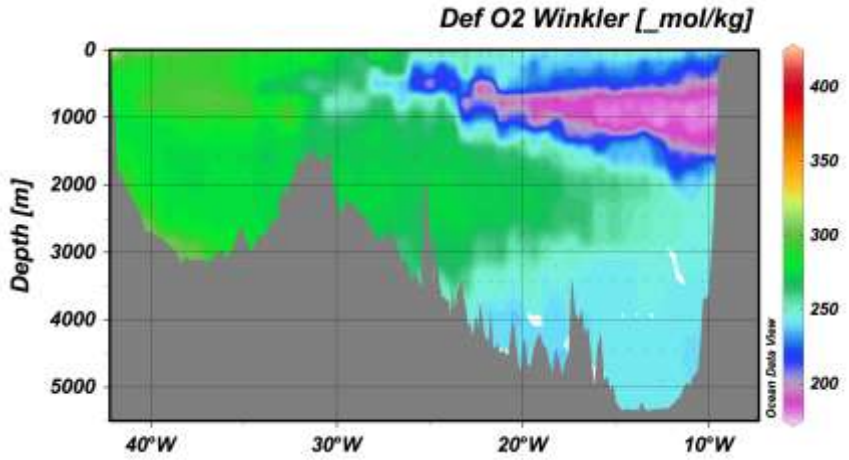
- **Project GEOVIDE: Ovide cruise conducted in April/May 2014: samples are being analysed**

Task 6.5: N2O and CH4 measurements at repeated hydrographic section

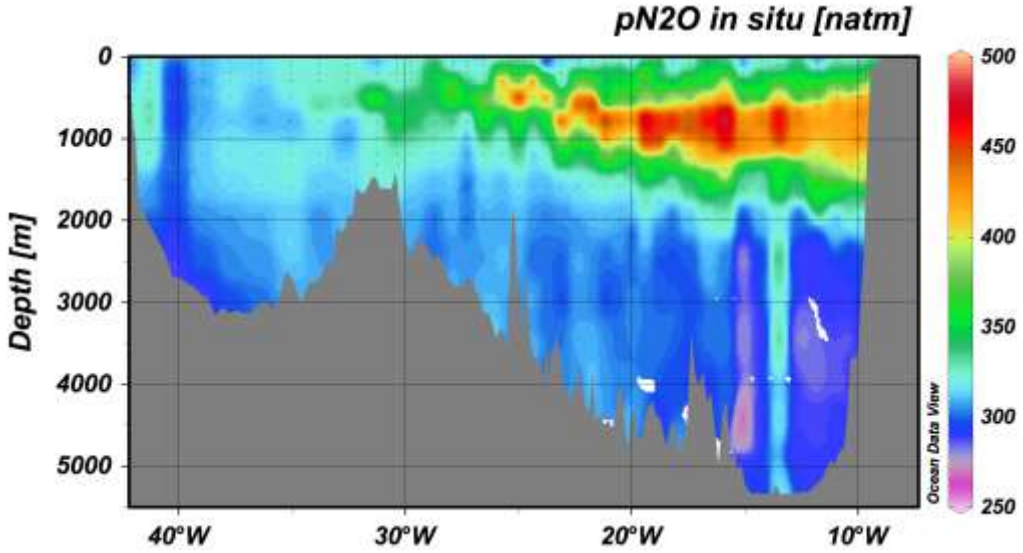
OVIDE Section

D 6.5 Report on repeated hydrographic section. Ready for submission

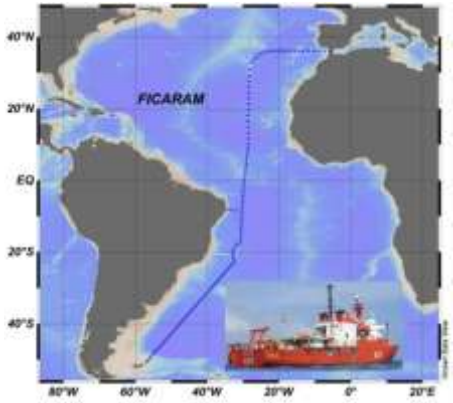




Please visit our poster…..



FICARAM-15 cruise

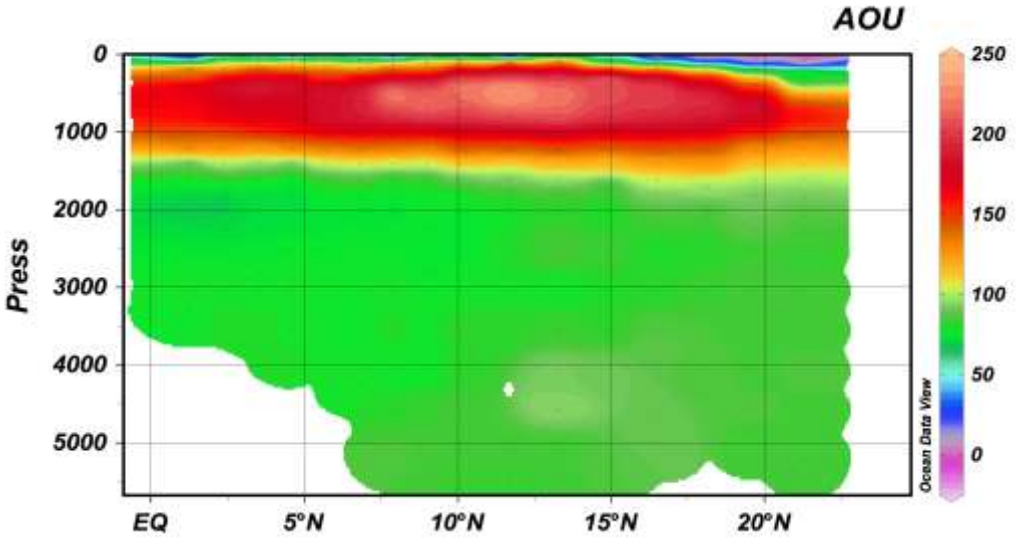


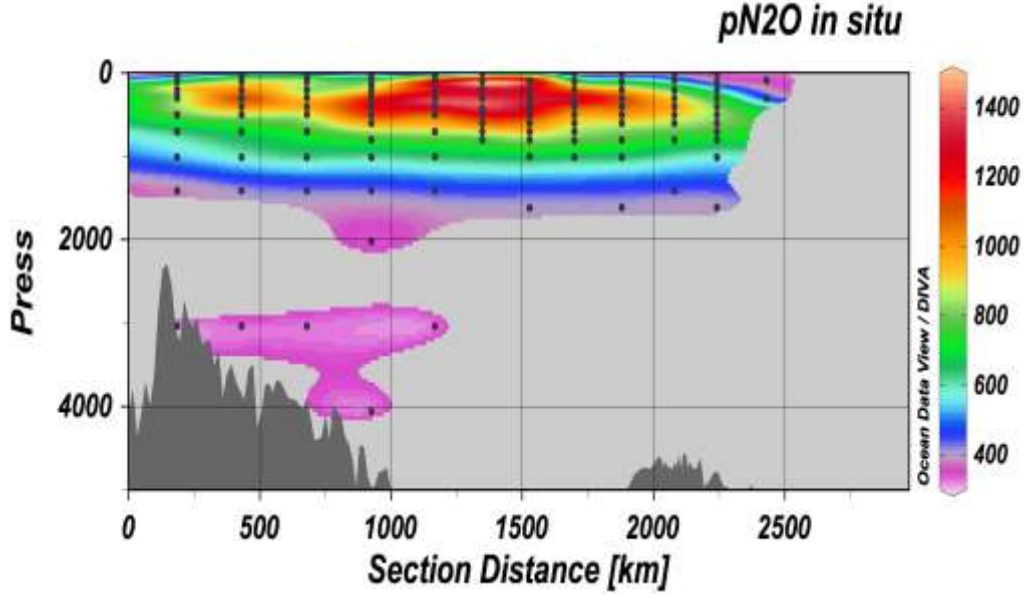
Temporal evolution of the anthropogenic carbon and evaluate the CO_2 absorption capacity of the South Atlantic region, the Equatorial zone, and the subtropical region of Azores-Gibraltar in the North Atlantic.

LEG 1: From Punta Arenas (Chile) to Recife (Brazil): 62 stations.

LEG 2: From Recife (Brazil) to Cartagena (Spain): 46 stations

Samples for N_2O and CH_4 were collected only in the Equatorial Atlantic, coinciding with the Oxygen Minimum Zone. This oceanic area is characterized for an intense node of N_2O production.





Thank you for your attention