



D4.3

Reference document for methane harmonized monitoring

WP 4 – Joint operations across the RI domains

LEADING BENEFICIARY: INGV

Author(s):	Beneficiary/Institution
Jean-Daniel Paris	CEA
Hélène Leau, Livio Ruffine, Thomas Giunta, Jean-Pierre Donval, Viven Guyader, Dominique Birot, Carla Scalabrin, Christophe Brandilly, Thibault Douillard	Ifremer
Mia Schumacher	GEOMAR
Manfredi Longo, Sergio Scire, Francesco Italiano, Gianluca Lazzaro	INGV
Roberto Grilli, Camille Blouzon	CNRS

Accepted by: Jean-Daniel Paris (WP 4 leader)

Deliverable type: REPORT

Dissemination level: PUBLIC

Deliverable due date: M46

Actual Date of Submission: 23 July 2019



ABSTRACT

Task 4.2 of the WP4 developed a joint pilot experiment to measure methane transfer from the seafloor to the atmosphere, in a pilot study involving RIs ICOS, Eurofleets, EMSO and ACTRIS. The pilot experiment developed joint monitoring strategy for methane detection at various levels starting from the seafloor and moving across the water column, the water/air interface and the atmosphere. The Romanian sector of the Black Sea is the selected location. This area hosts a large number of emission sites of methane-rich gases, from the continental shelf to the deepest part of the basin. It is consequently a good candidate for investigating the fate of marine methane, from the sedimentary column to the atmosphere by combining the expertise and technologies of six EU teams. The methodology applied integrates (1) sampling from the three spheres (lithosphere, hydrosphere and atmosphere) for laboratory measurements of methane concentration by well-proven standard methods together with $\delta^{13}\text{C}$ -CH₄ analysis, (2) *in situ* measurements of methane concentration and $\delta^{13}\text{C}$ -CH₄ into the water column and the atmosphere, and (3) the deployment of a seafloor observatory for a short monitoring period (4-5 days) to evaluate the temporal variability of gas fluxes.

- **Key words:** Acoustics survey, atmosphere, geochemical analysis, *in-situ* gas measurements, *in-situ* sampling, methane transfer, observatory, sediment, water-column

Project internal reviewer(s):

Project internal reviewer(s):	Beneficiary/Institution
Jean-Daniel Paris	CEA

Document history:

Date	Version
07/07/2019	Creation of the document
23/07/2019	Accepted by WP 4 Leader

DOCUMENT AMENDMENT PROCEDURE

Amendments, comments and suggestions should be sent to the authors (Jean-Daniel.Paris@Isce.ipsl.fr, Livio.Ruffine@ifremer.fr, francesco.italiano@ingv.it)



TERMINOLOGY

A complete project glossary is provided online here:

<https://envriplus.manageprojects.com/s/text-documents/LFCMXHHCwS5hh>

PROJECT SUMMARY

ENVRIplus is a Horizon 2020 project bringing together Environmental and Earth System Research Infrastructures, projects and networks together with technical specialist partners to create a more coherent, interdisciplinary and interoperable cluster of Environmental Research Infrastructures across Europe. It is driven by three overarching goals: 1) promoting cross-fertilization between infrastructures, 2) implementing innovative concepts and devices across RIs, and 3) facilitating research and innovation in the field of environment for an increasing number of users outside the RIs.

ENVRIplus aligns its activities to a core strategic plan where sharing multi-disciplinary expertise will be most effective. The project aims to improve Earth observation monitoring systems and strategies, including actions to improve harmonization and innovation, and generate common solutions to many shared information technology and data related challenges. It also seeks to harmonize policies for access and provide strategies for knowledge transfer amongst RIs.

ENVRIplus develops guidelines to enhance transdisciplinary use of data and data-products supported by applied use-cases involving RIs from different domains. The project coordinates actions to improve communication and cooperation, addressing Environmental RIs at all levels, from management to end-users, implementing RI-staff exchange programs, generating material for RI personnel, and proposing common strategic developments and actions for enhancing services to users and evaluating the socio-economic impacts.

ENVRIplus is expected to facilitate structuration and improve quality of services offered both within single RIs and at the pan-RI level. It promotes efficient and multi-disciplinary research offering new opportunities to users, new tools to RI managers and new communication strategies for environmental RI communities. The resulting solutions, services and other project outcomes are made available to all environmental RI initiatives, thus contributing to the development of a coherent European RI ecosystem.



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1. Rationale and approach

Methane (CH₄) is a major greenhouse gas emitted from both natural and anthropogenic sources. In a warming climate, methane emission from altered coastal seafloor have a potential to further increase significantly the greenhouse gas burden. Gas exploitation from hydrates has the potential to destabilize surrounding hydrates in the sediment and release significant amounts of methane in the water column. Currently, the cumulative effect of mechanisms regulating the injection of methane from the sediments through the water column to the atmosphere remain poorly known. These mechanisms include oxidation and transport through bubbling (see Figure 1). Sources can be linked to disturbances or leakages by offshore resources exploitation, spontaneous sediment sources, or destabilized methane hydrates especially in the Arctic. Gaining new systematic insights into the processes that govern the fate of methane through the sediment across the water column and providing more accurate estimates of marine source fluxes in the atmospheric methane budget are relevant to answer key societal questions such as ocean acidification, climate change and the development of chemosynthetic bacterial communities at deep sea.

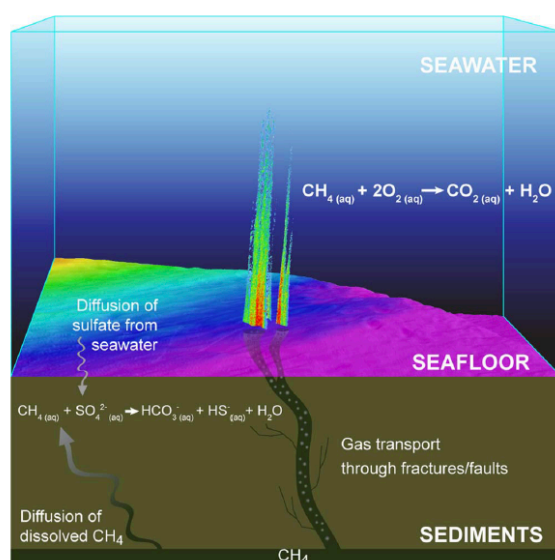


Figure 1. Processes regulating the flux of methane in the water column (from James et al., 2016)

Methane seeps discoveries are dramatically increasing with the improved detection capacities of the multi-beam acoustic sounders: gas hydrates, multiple small pockmarks, plumes from active faults, and from industrial production or storage sites. Their time variations due to climate change, seismic triggering and mud volcanoes need to be monitored. The task is organized around a joint pilot experiment on a RI platform at a site of interest. The pilot study experiment will include measurements from seismicity, seafloor gas bubbles, dissolved methane, sea surface, to atmosphere. Sensing technology will be compared and range from active acoustics, seismology, chemical and spectro-optical sensors, reference analysis of isotopes, etc. Monitoring of methane fluxes at the water-atmosphere interface will be addressed.

Earlier in ENVRIplus Task 4.2 innovative sensors on the seabed or along the water column (acoustic bubble counters, optical sensors for dissolved gas) have selected (see Milestone MS10), improved and integrated into a coherent end-to-end sensor system to meet future integrated usage in the frame of RIs. A new test bench has been designed (see Appendix 1) Improvement involves calibration, accurate modelling of the signals, processing and inversion strategies, and well-controlled ground-truthing operations. The chemical sensors need also improvements to follow the dissolution processes of the methane plumes.

This Pilot experiment involves design and implementation of a site experiment including deployment of an end-to-end sensor system at all levels from seismicity, seafloor gas bubbles,

dissolved methane, sea surface, as well as fluxes to the atmosphere. Sensing technologies will be compared within active acoustics, seismology, chemical sensors, analysis of isotopes,...

Overall this task shall better link discoveries of methane seeps and time series analysis of their variability with overall estimation of their impact on the global change. The outcome of Task 4.2 in ENVRIPLUS is:

1. a problem-solving demonstration of the 'agile' joint deployment and operation of several RIs toward a particular scientific issue and
2. to provide recommendations on the joint refinement to scientific and technical observation and analysis protocols across RIs.

2. Cruise presentation

Cruise general information:

- **Ship name:** MARE NIGRUM, operated by GeoEcoMar Romania
- **Date:** 1-8th April 2019
- **Zone:** Black Sea, Romania Exclusive economic zone
- **Territorial waters:** Romania
- **Subject:** Design and test of a joint pilot experiment on a RIs platform that aims to measure methane concentration from the seafloor to the atmosphere, and quantitatively gain insights into its transfer between the lithosphere and the atmosphere.

The Research vessel MARE NIGRUM

The chartering of a vessel to perform the ENVRI cruise was advertised publicly on the French website <https://www.marches-publics.gouv.fr/> on the 15 feb 2019. One offer was received, from GeoEcoMar operating the vessel MARE NIGRUM. A contract was then established between IFREMER and GeoEcoMar for the chartering of the vessel.

The research vessel (R/V) MARE NIGRUM was chosen to perform the cruise due to its location. It is the only RV operating in the Black sea, therefore allowing to reduce the transit time from port to survey area to its minimum, keeping the chartering costs to the minimum cost.

The operations and participants are described in Appendix 1.





Vessels details can be found on <https://www.geocomar.ro/website/en/nave-cercetare-mare-nigrum.html>

Cruise location :

The operation took place in two survey areas:

Northern box	Latitude (N)	Longitude (E)
Box		
N44.13,525639	E30.42,554935	
N44.12,794067	E30.43,973752	
N44.14,575678	E30.45,812485	
N44.15,295255	E30.44,440516	

Southern box	Latitude (N)	Longitude (E)
Box		
N43.52,634549	E30.12,190961	
N43.52,239174	E30.11,778255	
N43.52,662788	E30.10,947266	
N43.53,043985	E30.11,367805	

The map below shows the navigation route of the vessel during the cruise.

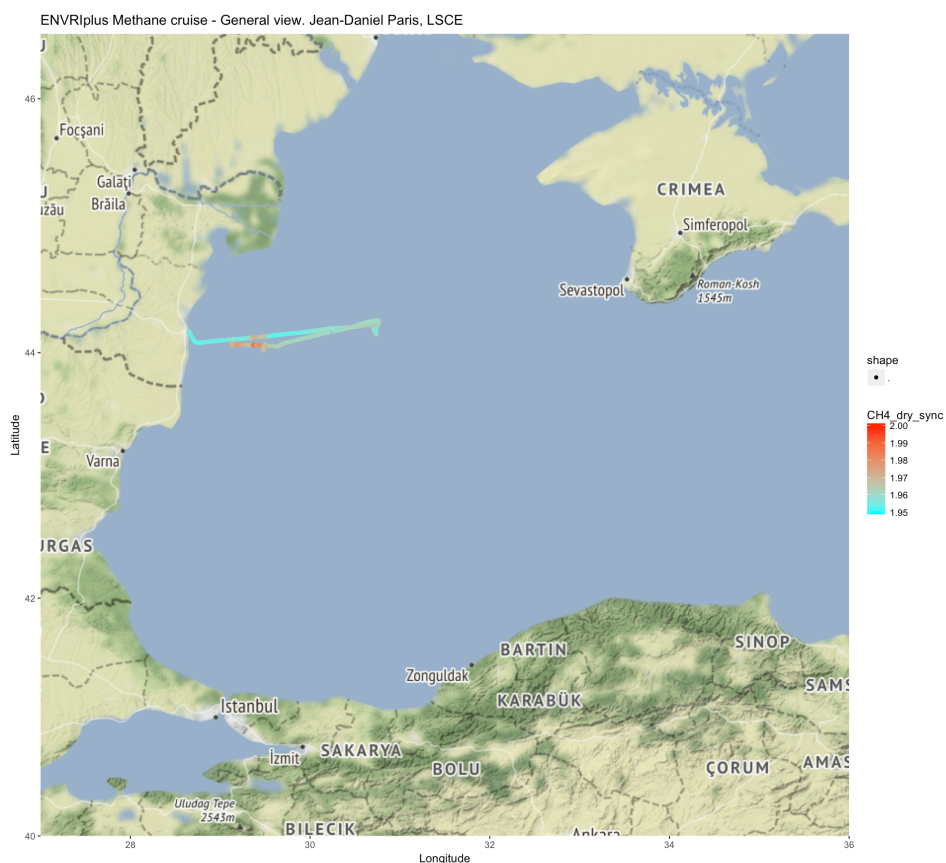


Figure 1: Location map of the study area

3. GIS mapping of flares

Instruments

To undertake the bathymetry mapping of the sites of interest and transit areas an ELAC Nautic SeaBeam 1050 was used to obtain information on the depth. It is a hull mounted multibeam echo sounder which was running throughout the whole cruise at a frequency of 50kHz. It counts 126 beams in total with a beam width of 1.5° and equi-angular beam spacing of 1.25°. The maximum depth for the SeaBeam 1050 is 3000m (L3 Communications ELAC Nautic GmbH (2011): SeaBeam 1050/1055 Medium Water Multibeam Systems).

To localize and investigate gas plumes sites a Simra EK80 Single Beam with ES70 transducer head was deployed. It operates at a frequency of 70kHz and is capable to give high resolution information about the water column and backscatter strength of objects in the water column. It is a split-beam transducer that is capable to locate objects within the beam accurately by comparing the phase deviations of returning signal in four sectors of the beam. Thus position and height of methane 'flares' can be examined easily (Kongsberg Maritime AS (2009): Simrad ES70 Single Beam Fish Finder, p. 2f).

Data Processing and Merging

The multibeam data were cleaned from spikes and outliers using HDPedit software. With MBSystems, the beams were corrected for sound velocity by implementing a sound velocity profile that has been acquired with the CTD rosette in the survey area. The cleaned and beam corrected data were exported as ASCII files (.xyz). In GMT (Generic Mapping Tools) the .xyz data were gridded using a nearest neighbour algorithm at a grid size of 7m. The final grid was loaded into QGIS to create a 2D bathymetric map of the main survey sites 'North Box' and 'South Box' or 'Shallow site', respectively (Figs. 1.1, 1.2).

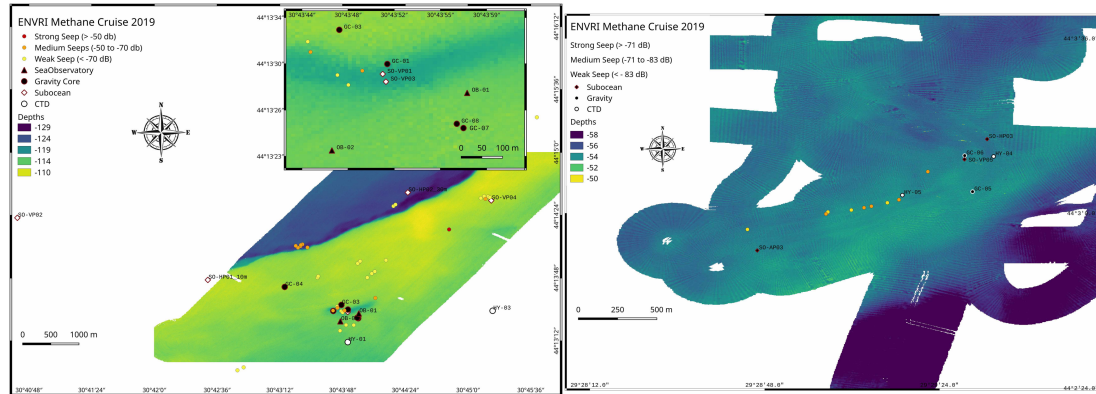
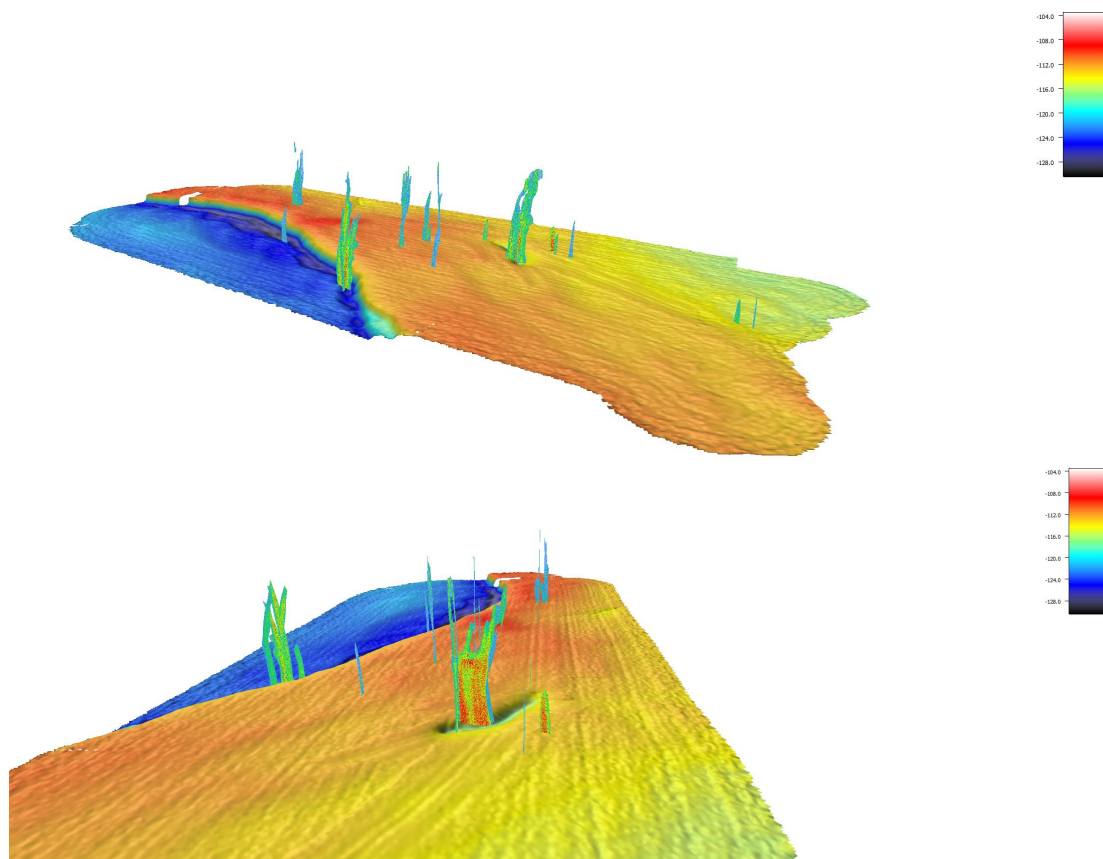


Figure 2: Distribution Map of the gas flares

The single beam data were examined with ESP-3 and QPS FMMidwater software. Basically, the positions of the seeps at the seafloor were geo-picked and exported as .xyz files to be displayed as points on the bathymetry map (Figs. 1.1, 1.2). Additionally, some well-defined flares were selected and exported as point clouds containing position and depth as well as backscatter strength values. The point clouds of the flares have been saved as .scene files which can be read by QPS Fledermaus software. The resulting flares are presented in the following figures. The flare locations represent the target of most of the operations.

To get a 3D impression, the .xyz bathymetry data were imported to Fledermaus along with the point clouds of the methane flares to get a 3D impression of the sites (Figs. 2.1, 2.2).

The single beam data will be further examined with the aim to estimate gas flow rate and volume.



4. Analysis of sediment cores, methane cycle in the sediment

The methane discharged from sediment into the ocean water column only represents a small fraction of all the methane being produced at depth in the sedimentary column, mostly through microbial methanogenesis. Indeed, as the methane migrates through the sedimentary column, a significant part is degraded by methanotrophic organisms in anaerobic conditions. In general, microbial degradation of methane is coupled with sulfate reduction, and is restricted to a narrow sedimentary horizon (usually less than 1m). As a part of the Envri+ campaign, 8 gravity cores were collected from shallow sediment layer of the Black sea to get insights into the methanogenesis and methanotrophy processes within the sedimentary column.

In addition to provide an estimation for the methane concentration of the fluid near the sediment/water column interface, one main aspect of this task was to better define the location of the methanogenesis/methanotrophy transition zone in shallow sediments from the Black sea. To achieve this goal, not only dissolved methane concentration profiles were measured, but Dissolved Inorganic Carbon (DIC) - which is one by-product from methanotrophic respiration - were measured *on board* by potentiometric titration together with the alkalinity. Because methane degradation is coupled with sulfate oxidation sulfate concentration profiles were also measured from the collected pore waters by liquid ion-chromatography.

Gravity cores

The gravity corer was deployed 8 times over the course of this campaign. It was deployed 6 times in the “Northern Box” (ENV-GC-01,02,03,04,07 and 08) and 2 times in the “Shallow Box” (ENV-GC-05 and 06). It should be noted that the gravity cores ENV-GC-03 and 04 came back on board empty, therefore were not usable for the study.

Overall, the gravity cores collected from the “Northern Box” were about 120 cm to 160 cm long, whereas gravity cores from the “Shallow Box” had a length of 240 cm.

Name	Date	Time (UTC)	Coordinates				Length recovered (cm)
			Lat °	Lat N	Lon °	Lon E	
ENV-GC-01	03/04/19	22:20:07	44	13.4997	30	43.8510	134 cm
ENV-GC-02	05/04/19	5:15:06	44	13.4863	30	43.7105	120 cm
ENV-GC-03	05/04/19	6:09:00	44	13.5440	30	43.7886	0
ENV-GC-04	05/04/19	6:23:12	44	13.7156	30	43.2460	0
ENV-GC-05	06/04/19	11:45:53	44	3.0742	29	29.5136	240 cm
ENV-GC-06	06/04/19	12:14:35	44	3.1979	29	29.4865	240 cm
ENV-GC-07	07/04/19	7:00:00	44	13°24,996	30	43°57,00	160 cm
ENV-GC-08	07/04/19	7:52:02	44	13°25,3260	30	43°56,4780	140 cm

Methane concentration

The procedure for methane concentration measurement in sediment pore waters is adapted from IODP standard procedure (Andr n et al., 2015). Sub-sample of 2 cc or 3 cc of fresh sediments is collected with a pre-cut syringe into a 20 mL headspace bottle, to which 5 mL of NaOH 2M is added. Methane concentration is then measured on the headspace, using a gas-chromatography with an FID detector. Concentration in the pore water is then derived from headspace concentration corrected by sediment porosity.

Dissolved Inorganic Carbon (DIC) and alkalinity measurement

Pore waters were collected using Rhizon samplers. They consist in hydrophilic, porous polymer tube with 2.5 mm in diameter and 50 mm in length [Seeberg-Elverfeldt et al., 2005]. The resolution at which Rhizons were inserted into the sediment was variable depending on the core features (from 10 or 40 cm). Soon after the collection of pore waters, the DIC was measured on board simultaneously with the alkalinity. Measurements were performed by direct titration with ultrapure 0.05 N HCl from a potentiometric titrator 848 Tritrino Plus from Metrohm.

Major dissolved elements (including sulfate)

Major dissolved elements present in pore waters were measured from the samples collected by Rhizon. Vials for major chemistry were pre-acidified with 50 microliters of HNO₃ 10N. Concentrations of anions and cations were measured at IFREMER on Dionex ICS200 ionic chromatograph. Anions (sulfate and chloride) were analyzed on an Ionpac AS-17C column of 250 mm in length and 4 mm in diameter equipped with a 4 mm ASRS suppressor. The detection limits were 1.5 and 5 ppm for sulfate and chloride, respectively. Major cations (magnesium and calcium) were analyzed on an Ionpac CS-12A column of 250 mm in length and 4 mm in diameter equipped with a CAES suppressor. The detection limit was 0.1 ppm for both species. All elements were quantified by comparing their peak intensity with equivalently diluted International Association for Physical Sciences of Oceans (IAPSO) standard seawater.



The latter was analyzed at the beginning of each run. The concentration values were determined with an estimated accuracy better than $\pm 3\%$.

Results & Discussion

Result for methane, sulfate and DIC are outlined in Figure 4 for the five cores on which these measurements were performed (ENV-GC-08 was collected for archive only).

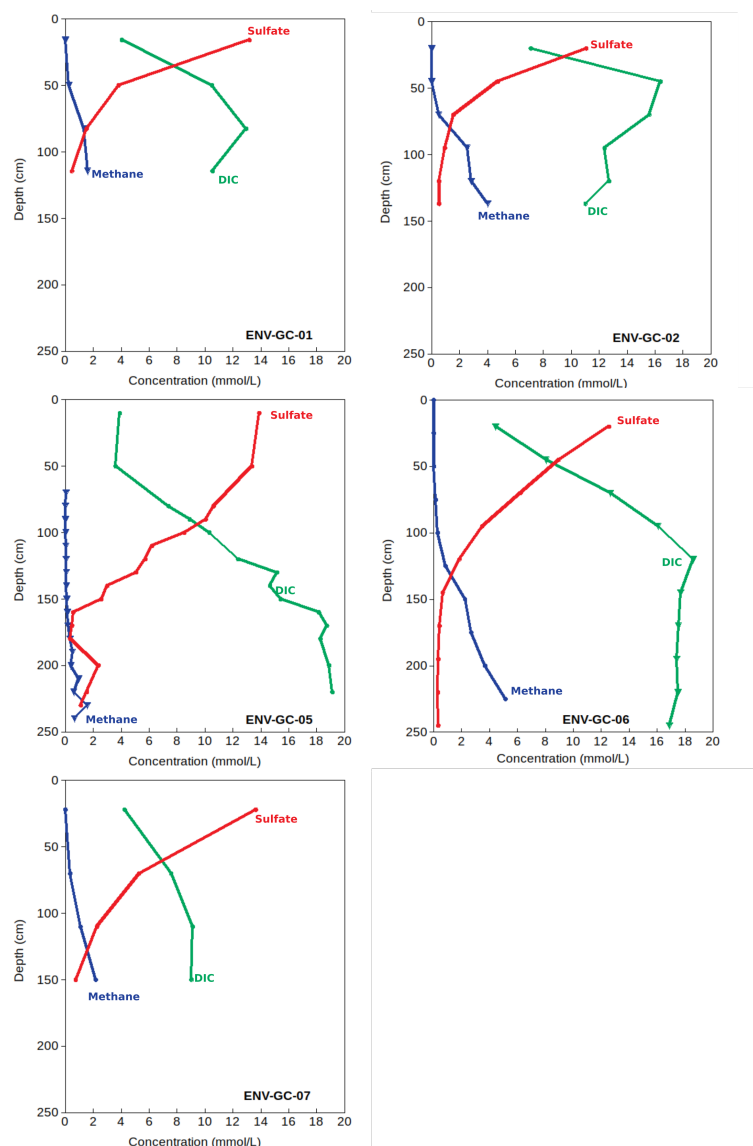


Figure 4: Methane, sulfate and DIC depth-concentration profiles, expressed in mmol/L

Methane concentrations range from near 0.001 mmol/L near the sediment/water-column interface (ENV-GC-06), to up to > 4 mmol/L (ENV-GC-02 and 04). Sulfate concentrations are very similar for the all 5 cores investigated. They roughly vary between ~ 14 mmol/L near the sediment-water interface, which is approximately the sulfate concentration at the bottom of the Black sea water column (Aloisi, 2004), to less than 0.2 mmol/L at deeper intervals. Dissolved Inorganic Carbon show wider range of variations from one core to another, and can reach a maximum of 19 mmol/L in ENV-GC-05. In all cores, it is remarkable that DIC maximum

seem to be observed near the depth where methane and sulfate concentrations cross each others. The specific horizon is called the Methane Sulfate Transition Zone, and represents the sedimentary interval where methane is degraded.

Overall, the concentration profiles of these 3 chemical tracers (methane, sulfate and DIC) are all very consistent with previous studies on shallow sediments from the Black sea (e.g. Jorgensen et al., 2001; Wallmann et al., 2006; Holmkvist et al. 2011). They are all exhibiting a shallow SMTZ, that must reflect the transition between a methanogenesis activity at a depth in the sediment (probably deeper than sampled by any of these gravity cores), and a methanotrophic activity : the anaerobic oxidation of methane- AOM at shallower depth coupled with sulfate reduction (SR). The fact that the DIC appears to be maximum at, or near the SMTZ, is also consistent with this general framework, as it reflects the maximum of methane degradation through AOM.

Although all five cores investigated show profiles suggesting similar processes with respect to the methane cycle, it can be observed that the location of the SMTZ occurs at different depth depending on the coring location. The SMTZ is about 70 cm depth for ENV-GC-01 and ENV-GC-02 ("Northern Box"), whereas it is closer to 120 cm depth for ENV-GC-06 ("Shallow site") and ENV-GC-07 ("Northern Box"). The reason for this variable depth of SMTZ remains to be investigated, but most likely results from variable penetration of sulfate within the sediment and/or upward methane fluxes.

The sulfate and methane profiles for ENV-GC-05 ("Shallow Box"), although sampled very close to ENV-GC-06, show some slightly more complex pattern. In particular, we can observe a slight increase of sulfate concentration at 200 cm depth, which could suggest the mixing with of a shallower fluid (with higher sulfate concentration) circulating at this interval. Nonetheless, this behavior could also result from sampling artifact during installation of Rhizon samplers onto the core. Further investigation is needed to better understand the sulfate pattern within the sedimentary column.

5. Analysis of ocean bottom sensors

The new generation of multidisciplinary seafloor observatory, built in the mainframe of the EMSO-Medit project, is a versatile underwater system able to operate in extreme environment up to the depth of 4000 meters. It is able to automatically record and store a large spectrum of long-term data coming from chemical-physical sensors using an open hardware architecture that allows of integrating any commercial underwater instrument.

The observatory is composed of three hard anodization Aluminum vessels, hosting electronic boards and batteries, connected together by underwater high-pressure type cables and connectors. Vessels and sensors are hosted on the, nylon-made, main frame structure (1m x 1m x 1.6m). The set of sensors used for during the ENVRI plus pilot experiment, the cruise, is composed by:

- Temperature: SeaBird SBE 3F
- Conductivity: SeaBird SBE 4C
- Depth (Pressure): SeaBird SBE 29
- pH: SeaBird SBE 18
- Turbidity: STM11
- Methane: METS K4
- Hydrophone: HTI 94SSQ

Many efforts were made in order to have a modular and fully customizable hardware and software system architecture, allowing to easily setup the data collection configuration of the multidisciplinary observatory, e.g. to adapt the acquisition rate and the power consumption to the battery capacity and sensors needs.

The electronic system was designed to be able to acquire from both analog and digital signals. It consists of eight analog synchronous channels with configurable front-end (current, voltage or high impedance input), each channel can accept wide band signals (0 Hz to 52 kHz) with 24-bit resolution. Digital inputs can communicate by serial protocols (USB, RS-232, RS-485, I2C, SPI, 1-Wire) or Ethernet (TCP-IP, UDP, FTP). The modular system includes also a dedicated power management board allowing to selectively power each sensor or all together. The special HW/SW design allows extremely low power consumption, thus obtaining extended autonomy, even with constrained battery volume resources. It is therefore possible to properly configure period and acquisition time to schedule sequences lasting even more than a year.

During the ENVRIplus cruise, the observatory was deployed two times:

1. ENV-OB-01 Deployed on 3rd April 2019 - Recovery on 07th April 2019;
2. ENV-OB-02 Deployed on 7th April 2019 - Recovery on 04th June 2019;

The observatory was setup to start acquisition on 18:30 (UTC) and from the launching date it started to acquire all parameters. The very first data of dissolved methane, turbidity and acoustic energy RMS, considered as a proxy of the gas flux, have shown low values that could be considered as the background. All those three parameters gave low values until the first gravity core (ENV-GC-01) was performed at 22:20 (UTC), on the same day, less than 200 meters away from the site of the observatory deployment [Figure 2]. The gravity core activity presumably induced the stripping of gas trapped in the shallower sediments. After ENV-GC-01, all parameters suddenly started to increase [Figure 5]. Dissolved methane reached high values around 3.5 $\mu\text{mol/l}$. The increasing of dissolved methane values was matched with the trend of turbidity ones. The latter have to be read as the measurement of the presences in the water column of both sediments and gas bubbles. Also the RMS values shadowed the trends of both turbidity and methane, being the noise generated from clusters of methane bubbles. From the beginning of April 5th all parameters showed a decreasing trend which lasted about 12 hours. On the same day at 05:15 (UTC) the second gravity core was performed more than 400 meters away from the ENV-OB-01. Only acoustics data has recorded a simultaneous variation correlated to core activity. Due to both effective double distances of ENV-GC-02 from the observatory and the weak presence of methane still trapped in the sediments, only a little delayed increment was recorded by all the measured



parameters. All values returned to the background values at the end of April 6th. For what concerning chemical-physical parameters (Temperature, Conductivity, pH, Hydrostatic pressure), they showed the typical features of the seawater close to the seafloor without any significant variation over the time. It is worth noting that the collected pH values (about 7.8) are lower with respect the normal seawater [Fig. 4].

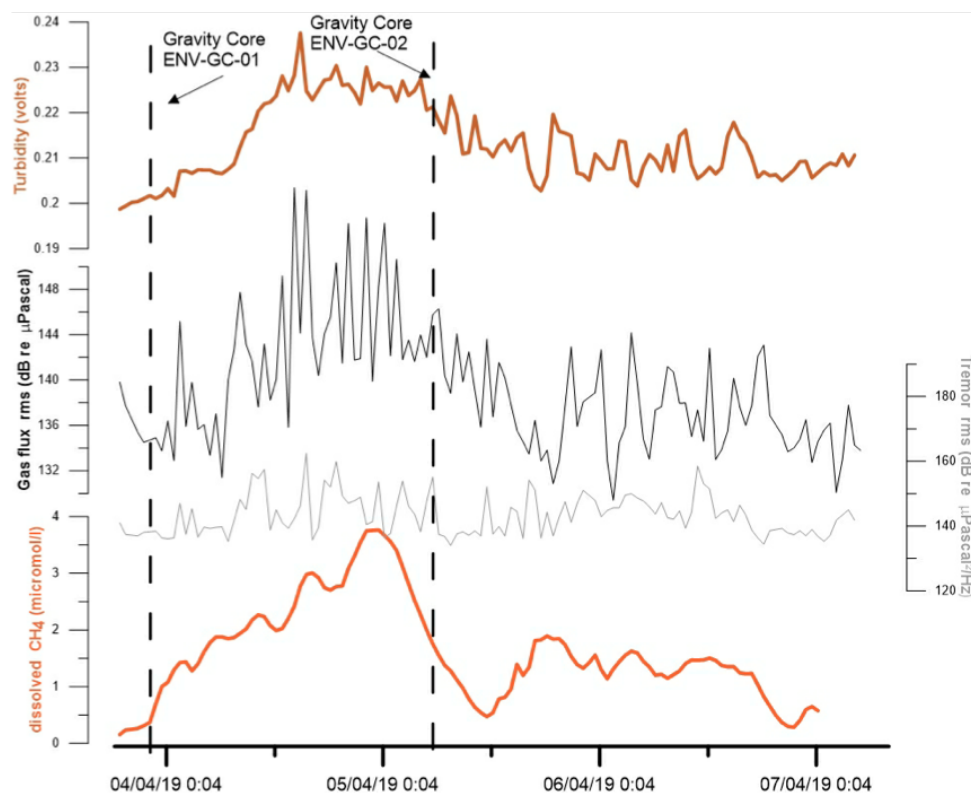


Fig. 5. Variations over a 3 days-long time period of: dissolved methane (orange curve), tremor (light grey curve), gas flux RMS (black curve), Turbidity (brown curve). Vertical dashed lines represent gravity core activities

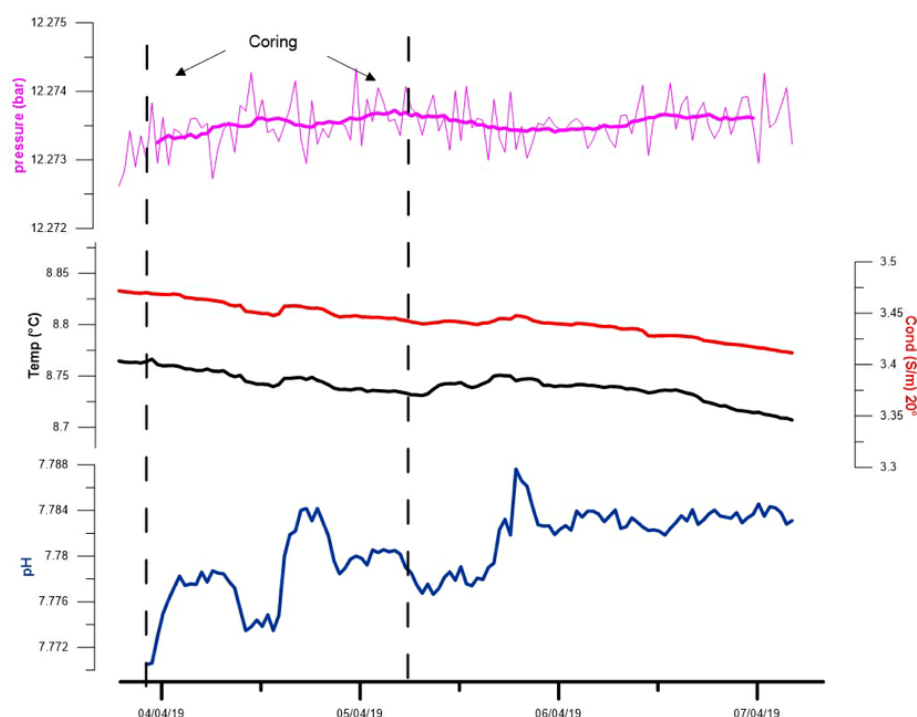


Fig. 6: Variation over 3 days-long period of chemical-physical parameters: pH (blue curve), Temperature (black curve), Conductivity (red curve), Hydrostatic pressure (violet curve). Vertical dashed lines indicate gravity core activities

Methane bubbles coming from flares radiate significant broadband and narrowband acoustic pressure waves. Investigating the energy changes as a proxy of gas flow is the main goal of passive acoustic measurements. Acoustic signals were sampled at 100 kHz with a 24-bit resolution A/D converter. The used hydrophone, based on a piezoceramic sensor element, was HTI-94-SSQ with a -198 dB re 1 V/ μ Pa omnidirectional response sensitivity within 2 Hz to 30 kHz frequency band, connected to a 40 dB fixed gain input channel. Each 5s-long acoustic record was processed using spectral analysis, to extract power magnitude time-series for different acoustic frequencies bands of interest. Every acoustic record was down-sampled, in order to exclude high frequency induced noise, then low-pass filters were applied to remove inducted aliasing effects. FFT spectral analysis, using a non-zero Hanning window function, was then applied together with 9-pole band-pass Butterworth filter to selectively analyze each band (choosing 5s-long segment window in order to mitigate impulsive noise and highlight time-continuous signals). Acoustic average pressure (intensity magnitude) modulation, represented with RMS (Root Mean Square) and frequency bins peaks values were then extracted from every selected frequency range. Chronological metadata series were used to analyze the magnitude modulation along time and thus provide flares flow rate changes.

Methane gas concentration was measured using a Mets K4 sensor. Following datasheet specifications, in order to collect good quality data, prior to each acquisition the observatory electronics management software was configured to power-on the sensor for 20 minutes, in order to warm-up and stabilize its electronics. However initial set-up operations described are intended to be done prior to each deployment, after the sensor has been out of water for a period of time. In the specific scenario described in this installation, the sensor was constantly submerged, the membrane together with sensor detector are supposed to be in stable conditions; it is furthermore

reasonable to presume that there is no need for such a long warm-up period. However, checking of such assumptions is required using the newly built high-pressure calibration bench.

The operations to recover the observatory started on 07th April at 03:23 (UTC). A small crowd, composed by two researchers and two sailormen, was launched with a motor ship to begin the approach with the observatory. The submarine acoustic releaser was triggered by a remote controller transducer at 03:28 (UTC) and after 90 seconds it was possible to see the bentospheres cluster on the sea surface. The system was hooked to the boat and then dragged to the side of the vessel, where it was fastened to the crane hook and lifted to the main deck at 04:10 (UTC).

6. Intercomparison of CH₄ sensors during vertical profiles

Vertical casts on the water column have been performed. The whole system was equipped with the *in situ* SubOcean probe, , the ISMS sensor that however had detection limit of dissolved CH₄ above the observed concentrations, and a commercial methane sensor from Franatech. Besides, discrete water samples were taken from the cast for laboratory measurement at both Ifremer and INGV. During the vertical casts the ship was considerably drifting (in general around 1.5-2 knots) from the targeted location due to water currents and wind, and a lack of dynamic positioning system. Because the presence of flares induces a high spatial variability of dissolved gases in the water column, with methane dissolving away from the emission vent, the drifting of the ship makes the intercomparison challenging. Consequently, there is a difference in location between the SubOcean and the hydrocast.

In this intercomparison we also include the gravity core results, which better highlights the large losses in CH₄ while going from the sediment to the water column.

Figure shows the locations at the deeper site (100m depth) where the casts were performed. Gravity core (GC) and the Observatories (Ob) are represented by a single point, while the spatial distribution is reported for the HY and SO casts. When necessary, the direction of the cast (Bottom to Top for the HY and bottom measurements for the SO) are highlighted for better clarity. A zoom on the important area for the intercomparison is reported on the right-hand side of the figure.

A similar graph has been produced for the shallower site (Figure) with the location of the GC, HY and SO.

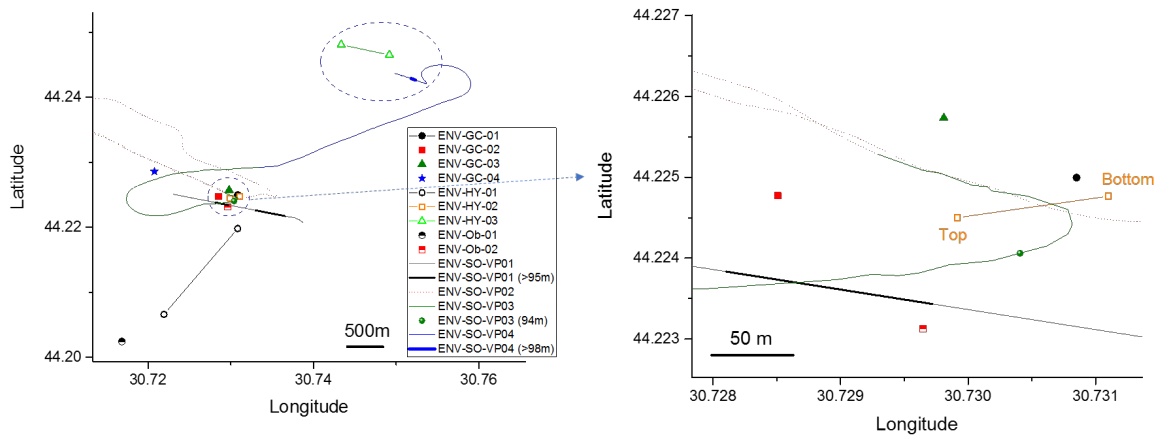


FIGURE 7. LOCATIONS OF THE GRAVITY CORES (ENV-GC), HYDROCASTS (ENV-HY), OBSERVATORY DEPLOYMENTS (ENV-Ob) AND IN-SITU SUBOCEAN VERTICAL PROFILES (ENV-SO) FOR THE NORTHERN SITE. LEFT SIDE: FULL AREA, DASHED BLUE CIRCLES HIGHLIGHT TWO AREA FOR INTERCOMPARISON. RIGHT SIDE: ZOOM ON THE INTERCOMPARISON SITE.

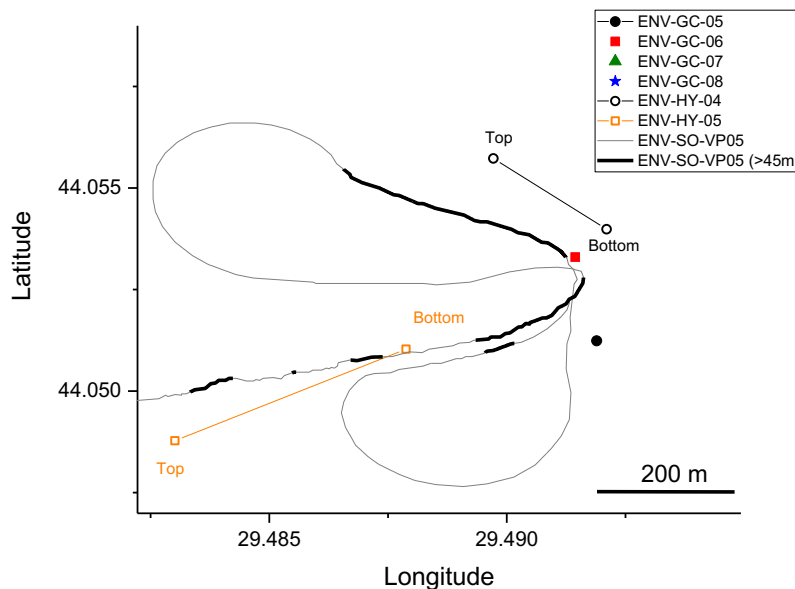


FIGURE 8. LOCATIONS OF THE GRAVITY CORES (ENV-GC), HYDROCASTS (ENV-HY), OBSERVATORY DEPLOYMENTS (ENV-Ob) AND IN-SITU SUBOCEAN VERTICAL PROFILES (ENV-SO) FOR THE NORTHERN SITE.

At the Northern site, the intercomparison was focused on the ENV-SO-VP03, ENV-HY-02 and ENV-GC-01 profiles (Figure). Close to the seabed those profiles are quite close (about 50 m away from each other) making relevant the comparison. At shallower depths (above 60 m) the distance between the instruments is significantly different, (see Figure for the larger map) making the agreement less pronounced. Between 60 and 90 m *in situ* and discrete measurements agrees well. On the left-hand side of Figure a log plot is proposed including the results from the gravity cores, thus highlighting the strong decrease in methane concentration from the sediment to the water column.

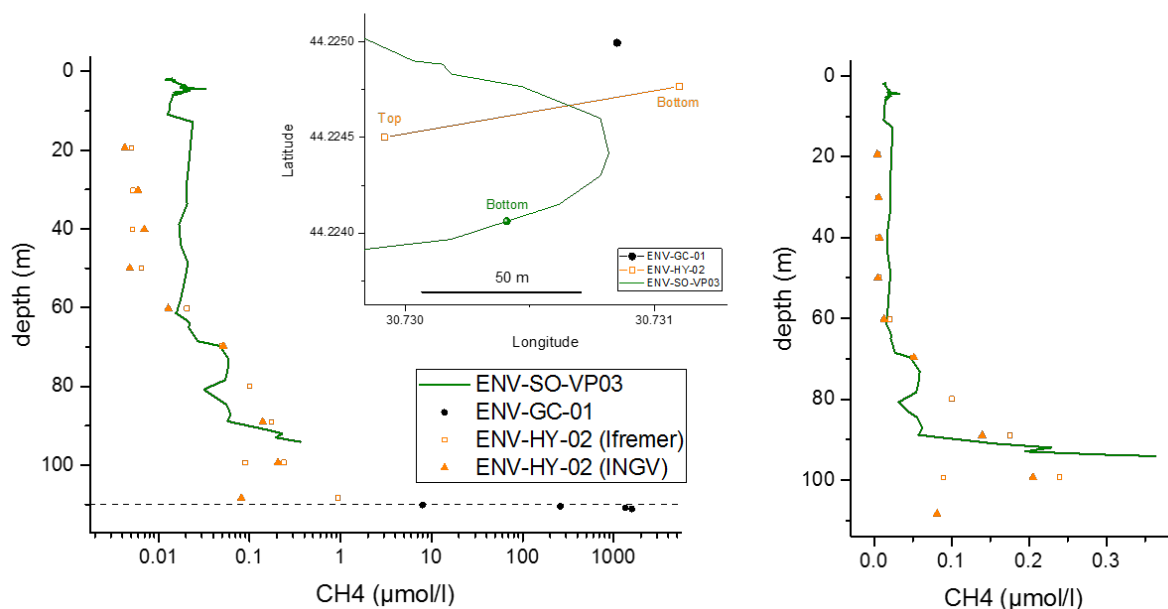


FIGURE 9. INTERCOMPARISON BETWEEN SUBOCEAN, SO, HYDROCASTS (DISCRETE MEASUREMENTS) HY AND GRAVITY CORE GC AT THE DEEPER SITE. DATA ARE WITHIN 50 M DISTANCE AT DEEP WATER. THE COMPARISONS IS LESS RELEVANT FOR SHALLOWER WATERS WHERE LOCATIONS ARE NO LONGER MATCHING. THE DASHED BLACK LINE MARKS THE SEABED. (LEFT: LOG, RIGHT: LINEAR PLOT)

At the shallow site a more spatial homogeneity has been found, visible from the ENV-SO-VP05 data in Figure (grey squares with the average represented by the black line). Here the probe was dragged up and down sequentially while the ship was drifting over the flares. In the insert map, SO data below 45 m of depth are represented by a black thick line (as in Figure) in order to visualize where the consecutive vertical profiles were located. In the water column, a relatively good agreement between the different measurement techniques was founded. All techniques highlighted this “S” shape profile, however the Subocean seems systematically lower than the discrete measurements. One should bear in mind that these profiles were taken not only at different location but also at different time.

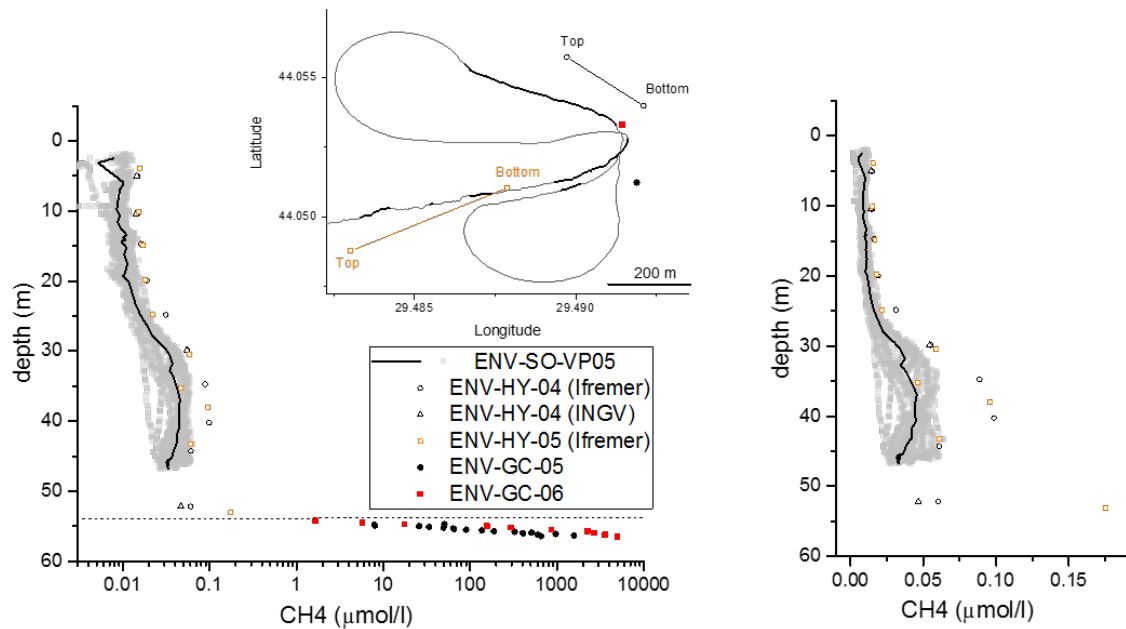


FIGURE 10. INTERCOMPARISON BETWEEN SUBOCEAN, SO, HYDROCASTS (DISCRETE MEASUREMENTS) HY, AND GRAVITY CORE GC AT THE SHALLOWER SITE. LEFT SIDE LOG SCALE, RIGHT SIDE LINEAR. THE DASHED BLACK LINE MARKS THE SEABED.

7. Intercomparison of laboratory-based measurements during vertical profiles

Objectives

The objectives of this study can thus be summarized as follows: 1) Quantify CH₄ in the water column from rosette bottles with a resolution of ~5-10 m, 2) Analyze on shore the CH₄ by two different methods: Headspace and Purge and Trap, and 3) Compare the results from the two laboratories (Ifremer and INGV- Palermo)

Finally, these data will be integrated in the global study of CH₄ migration from the bottom to the atmosphere, with an assessment of the reliability of the deployed methane sensors.

Finally, these data will be integrated in the global study of CH₄ migration from the bottom to atmosphere. In complement, they will be a guideline for characterization of associated sensors.

Material, sampling and analytical methods

Material - For the sampling of seawater, a CTD rosette (photo 1) was deployed. Ifremer's CTD-Rosette consists of a Seabird 911+ CTD (Conductivity; Temperature; Depth) mounted on a carousel with 16 Niskin sampling bottles (8 l). CTD-Rosette allows the connection of several sensors. During this cruise, the system was equipped with an altimeter, an oxygen optode, a methane sensor (METS Sensor-Franatech) and an *in situ* Mass Spectrometer (ISMS-Gaspard) for detection of CH₄ anomalies in the seawater column. Information from the sensors is received in real time on board,

allowing establishing a sampling strategy as a function of the recorded anomalies in the water column.

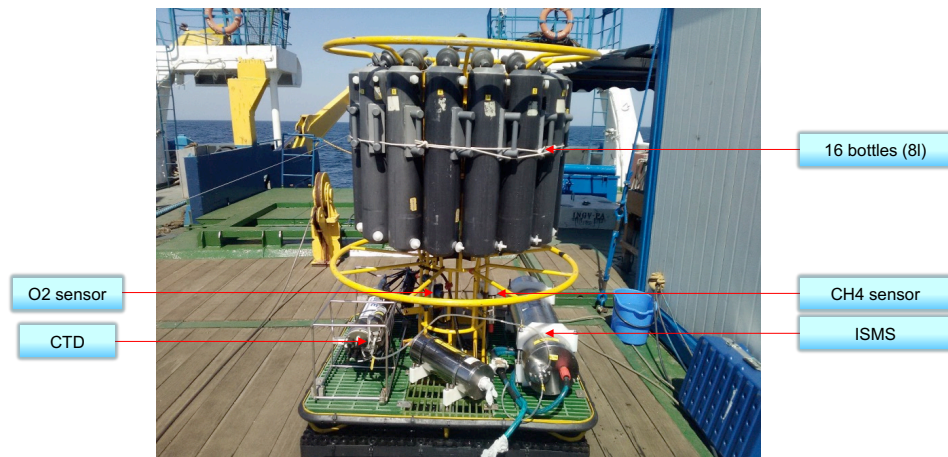


Photo 1: IFREMER CTD-Rosette

Sampling - From the 8L Niskin bottles, subsampling was performed for onshore analysis. For CH₄ analysis, subsampling was performed as follows:

- 125ml glass bulbs devoted to the analysis of methane by purge and trap method (IFREMER). The bulbs are allowed to overflow at least two volumes of seawater. A particular care is taken to exclude air bubbles during sampling to prevent contamination. During the filling, sodium azide is added to prevent future microbial activity.
- 10ml vials devoted to the analysis by Headspace method (IFREMER). At the beginning of the cruise all 10ml vials were flushed with air zero to avoid introducing methane in the initial gas phase. With a gastight syringe, simultaneously 5ml of seawater are transferred into the vial while a second needle is introduced to keep a pressure closed to atmospheric pressure. The vials are then stored upside down. Note that before the cruise a small quantity of sodium azide was added to each vial.
- 122 ml vials devoted to the analysis by Headspace method (INGV): Vials were filled by using a silicone tube connected to the 8 L Niskin bottle. The silicone tube was inserted in the vial down to the bottom to completely fill the vial from the bottom to the top displacing all the air contained. Once the vial was filled, it was completely submerged in sea water coming from the same Niskin bottle, keeping the silicone tube at the bottom of the vial and allowing the overfilling of the sample. Then the tube was slowly removed, taking care to avoid any air bubble and the vial was sealed by a PTFE septum using special crimping pliers. No chemical or poisoning product was added to the water sample to stop possible microbial activity.



Photo 2 and 3: Subsampling from IFREMER Rosette



Photo 4: 125ml bulbs



Photo 5: 10 and 20ml vials

Analytical methods on shore

The Ifremer methods have been described by Donval et al [1] et Donval and Guyader [2]. Here, we give a brief description of these two methods.

The *Purge and trap* method used here is based on Swinnerton et al. and modified by Charlou et al.. As previously mentioned, the seawater is sampled in a 125ml glass bulb. Once in the laboratory, CH_4 is stripped from seawater with He carrier gas, trapped on activated charcoal at -80°C , and detected and quantified with a flame ionization detector after separation on a packed column. The calibration is performed by injection of commercial gas standards. The limit of detection is 0.03nmol/l , the precision based on five replicates from the same rosette bottle is within $\pm 2\%$ (confidence level 95%) and accuracy 5%. It should be noted that the CH_4 equipment is set up in a portable clean air-conditioned container, allowing one CH_4 analysis every 6 min thank to 2 extraction kits.

Headspace method consists on putting a seawater volume in a sealed vial and keeping it in equilibrium with a gaseous phase. On shore, the vial are shaken. After a step of equilibration, they are automatically analyzed by means of a headspace sampler connected to a Gas Chromatograph which is the same instrument tat has been used for the Purge and Trap method. The limit of detection is 5nmol/l and the precision is $\leq 10\%$ for low concentration, $\leq 5\%$ for medium concentration (confidence level 95%)

The INGV method have been reported in Capasso, Inguaggiato, Inguaggiato, Rizzo and Italiano et al. The method here briefly described is based on the equilibrium of gases between liquid and gas phase in a head-space. 7 cc of high purity host gas is injected in the 122 cc sample vial to create a head space where the dissolved gases can re-equilibrate. A second needle is used to allow the same water volume of escaping from the vial. The used host gas depends on the gas species to be determined. In the case of the Black Sea samples, we used pure Ar.

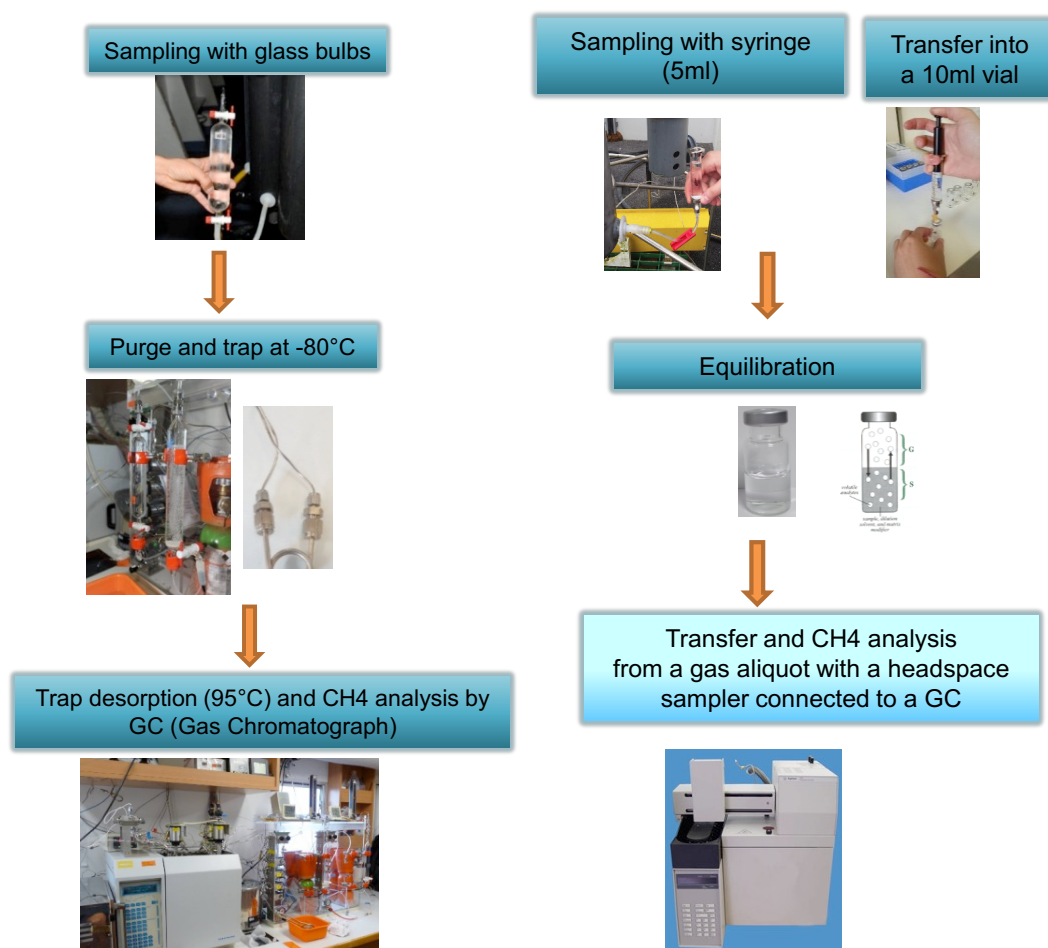


Figure 11: step diagram for CH₄ analysis by purge and trap (left) vs headspace method (right)

After a 24 hours-long equilibrium period at known temperature in thermostatic bath, the vial is connected to a device to restore atmospheric pressure. Then the gas mixture is extracted from the head space by using two syringes: one syringe to introduce millipore water and another one with stopcock to collect the gas sample.

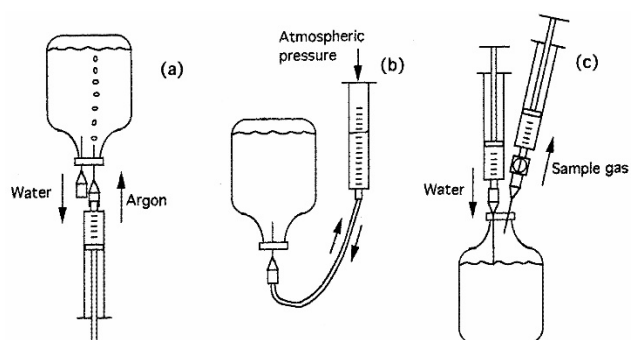


Figure 12: Creation of headspace before the CH₄ analysis

Before admitting the gas sample to the GC column, the syringe containing the gas sample is then directly connected to the inlet system of the GC equipped with vacuum pump to pump out any air from the needle. The analytical precision ($\pm 1\sigma$) is always better than $\pm 3\%$. The CH₄ detection limit is about 0.4 nmol/l

The quantity of dissolved gas per liter of water is calculated using the following relation:

$$C_i = [\chi_i^* (G + \gamma_i^* w) / w] * 10^3$$

where C_i is the concentration of the i^{th} gas, expressed in cc/liter of water at STP (25°C, 1 atm), χ_i is the molar fraction of the i^{th} gas in the gas phase, G are the concentration at STP of extracted gases, w the volume (ml) of water in the sample analyzed and γ_i is the solubility coefficient (β) of the gas i expressed in cc/ml at STP.

Results

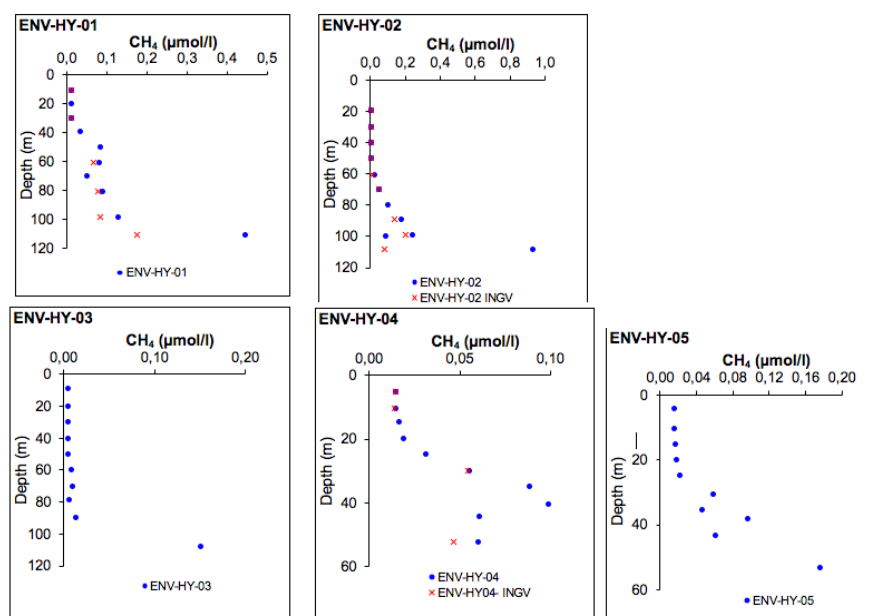


Figure 13: Comparison of CH₄ profiles

For the first three hydrocast were taken at the Northern site at water depth of around 120m and the minimum CH₄ value was 4,2nmol/l. We can note for HY01 a maximum value of 0,4μmol/l at 99m, HY02 0,9μmol/l at 108m, and a value of 0,15μmol/l. At the shallow site, the seafloor was less than 60m depth and the minimum value of methane was higher, around 15nmol/l. On the other hand the maximum value of methane is 0,1μmol/l at 40m depth for HY04 and 0,17μmol/l for HY05. To go further with the data analysis, these results will have to be examined by considering the presence of flange detected by acoustic and the profile of oxygen which define the anoxic zone.

Intercomparisons between methods and labs

Considering overall the plot 1 (Figure 13), there is a good agreement between the two methods on the range of the concentrations studied. However for the low values we can note a variation significant difference between the two methods. This difference is linked to the accuracy of the head-space (HS) method when the values are closed to its limit of quantification (~20nmol/l). In the case of IFREMER HS method, an automatic headspace sampler is used and a constraints a specific ratio between gas and liquid phase (ratio of 1) is fixed. It requires likewise a dilution of gas phase before a partial injection of the gas phase. For the low CH₄ concentration, the purge and trap (PT) method (very high sensitivity method) or a specific HS method developed for onboard analysis should be applied.

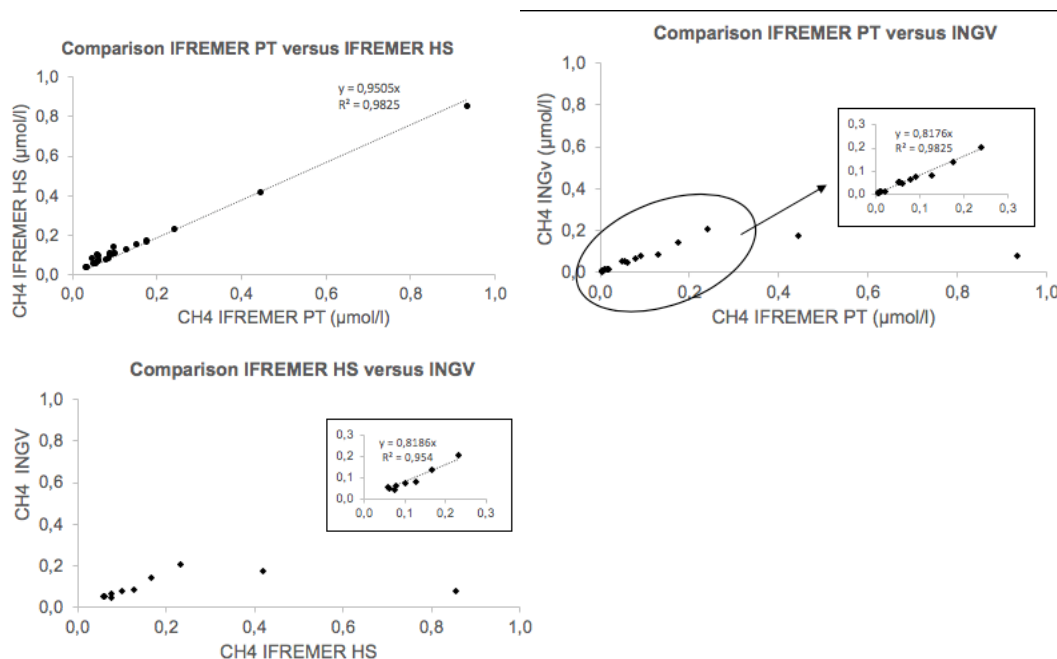


Figure 14: Comparison of methods between Ifremer and INGV- Palermo

The accordance between the IFREMER PT and INGV HS results is good ($R^2=0.98$) as also shown by Figure 14 with an almost perfect overlapping of data for all the samples taken in shallow water. The two deeper samples collected close by the seafloor display high methane content (0,4 and 0,9 $\mu\text{mol/l}$ from PT method), with a significant difference of CH_4 concentration measured by INGV and IFREMER laboratories. The slope of 0,8 obtained from the data fitting means that globally the INGV values are lower than IFREMER PT values.

Figure 14 confirms the already mentioned problem on the two points of high value:

- a possible explanation could be found in the different methods to collect and treat samples (use of sodium azide by IFREMER, not by INGV).
- The presence of living bacteria in the water samples for some days might be responsible for microbial CH_4 consumption with a lowering of the pristine CH_4 content. The marked discrepancies indeed involve only samples collected close to the sea-floor sediments, where the methanotrophic activity is higher.

Instead, all the other data coming from the water columns are very coherent, with negligible discrepancies, despite different treatment of the sample.

In conclusion, these first results are interesting and encouraging. It is likely that the number of samples are not sufficient to establish a critical comparison of methods and analytical procedures, especially for the high ranges of methane concentration studied in this context.

8. Vertical profiles of CH_4 in the water column

Samples and data were collected using a CTD-Rosette consisting of a Seabird SBE-911+ CTD associated with a water carousel. It is a multi-instrumented device that allows acquiring physical and chemical data all along the water column, and sampling water in 8 liters Niskin bottles at different depth from the seafloor to the surface. The main parameters recorded by the CTD are Conductivity, Temperature and Depth. Derived properties such as salinity or sound velocity are calculated from these three parameters, and they are useful for example for multibeam echosounders calibration. On the Envri Methane cruise, the CTD-Rosette was also equipped with

an oxygen Sensor (Aanderaa Optode 4831F), a methane Sensor from Franatech, and an *In Situ* Mass Spectrometer (ISMS-Gaspard). All data from the sensors are received in real time on board, allowing establishing a sampling strategy as a function of the recorded anomalies in the water column. For compatibility reasons, data rate acquisitions have been degraded to 1 Hz.

Aanderaa optode uses Optical lifetime-based luminescence quenching measurement principle.

The ISMS-Gaspard is a prototype based on the separation of gases from seawater through a membrane (membrane inlet mass spectroscopy). Gases are ionized by a filament, separated by mass with a quadrupole, and then measured by a commercially available mass spectrometer. This apparatus have been qualified for 4500 m depth deployment.

Results and discussion

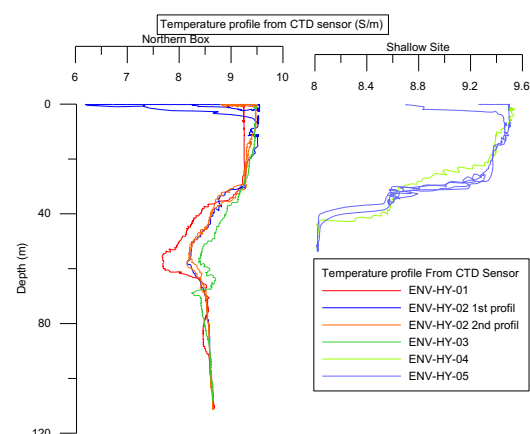


FIGURE 15: TEMPERATURE PROFILE FROM CTD

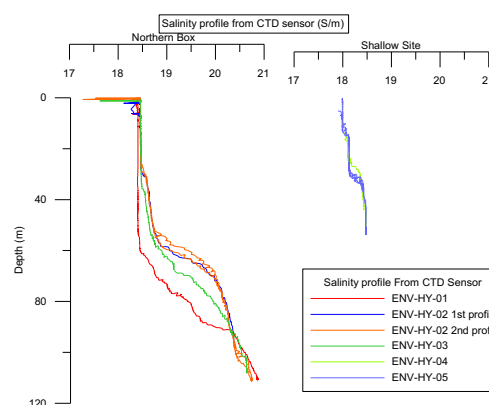


FIGURE 16: SALINITY PROFILE FROM CTD

Results of physical data (Figure 15 and 16) show a large variability in water masses due to time and spatial variations. This is particularly well illustrated by the difference between the first and the second profiles of the ENV-HY-02 operation, which shows significant variability even at low time and spatial scales. Those differences can also be seen between the Downcast and the Upcast of the 2nd profile where an important drift of the ship have been observed.

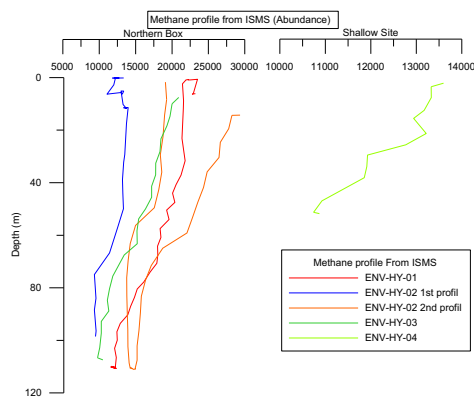


FIGURE 17: METHANE PROFILE FROM ISMS

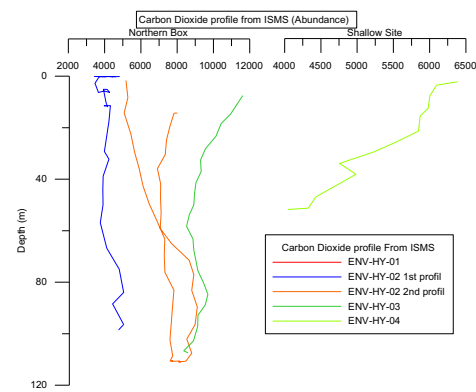


FIGURE 18: CARBON DIOXIDE FROM ISMS

These results from ISMS data show that the ISMS configuration was not adapted for those environments, which lead to a too high limit of detection for methane and carbon dioxide measurements. H_2S and CO_2 analysis are possible by ISMS thanks to a particular mounting. The water vapor trap is bypassed in order to avoid the trapping of CO_2 and H_2S . Indeed, these gases are quite soluble in water and are captured in the water vapor trap. Consequently, water vapor pressure is higher in the mass spectrometer with this configuration. So, the high sensitivity detector is not operable in this poor vacuum quality. When we defined the best measure configuration, we considered a predictable high methane concentration in the water column, higher than $1 \mu\text{mol/L}$. In reality, the concentration is below ($\sim 100 \text{ nmol/L}$) and is out of range for the chosen ISMS configuration.

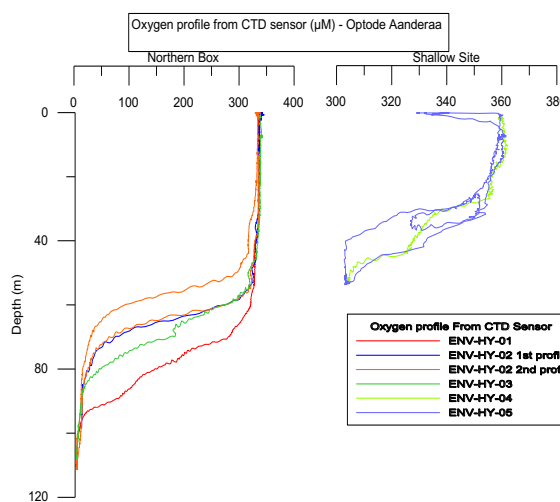


FIGURE 19: OXYGEN PROFILE FROM CTD SENSOR

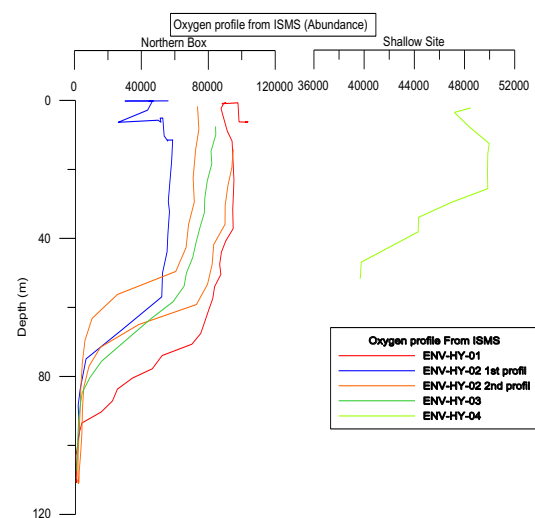


FIGURE 20: OXYGEN PROFILE FROM ISMS

Oxygen profiles confirm the heterogeneity of the water masses in the water column. The profile shape is confirmed by the ISMS data and validates the fast response time of the ISMS. However, an important offset of the ISMS measurements is observed for the highest values which is not confirmed by the optode ones. An explanation would consist in the ISMS presented values; figures show abundance vs depth. Abundance is directly linked to ionic current measured by the m/z detector. This current is proportional to the amount of ionized gas present in the spectrometer. This amount is affected not only by the gas concentration in seawater but also by (i) the membrane gas permeability and by (ii) the vacuum quality. These parameters depend on the water flow on the membrane and the possible membrane clogging (case (i)), and the presence of relatively high quantity of water vapor in the spectrometer due to the trap absence (case (ii)).

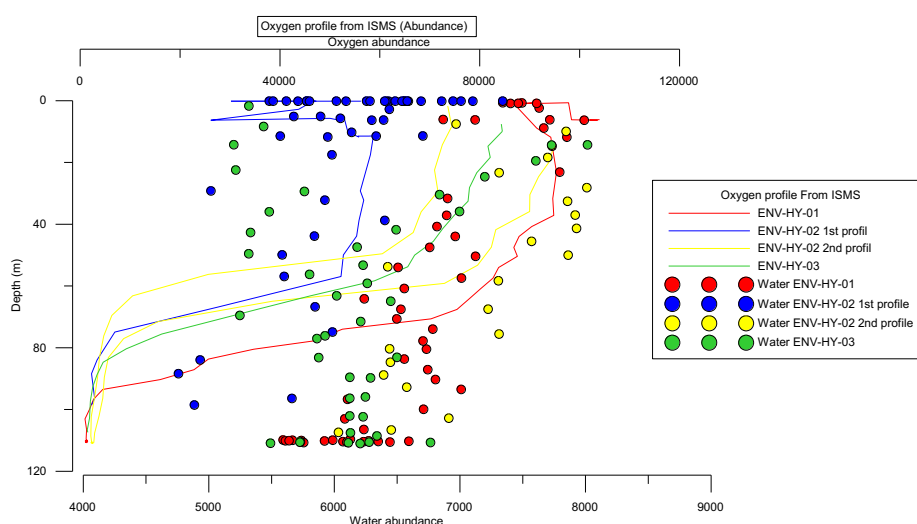


Figure 21: Oxygen and water abundance from CTD

9. Intercomparison of near-surface CH₄ sensors

Surface measurements were performed by both the LGR and Franatec instruments, the SubOcean probe, and by the discrete measurement from the hydrocasts (HY).

In order to compare *in situ* and discrete measurements, data points from the continuous SO measurements performed during the atmospheric survey (AP01 and AP03) were selected (thick black lines on Figure 12 and Figure 13) at the nearest location to the HY casts, and averaged. 100 SO data points were used for comparing HY-01, -04 and -05, and 400 points (100 per leg) for HY-02 and -03.

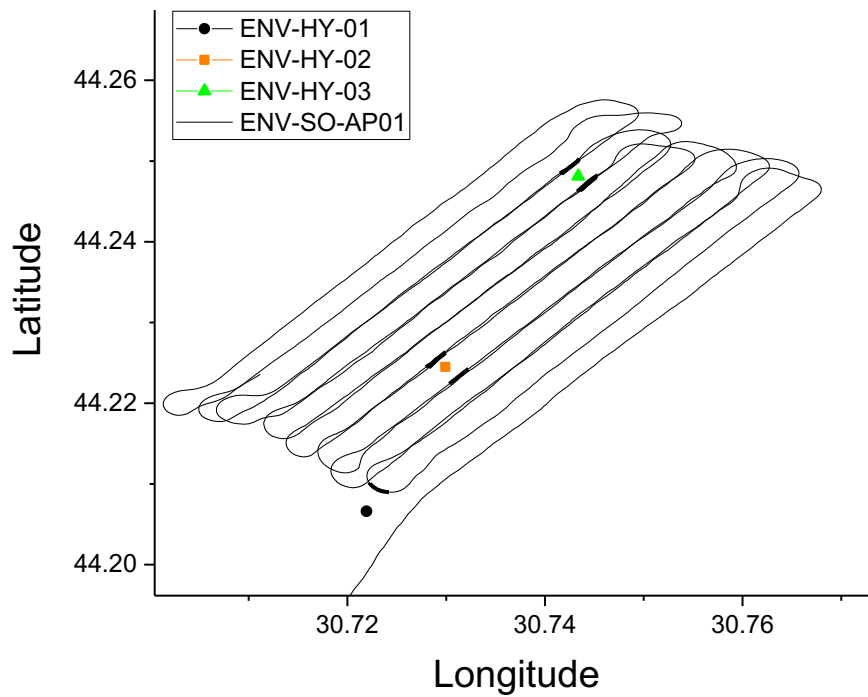


Figure 22. Locations of the continuous surface atmospheric survey (AP) and discrete sampling during the hydrocast (HY) for the deep site. The location of the HY corresponds to the location where surface sample was performed. In dark black is the locations of the SO data points used for the comparison.

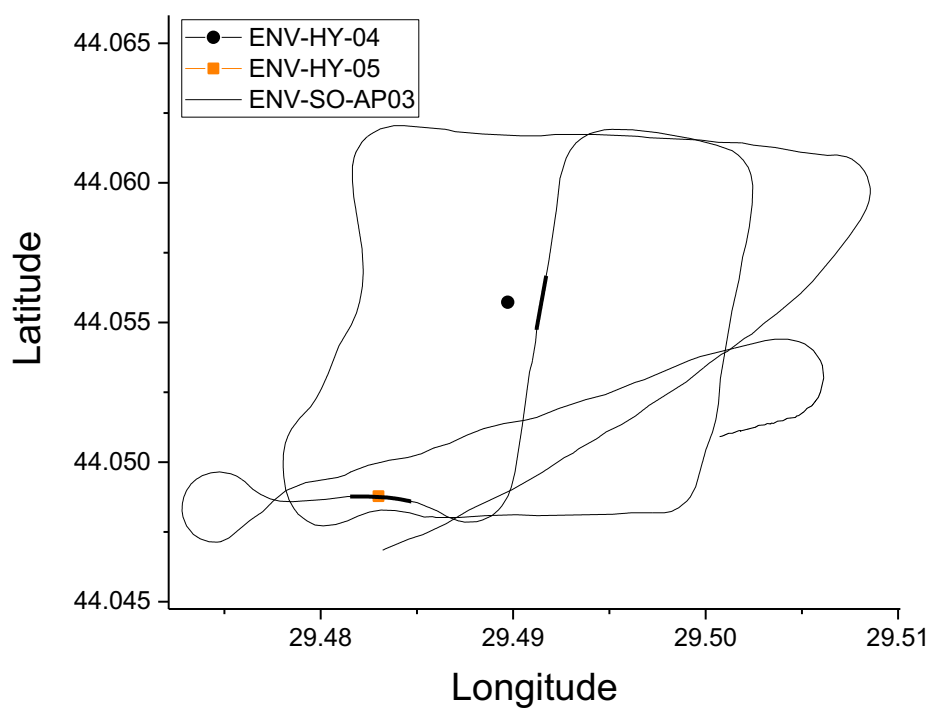


FIGURE 13. LOCATIONS OF THE CONTINUOUS SURFACE ATMOSPHERIC SURVEY (AP) AND DISCRETE SAMPLING DURING THE HYDROCAST (HY) FOR THE SHALLOW SITE. THE LOCATION OF THE HY

CORRESPONDS TO THE LOCATION WHERE SURFACE SAMPLE WAS PERFORMED. IN DARK BACK IS THE LOCATIONS OF THE SO DATA POINTS USED FOR THE COMPARISON.

A summary of the comparison is reported in **Erreur ! Référence non valide pour un signet.** and Figure . Very good agreement is found of the shallow site, where the SO and DS measurements agreed within the accuracy of the measurements represented by the error bars in Figure . This highlight a good homogeneity of the water masses at this area, since the measurement were not carried out at the same time and depth, as well as the robustness of the two methods for measuring background concentrations. The latter are reported in **Erreur ! Référence non valide pour un signet.** Regarding the deeper site, the discrepancies are larger, particularly for the HY-01, where with the DS method at concentration of 10.7 nM was measured against the 2.84 nM of the in situ SO probe. This may be due to the large distance (300 m) between the two measurement locations. Unfortunately, there are not closer data of the SO probe to the HY-01 location for a better comparison.

TABLE 1. COMPARISON OF THE DATA. THE SUBOCEAN (SO) DATA CORRESPOND TO THE AVERAGE OF CONTINUOUS MEASUREMENTS NEARBY THE HY LOCATIONS.

		Depth SO /m	CH ₄ SO /nM	Accuracy SO (12%)	Depth HY /m	CH ₄ HY /nM	Accuracy DS (5%)	Notes
<i>Deep Site</i>	HY-01	5.9	2.84	0.34	10.4	10.77	0.54	300 m distance
	HY02	5.2	1.69	0.20	19.4	4.68	0.23	Between two lines
	HY-03	4.6	2.78	0.33	8.6	4.23	0.21	Between two lines
<i>Shall ow Site</i>	HY-04	5.0	12.79	1.53	5.0	14.59	0.73	140 m distance
	HY-05	3.6	13.49	1.62	3.9	15.52	0.78	Well superposed

At the deeper site, for the entire AP01 dataset, the SO instrument measured an average CH₄ concentration of 2.23 ± 0.78 nM, while the average over the 3 selected locations corresponding to HY-01, -02, and -03 is of 2.44 ± 0.65 nM against the 6.56 ± 3.65 of the DS measurements. On the latter, if we remove the HY-01 data point, the average drop to 4.45 ± 0.31 nM (all errors here are expressed as 1σ).

On the shallow site, the averages values for the entire AP03 SO dataset is 12.49 ± 2.77 nM while only accounting for the locations of the HY-04 and -05 the averages are 13.14 ± 0.49 and $15.06 \pm$

0.66 nM for the SO and DS, respectively. Both techniques confirm the higher level of CH₄ at the shallow site with respect to the deep site.

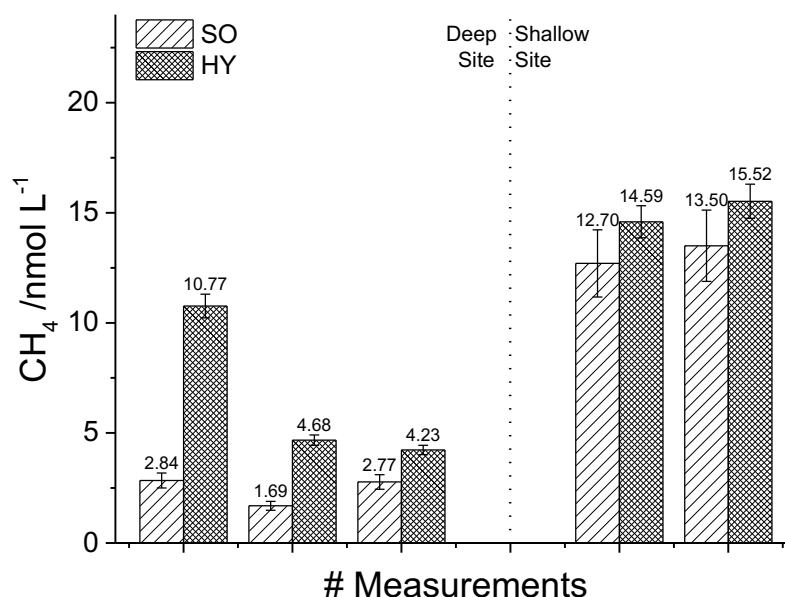


Figure 24. Comparison on surface waters between the in situ Subocean data (SO) and the discrete measurements performed on the samples collected during the hydrocasts (HY). The graph reports the data in A summary of the comparison is reported in **Erreur ! Référence non valide pour un signet.** and Figure . Very good agreement is found of the shallow site, where the SO and DS measurements agreed within the accuracy of the measurements represented by the error bars in Figure . This highlight a good homogeneity of the water masses at this area, since the measurement were not carried out at the same time and depth, as well as the robustness of the two methods for measuring background concentrations. The latter are reported in **Erreur ! Référence non valide pour un signet.** Regarding the deeper site, the discrepancies are larger, particularly for the HY-01, where with the DS method at concentration of 10.7 nM was measured against the 2.84 nM of the in situ SO probe. This may be due to the large distance (300 m) between the two measurement locations. Unfortunately, there are not closer data of the SO probe to the HY-01 location for a better comparison.

Table 1. HY data are average between the IFREMER and INGV analysis. SO data are average from data points nearby the location of the discrete samples. Error bars are the respective accuracies (12% for SO and 5% for HY).

10. Hotspot flux estimate from closed chamber

High resolution CH₄ and CO₂ diffuse flux meter by WEST Systems (TDLAS LDL = 100 ppb), equipped with customized floating accumulation chamber was used in order to evaluate any possible methane fluxes coming from the flares and released from the water surface to the atmosphere.



Figure 25: customized accumulation chamber and fluxmeter equipment during on-field measurement

With this aim on April 4th at 14:20 (UTC) the safety boat was launched on the sea surface, in order to make possible flux measurements as close as possible to the flares sea bottom vertical, at a certain distance from the R/V. Unlikely the sea was slightly rough, a not optimal condition considering that, for better acquisitions of gas flux, floating chamber needs quite flat sea surface. The small boat with three researchers and two sailormen moved away from the vessel and stopped approximately in a position just above flares. After the necessary time for the warm up of the fluxmeter, the concentration in the air was acquired (2.1 ppm). The floating accumulation chamber was placed on the sea surface to collect methane released across the seawater surface. Meanwhile, the sailorman kept the position by using outboard engine.

Measurements were repeated several times, trying also to change the position, seeking in the direction of surface currents, considering that the shallow depths down to about 50 meters were dominated by strong currents. In no case there was a substantial accumulation of methane in the chamber (concentration record was stable at 2.1 ppm), that means there was no methane flux from the sea surface nearby the vertical of the flares detected by acoustics. Likely the flares were pushed away by the currents and so if methane reached the atmosphere it could happen somewhere far from the vertical bottom sources.

11. Mapping of atmospheric CH₄

The CO₂, CH₄ and CO molar mixing ratio in the atmosphere were measured in situ from an inlet located on the front mast of the ship and injected into an analyzer located in the radio cabin on the navigation bridge. Measurements were done using a Cavity ringdown spectroscopy analyzer Picarro G2401. Four different calibration gases bracketing typical ambient concentrations were injected in the analyzer before and after the campaign for calibration purposes to ensure traceability to ICOS standards. The injection sequence consists of four 20-min injections of each of the four gases. An additional target gas was injected at higher frequency (twice daily) to assess measurement accuracy. The data has been documented and processed following ICOS standard procedure (Hazan et al., 2016), including the propagation of the calibration and threshold-based filters. The mean drift of measured concentrations from calibration cylinders between two

sequences is of 0.05 ppm and 0.5 ppb CH₄, significantly below the drifts typically observed at fixed observatories (Hazan et al., 2016). Target injections show a small residual bias (after calibration) below 0.3 ppb CH₄. The processed data is reported as 1-min averages.

Meteorological parameters such as wind speed and direction, pressure and temperature as well as GPS position and course, were acquired thanks to a Vaisala meteorological station at the starboard side of the bridge.

The measurements have been filtered to remove any possible influence from the ship exhaust using a very conservative set of thresholds on CO and CO₂ measurements, as these are the most sensitive measurements to exhaust. All measurements were relative to a background value defined as the 10th percentile of observed concentrations.

Measured excess concentrations are presented in the following Figures.

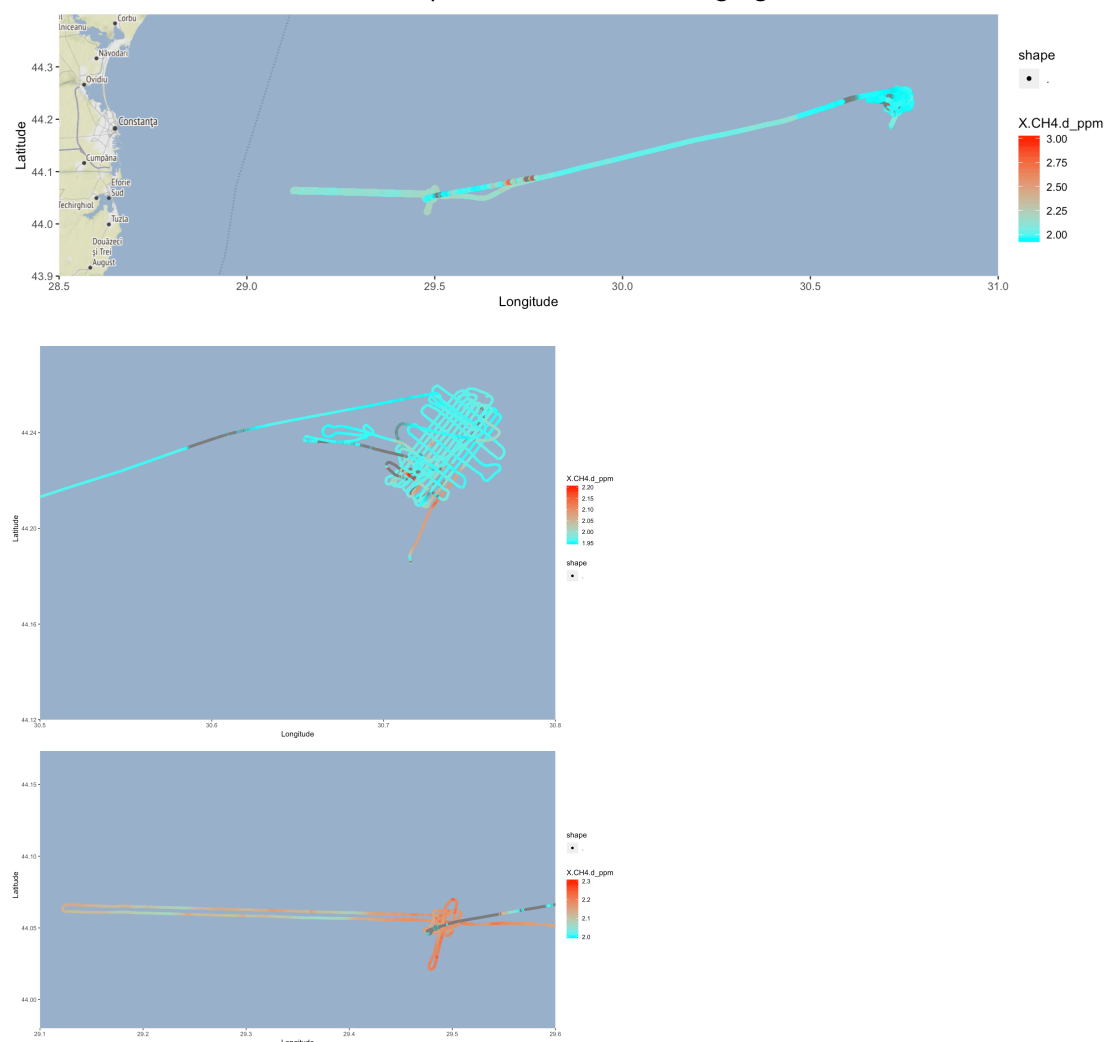


Figure 26: maps of atmospheric CH₄ distribution with zooms over the Northern and Southern boxes

Significant excesses of up to 30 ppb are found in the vicinity of the shallower site, and consistent with the water column enhancements and the distribution of the plumes. The deeper site has shown no clear, general release of CH₄ although a few enhancements have been observed. Overall

the methodology to derive precise fluxes from the observations through mass balance approach will generate valuable research out of this activity.

12. Data management

The cruise and the sensors have generated a wealth of heterogeneous, high quality data. High volume of raw data from the echo beam sounder have been collected, the other sensors tend to generate smaller volume of data. The data obtained during the cruise are shared among participants using the EUDAT service B2DROP. A PID is being associated to the dataset through B2SHARE. Once the data processing will be fully completed and the quality fully controlled, the data will be made fully available to the community. Data archiving is secured by each participant separately, involving among other PANGEA for the echobeam sounder and the ICOS database for the atmospheric measurements.

13. Conclusion and recommendations

This cruise has allowed to probe the feasibility of an agile deployment to address an interdisciplinary scientific question that required mobilizing resources from several research infrastructures. This deployment involved 4 RIs from 2 different domains: ICOS, EMSO, Eurofleets, ACTRIS.

Methane is a powerful greenhouse gas, and accordingly it is important to decipher the different sources that can provide input to the atmosphere. Over the last decades, the discovery of cold seeps on continental margins has shed the light on large sources of marine (microbial) methane. Indeed, due to the important accumulation of organic matter on continental margins, large volume of methane is generated within the sediment and a fraction of it is discharged in the water column. The ocean is a powerful machine capable of mitigating marine methane input to the atmosphere, yet at certain conditions, injection to the atmosphere is possible and it is important to know when these conditions are met and to quantify the release in order to better understand the dynamics of marine methane.

The Envri Methane cruise aimed to develop a procedure combining several RIs to detect, monitor and quantify marine methane from the lithosphere to the atmosphere. The applied procedure combined *in situ* measurements and laboratory analyses. Overall, there is a good agreement between the methane *in situ* measurements using the SubOcean probe and the Franatec sensor. The *in situ* mass spectrometer (ISMS) was not set to the appropriate range of methane concentrations found in the Black sea. Therefore, the methane measurements were not exploitable. However, good agreement on the oxygen concentration has been observed between the ISMS and the CTD-connected optode. Because methane concentration is highly variable even within an area of a couple of meters square, standards method (purge-and-trap and headspace) are required to assess the efficiency of *in situ* measurements. Thus, a comparison of onshore analytical procedure, from the sampling onboard through the storage to the final analysis on shore, has been undertaken between two laboratories involved in the cruise. Again, there is a good agreement between the results obtained from the different laboratory. Major discrepancy is observed from

water samples collected near the seafloor where methanotrophy is expected to be more important. The combination of RIs turned out to be an appropriate to study the dynamics of marine methane from the lithosphere to the atmosphere.

The main scientific outcomes from the cruise can be summarized as follows:

- Methane concentration drastically decreases from the lithosphere to the atmosphere, highlighting its degradation and dispersion along the pathway to the atmosphere.
- The seafloor observatory effectively detect changes in methane concentration over time. In our case, the change was induced by the coring operation, highlighting how sensitive methane emissions can be regarding environmental or anthropogenic perturbations.
- The atmospheric measurements show a more important contribution of marine methane to the atmosphere at shallow water depth.

However, several limitations have been identified, and would require improvement to better quantify marine methane injection to the atmosphere.

- The first limitation was the lack of dynamic positioning on the ship. Indeed, the high variability of the methane concentration in the water column requires the ability to stay at station for the sake of a more reliable comparison of sensor and methods, both *in situ* and onshore.
- The second improvement would be the harmonization of the storage procedure of the seawater samples. Here, we use the same samples for the onshore analyses, but the storage procedures were different, introducing bias in the results.
- The use of a multibeam instead of a single beam would allow a faster detection of the gas flares. Water column data acquisition and processing should be improved for allow gas flux estimations.
- Finally, for a better quantitative assessment of methane fate, the fluxes at the interface (sediment- seawater and surface water- atmosphere) would be better characterized. This requires further deployments of the seafloor observatory after a thorough calibration of the methane sensor, and the development of the analytical method for measuring the surface water methane concentration.

Additional sensors have been experimented. The floating chamber measurement has been challenging to deploy due to the difficulty to position exactly on top of bubble plumes. The diffusive flux measurement through an air extractor has been of limited use due to the lack of zero gas for equilibration.

Overall the end-to-end sensor system has demonstrated its value. The integration and deployment on ship has been validated. The insight provided meets the initial requirements.

Agreement on data sharing and joint analysis has been instrumental in fully realizing in due time the full potential of this experiment.

From this experiment we derive a set of **high-level recommendations**:

- The community needs to establish a **blueprint** for joint operations of Research Infrastructures on cross-cutting challenges with modular well characterized subsystems
- We need to elaborate the concept of a **systematic monitoring capability based on existing Research Infrastructures** to detect large scale changes in methane fluxes in European/global waters, as it has proven feasible and will provide key information to monitor this problem

- We need to enable through the development of a community and through appropriate funding, joint actions of Research Infrastructures on sensors and observatories
- It is important to establish a European network of best practices and capacity building for harmonized monitoring
- We need to promote intercomparison exercises and harmonization/standardisation of sensor test practices to increase readiness for future ad hoc joint deployments on other questions.

IMPACT ON PROJECT

This deliverable summarizes the findings from Task 4.2. It is the last deliverable of WP4, and constitutes an ambitious joint pilot study. Although this deliverable has reached its objective to demonstrate the feasibility of joint deployment, it has attracted interest from RIs and further research is anticipated to take place on this successful activity.

IMPACT ON STAKEHOLDERS

This report highlights the value of combining research infrastructures to address key scientific questions. The scientific mission of environmental research infrastructures is defined at their inception. When need arises, specific deployments and studies can require an ad hoc association of RIs that together to mobilize the knowledge and observational resources required to unlock emerging knowledge gaps.

References

Aloisi, G., Drews, M., Wallmann, K., Bohrmann, G., 2004a. Fluid expulsion from the Dvurechenskii mud volcano (Black Sea): Part I. Fluid sources and relevance to Li, B, Sr, I and dissolved inorganic nitrogen cycles. *Earth and Planetary Science Letters* 225, 347-363.

Capasso, G., Inguaggiato, S., 1998. A simple method for the determination of dissolved gases in natural waters. An application to thermal waters from Vulcano Island. *Appl. Geochem.* 13, 631–642.

J.L. Charlou, L. Dmitiev, H. Bougault, H.D. Needham, Hydrothermal CH₄ between 12°N and 15°N over the Mid-Atlantic Ridge, *Deep Sea Res.* 35 (1988) 9625–9642.

J.P. Donval, J.L. Charlou, L. Lucas, Analysis of light hydrocarbons in marine sediments by headspace technique: optimization using design of experiments, *Chemom. Intell. Lab. Syst.* 94 (2008) 89–94.

J.P. Donval and V. Guyader, Analysis of hydrogen and methane in seawater by “Headspace” method: Determination at trace level with an automatic headspace sampler, *Talanta* 162 (2017) 408–414



Hazan, L., Tarniewicz, J., Ramonet, M., Laurent, O., & Abbaris, A. (2016). Automatic processing of atmospheric CO₂ and CH₄ mole fractions at the ICOS Atmosphere Thematic Centre. *Atmospheric Measurement Techniques*, 9(9), 4719-4736.

Holmkvist, L., Kamyshny, A., Jr., Vogt, C., Vamvakopoulos, K., Ferdelman, T.G., Jorgensen, B.B., 2011. Sulfate reduction below the sulfate-methane transition in Black Sea sediments. *Deep-Sea Research Part I-Oceanographic Research Papers* 58, 493-504.

Inguaggiato, S., Rizzo, A., 2004. Dissolved helium isotope ratios in ground-waters: a new technique based on gas–water re-equilibration and its application to Stromboli volcanic system. *Appl. Geochem.* 19, 665–673.

Italiano, F., Bonfanti, P., Ditta, M., Petrini, R., and Slejko, F.: Helium and carbon isotopes in the dissolved gases of Friuli region (NE Italy): geochemical evidence of CO₂ production and degassing over a seismically active area, *Chem. Geol.*, 266, 76–85, <https://doi.org/10.1016/j.chemgeo.2009.05.022>, 2009.

Italiano, F., Yuce, G., Uysal, I., Gasparon, M., and Morelli, G.: Insights into mantle-type volatiles contribution from dissolved gases in artesian waters of the Great Artesian Basin, Australia, *Chem. Geol.*, 378, 75–88, <https://doi.org/10.1016/j.chemgeo.2014.04.013>, 2014.

James, R. H., Bousquet, P., Bussmann, I., Haeckel, M., Kipfer, R., Leifer, I., ... & Treude, T. (2016). Effects of climate change on methane emissions from seafloor sediments in the Arctic Ocean: A review. *Limnology and oceanography*, 61(S1), S283-S299.

Seeberg-Elverfeldt, J., Schlüter, M., Feseker, T., Kölling, M., 2005. Rhizon sampling of pore waters near the sediment/water interface of aquatic systems. *Limnology and oceanography: Methods* 3, 361-371.

Wallmann, K., Drews, M., Aloisi, G., Bohrmann, G., 2006. Methane discharge into the Black Sea and the global ocean via fluid flow through submarine mud volcanoes. *Earth and Planetary Science Letters* 248, 545-560.

J.W. Swinnerton, V.J. Linnenbom, Determination of the C₁ to C₄ hydrocarbons in seawater by gas chromatography, *J. Gas Chromatogr.* 5 (1967) 570–573.



Appendix 1: design and implementation of a test bench for dissolved methane sensors under hyperbaric conditions

Methane is the most common organic compound found on continental margins. In the sediment column, methane is generated through organic matter degradation, either by microbial processes in the shallow sediment or by thermal cracking at greater depths. It is a key chemical compound in biogeochemical processes such as carbonate precipitation, and is part of the energy chain of many chemosynthetic communities found in cold seepage areas. Thus, the methane generated in the sediment is largely degraded in the same environment. However, a larger or smaller fraction is released into the water column. It is estimated that gas emissions on the ocean floor represent about 65 Tg of methane, and about 5-20 Tg reach the atmosphere. Such estimates need to be more constrained. However, these values also illustrate the ability of the water column to capture this methane through various physical and biogeochemical processes, leading to a heterogeneous distribution of methane in the water column. Quantifying these processes is an essential step in improving our estimates of the ocean methane budget, more accurately assessing its contribution to atmospheric methane, and better understanding the influence of climate change on this capture capacity. In this context, a reliable measurement of methane concentration in the water column is essential. These reasons have encouraged us to undertake a detailed qualitative and quantitative study of in situ methane measurement sensors. The development of the test bench is in line with this theme.

There is no doubt that the progress in knowledge being made in this field will greatly benefit from the use of in situ dissolved methane measurement devices providing reliable, high frequency measurements and, if possible, real-time access. Consequently, work has been conducted worldwide over the past twenty years to meet this challenge and some - rare - equipment is even commercially available. However, in view of the advantages they offer, their use for oceanographic studies appears extremely limited or even confidential. One possible cause could be the lack of documented data on the influence of environmental conditions - and first and foremost hydrostatic pressure - on the quality of the measurement provided by the device.

To address this uncertainty, Task 4.2 of the Envri+ project proposed to design and implement a calibration bench to assess the accuracy and robustness of the measurements provided by these devices in concentration, hydrostatic pressure and temperature ranges that correspond to the potential operational conditions.

Development of the test bench

Specifications and design choices

The device has been designed to meet the following requirements:

- a) Containment of a volume of water between 0 and 35 PSUs in sufficient quantity (approximately 80 litres) to allow simultaneous testing of two sensors already available at IFREMER: the METS sensor from Franatech and the HydroC® sensor from Contros;
- b) The injection into this volume of controlled quantities of gaseous methane or methane saturated solution to obtain concentrations of dissolved methane between 100 nM and 1 mM;

- c) Control of environmental test conditions from 5°C to 20°C for temperature and from 0 to 200 bar for hydrostatic pressure;
- d) Sampling under test conditions (pressure and operating temperature) of sufficient volumes of water (approximately 10 mL) to determine the dissolved methane concentration of the test medium by reference chromatographic methods.

Description

To achieve the objectives defined above, the equipment consists of the association of two sub-assemblies:

- a) The first element allows the injection of methane gas volumes and samples for reference measurements;
- b) The second element consists of a measuring medium containment chamber placed inside a hyperbaric chamber imposing the desired temperature and pressure conditions.

The injection and sampling subassembly

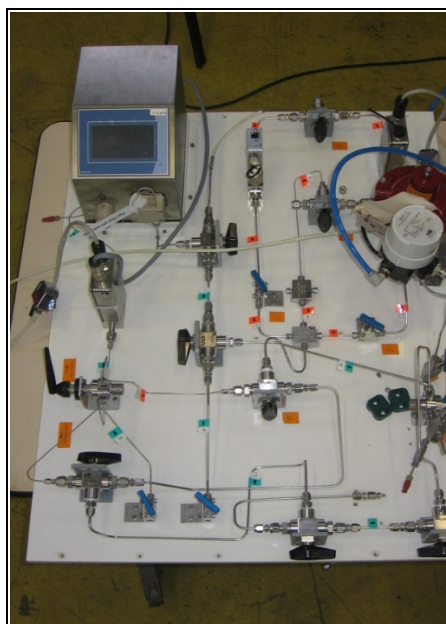


FIGURE 2: UNIT FOR INJECTING PRECISE VOLUMES OF GAS INTO THE TEST CHAMBER AND HYDROSTATICALLY SAMPLING THE MEDIUM OBTAINED FOR CONTROL BY REFERENCE METHODS UNDER HYDROSTATIC PRESSURE

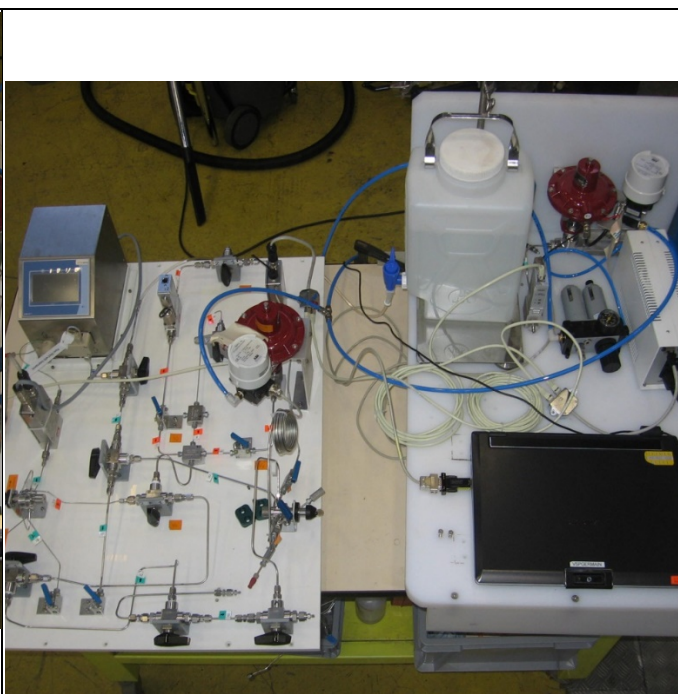


FIGURE 3: THE INJECTION AND SAMPLING MODULE, AS WELL AS THE ASSOCIATED CONTROL AND MONITORING SYSTEM

This module allows you to:

- a) introduce into the circuit precise quantities of methane gas or methane saturated solution that may be between 1 mL and several litres;

- b) homogenize the concentration of dissolved methane throughout the system by means of a circulation pump operating under high hydrostatic pressures;
- c) Isolate a volume of water (possibly under pressure) in such a way as to allow the concentration of dissolved methane to be determined by reference methods.

It consists of the assembly of the following different elements:

- A water circulation pump that can operate up to a pressure of 400 bar. It will be used, by circulating the water contained in the circuit, to convey the gas or methane saturated solution introduced to the measuring chamber and allow the homogenization of the methane concentration between the chamber and the circuit;
- A Coriolis flowmeter for measuring water flow between 0 and 40 g/min;
- A Coriolis flowmeter for gas flow measurement between 0 and 2 g/min. The association of this flowmeter with a Badger valve allows to determine the exact quantity of methane introduced into the circuit;
- A first six-way/two-position valve with an interchangeable injection loop is also installed for the introduction of very small volumes (between 1 and 10 mL);
- A set of valves allowing the methane gas or methane saturated solution to enter the circuit and be transported to the measuring chamber by means of a drive with the circulation pump;
- A second six-way/two-position valve also equipped with a removable injection loop for sampling the measuring medium for reference analyses;
- The various flow control and adjustment equipment (pump, flowmeters, Badger valve) are connected by a field bus and controlled by a dedicated computer system.

Containment and hyperbaric chamber

The second part of the test bench consists of a large hyperbaric chamber, in which the waterproof enclosure containing the sensors is placed. This chamber, which has an internal volume of approximately 80 litres, is filled with the measuring medium whose methane concentration can be modified by adding methane gas or methane saturated solution with the injection system. The enclosure has a membrane to isolate this measuring medium from the water in the hyperbaric chamber while transmitting hydrostatic pressure.



FIGURE 3: THE HYPERBARIC CHAMBER AND ELEMENTS OF THE CONTAINMENT OF THE TEST MEDIUM ALLOWING SENSORS TO BE SUBJECTED TO HIGH HYDROSTATIC PRESSURES AND A REGULATED TEMPERATURE BETWEEN 4 AND 20 °C.



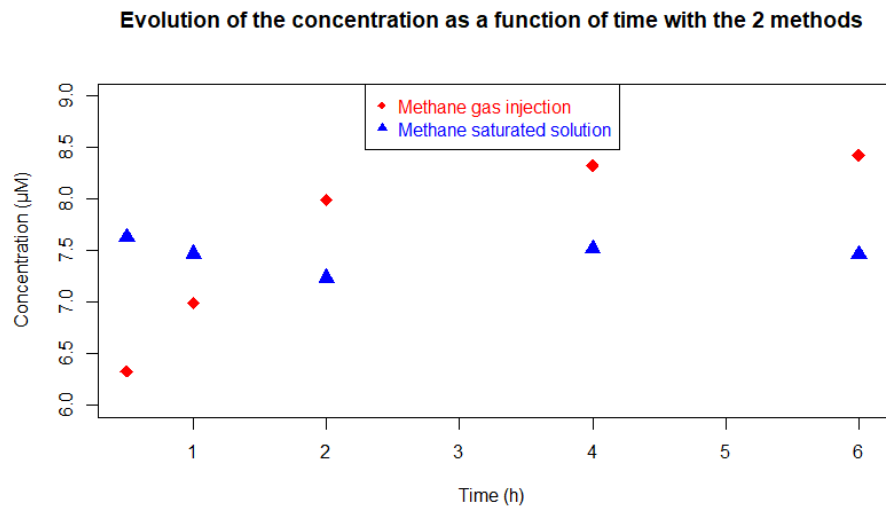
FIGURE 4: THE CONTAINMENT CHAMBER OF THE TEST MEDIUM WITH THE COVER PROVIDED WITH ELECTRICAL AND FLUID PASSAGES FOR CONNECTION TO THE OUTSIDE OF THE HYPERBARIC CHAMBER.

Evaluations of the bench

As the test bench was developed, evaluations were carried out on some of these sub-assemblies and we have defined a procedure to improve its efficiency:

- a) Pressure qualification of the bench system up to 160 bar. The current configuration of the circulation pump does not allow us to achieve the target of 200 bar. This requires minor modifications. However, this 160 bar limit is currently more than sufficient to evaluate our sensors.

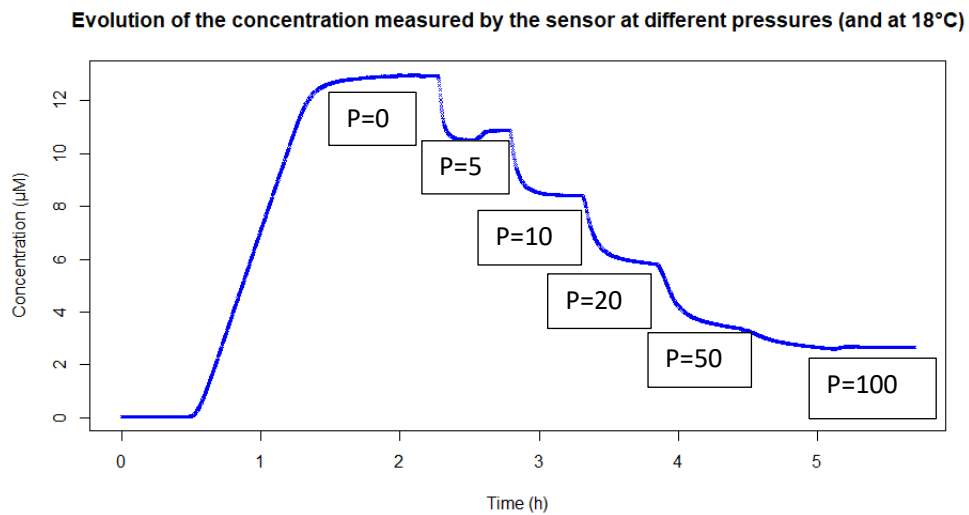
- b) A procedure has been defined to accelerate the homogenization time of the methane concentration following its introduction into the measuring medium (see figure below).



First characterizations of the methane sensor (METS)

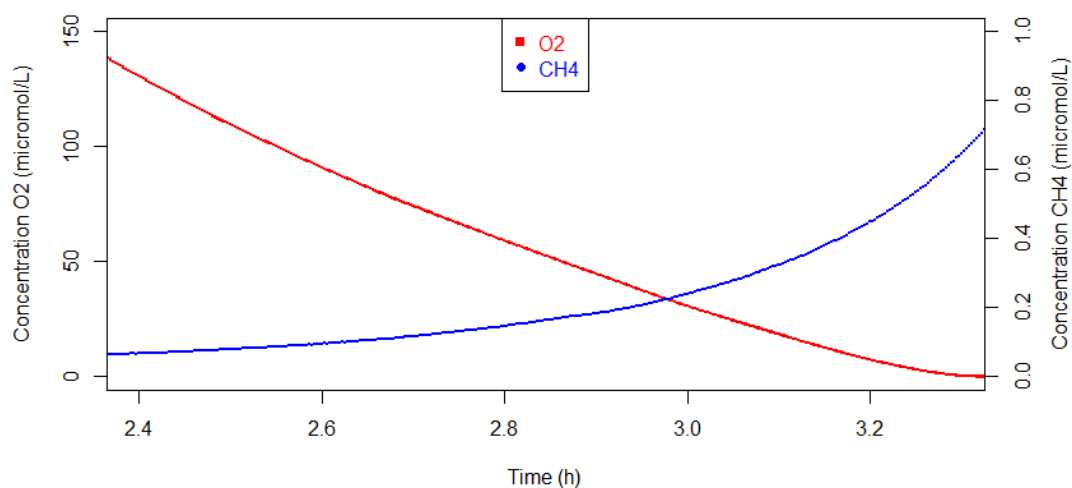
Brief characterizations were carried out with this bench on the METS methane sensor (from Franatech) used on the ENVRI methane campaign. These first experiences highlighted:

- a) A dependence of the signal delivered by the sensor on hydrostatic pressure ;



- b) An impact of dissolved oxygen concentration on the sensor response

Evolution of the concentration of O₂ and CH₄ as a function of time



Conclusion

The technical development carried out as part of the ENVRI project is already of obvious interest.

The first brief characterization experiments carried out on the METS methane sensor make it possible to identify and start quantifying the impact of environmental parameters (pressure, dissolved oxygen concentration) on the measurement delivered by the sensor.

These results make it possible to consider the influence of these parameters in the modelling of the sensor response to obtain improved coherence between the data provided by these devices and the analyses carried out on samples.

Appendix 2: Cruise log book and participants

Cruise description:

The cruise was carried out following the schedule summarized below (time in UTC)

1 st and 2 nd april 2019		Mobilisation	Port of Constanta, Romania
2 nd april 2019	20h00	Start transit to Northern box	
3 rd april 2019	06h02	Start operation on Northern box	
5 th april 2019	15h40	End operation on Northern box Start transit to Shallow site	
6 th april 2019	00h03	End of transit Start of operation on Shallow Site	
6 th april 2019	20h00	End of operation on Shallow site Start transit to Northern box	
7 th april 2019	10h04	End of operation on Northern box (observatory recovery) Start transit back to port	
8 th april 2019		Demobilisation	Port of Constanta, Romania

Cruise operations

The table below summarizes the type of operation performed during the cruise, together with the equipment used and total number of samples recovered.

Each equipment is described in the sections addressing the results.

Operation	Equipment	Nomenclature	Total number
Bathymetry	Hull mounted ELAC Nautik Seabeam 1050D		water column Profiles during acoustic survey
Sediment core	Gravity corer	ENV-GC	8 cores
Acoustic survey in water column	EK 80		water column Profiles

<i>In situ</i> measurement of methane concentration and stable isotope ratio in the water column	Subocean and Franatec methane sensor	ENV-SO-VP ENV-SO-HP ENV-SO-AP	5 Vertical profiles 3 Horizontal profiles 3 Atmospheric profiles
<i>water column sampling for laboratory analysis</i>	CTD equipped with a Rosette and a Franatec methane sensor	ENV-HY	5 CTD casts
<i>In situ</i> measurement of methane concentration at sea surface	Los Gatos FGGA		Profiles
<i>In situ</i> measurements in the atmosphere	Picarro G2401	ENV-AP	Atmospheric profiles
<i>In situ</i> surface flux	Prototype floating chamber		1 deployment
Deployment of seafloor observatory	EMSO type	ENV-OB	2 deployment 1 recovery

Cruise participants:

The cruise was lead by Livio RUFFINE, IFREMER, Laboratoire “Cycles géochimiques et ressources”, livio.ruffine@ifremer.fr. The institutions listed below participated to the cruise:

- GeoEcoMar (Romania - EMSO)
- Ifremer (France – EMSO, Eurofleets)
- LCSE- CEA/CNRS (France, ICOS)
- INGV- Palermo (Italy, EMSO)
- IGE- Grenoble (France, ACTRIS)
- Geomar (Germany, ICOS)

The RIs involved are:

- European Multidisciplinary Seafloor and water-column Observatory- EMSO
- Integrated Carbon Observation System- ICOS
- European Aerosol, Clouds, and Trace gases Research Infrastructure- ACTRIS
- Alliance of European research fleets- EuroFleets

We thank the ship’s team of operators and captains for full collaboration that enabled the 24-7 operations.