

# Hydrothermal versus microbial MEthane release From very shallow coastal systems: can differently sourced emISSIONS directlY escape into the atmosphere? (MEFISTO)

**Deliverable 2.** Pre-survey in Southern Tyrrhenian Sea (March 21-23, 2024) - *Report of the activity* -

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## 1. SUMMARY

MEFISTO pre-survey campaign in the hydrothermal vent area off the island of Panarea (Aeolian Archipelago, Southern Tyrrhenian Sea) was carried out jointly by OGS and INGV operational units in March 21-23, 2024. The survey had the principal objective of detecting at least three sites with different methane ( $\text{CH}_4$ ) emission magnitudes, corresponding to the stations that would have been sampled during the successive field campaigns.

The survey, functional to the implementation of the experimental design, was originally intended as a visual investigation performed by mean of a remotely operated vehicle (ROV). However, the visual identification of the emission sites and the photogrammetric analyses of the seafloor were carried out using GoPro cameras mounted on divers' mask. This change to the original approved plan was due to logistical and scientific reasons. In fact, given the complexity of the rocky seabed in several of the areas investigated around the island and the generally shallow water depth (usually no more than 10 metres), the MEFISTO research team preferred to simplify and speed up the activity by entrusting the mapping of the hydrothermal vent area and the identification of the emission sites to the divers of the INGV operational unit. It should also be noted that in the Aeolian Archipelago the leaking gases generally have an extremely high  $\text{CO}_2$  content (95-98%), which means that the mere identification of bubble streams does not per se indicate  $\text{CH}_4$  emissions. Therefore, the visual survey was implemented, in each investigated site, by the deployment along the water column of a multi-parametric probe equipped with a  $\text{CH}_4$  sensor and by the measurement of the  $\text{CH}_4$  efflux at the water-air interface through a floating accumulation chamber.



MEFISTO research party during the pre-survey and first sampling campaign in the hydrothermal vent area off Panarea Island (March 20-23, 2024).

Visualising all this data in real time allowed the target areas to be selected quickly and correctly, which in turn enabled the MEFISTO research team to carry out the sampling directly during the survey and thus complete the first campaign in the southern Tyrrhenian Sea earlier than originally expected.

Thanks to the support of the M/N Corvo vessel and its crew, more than 250 water samples, 50 pore-water samples, 40 hydrothermal fluid samples, 20 sediment samples, over 15 hours of overnight passive hydroacoustic, accumulation chamber measurements and high-resolution video recordings as well as 8 multi-parametric probe casts were collected in just 30 hours of work at sea.

This report provides the preliminary CH<sub>4</sub> and CO<sub>2</sub> results from the accumulation chamber and multiparametric probe measurements, as well as the most informative images taken by divers during the investigations of the emission sites.

## 2. MEFISTO RESEARCH PROGRAMME AND OBJECTIVES

### 2.1 General scientific background

Methane (CH<sub>4</sub>), accounting for about 30% of the ongoing atmospheric warming, is today recognized as one of the most powerful greenhouse gases (GHGs), being an even stronger absorber of Earth's emitted thermal infrared radiation than carbon dioxide (Simson, 2021). Atmospheric CH<sub>4</sub> concentrations, which increased by only 700 ppb during the millennium before industrialization, are now more than 2.6 times above estimated pre-industrial equilibrium levels, reaching 1857 ppb in 2018 (Saunio et al., 2020). Such an increase is largely the result of anthropogenic emissions related to human activities, including agriculture, production and utilisation of fossil fuel and waste management practices (Ciais et al., 2014). Nevertheless, since the lifetime of CH<sub>4</sub> in the atmosphere barely exceeds 10 years (Prather et al., 2012), the concentrations and therefore the radiative forcing of this potent GHG are thought to be scaled down in a few decades by just stabilising or reducing the anthropogenic emissions (Shindell et al., 2012). Such an approach is considered an effective and realistic way to rapidly mitigate climate change, making it possible to limit the global temperature rise to 1.5-2.0 °C, as targeted by the Paris Agreement (Nisbet et al., 2019).

In order to verify future emission reductions, a precise quantification of the global CH<sub>4</sub> budget is actually needed but, according to the most recent modelling, important uncertainties still affect the calculations, since global emissions were estimated to range between 576 Tg CH<sub>4</sub> / yr and 737 Tg CH<sub>4</sub> / yr (Saunio et al., 2020). The most important source of uncertainty is attributable to natural emissions, accounting for 40% of the global CH<sub>4</sub> budget, 1-13% of which is due to the oceans (Kirschke et al., 2013; Saunio et al., 2016). However, while the open ocean CH<sub>4</sub> emissions are relatively well constrained and are driven by variations that are steadily linked to the organic matter cycling, the global marine flux appears to be mostly influenced by shallow near-shore environments (0-50 mbsl), where CH<sub>4</sub> released from the seafloor can escape to the atmosphere before oxidation (Weber et al., 2019). Here, many forcings can severely affect the amount of CH<sub>4</sub> that reaches the air-sea interface, above all water depth, currents, tides, temperature, water column stratification and microbial methane oxidation (Boles and Clark, 2001; Jordan et al., 2022; Mc Ginnis et al., 2006), but due to limited and scarce data, the actual contribution of coastal areas to atmospheric CH<sub>4</sub> is still quite uncertain (Weber et al., 2019).

### 2.2 The MEFISTO project

The MEFISTO project aims to reduce the abovementioned uncertainties in the estimates of the natural CH<sub>4</sub> fluxes by providing new data on the emissions from shallow near-shore marine environments, where, rapidly bypassing the water column by bubble transport, this powerful GHG can be directly released into the atmosphere (Weber et al., 2019). The lack of data on CH<sub>4</sub> fluxes in coastal areas has

significant implications for the accurate calculation of the atmospheric budget for this gas and the accuracy of this estimate is crucial for verifying potential emission reductions associated with the adoption of effective climate change mitigation strategies. The MEFISTO project, combining classical physical, chemical, and molecular methods with innovative hydroacoustic approaches, will help to fill this knowledge gap by focusing on the study of two Italian shallow coastal areas: a seepage zone recently identified in the Gulf of Trieste, centred on the Bardelli outcrop (Northern Adriatic Sea) and the hydrothermal vent area off the Panarea Island (Aeolian Archipelago, Southern Tyrrhenian Sea).

The project has three main objectives: 1) to ascertain possible differences in the water column degassing pathways and fates between microbially sourced and volcanic-related CH<sub>4</sub> emissions; 2) to assess the main physical and biological forcings (i.e., water depth, currents, tides, temperature, water column stratification and microbial community structure and composition) favouring or preventing the release of CH<sub>4</sub> to the atmosphere from the two investigated marine shallow areas; 3) to eventually develop local emission estimates that will contribute to the refinement of the global atmospheric CH<sub>4</sub> budget.

### 2.3 Volcanic-related CH<sub>4</sub> emissions: the hydrothermal vent system off the Panarea Island (Aeolian Archipelago, Southern Tyrrhenian Sea)

The Aeolian Archipelago is the expression of the volcanism migrating south-eastward from the Central and Southern Tyrrhenian Sea during the Lower Pleistocene. Submarine emissions of CO<sub>2</sub>-rich gases and thermal water outflow is documented in this area since the Roman Age (De Astis et al., 2003). The archipelago includes the active volcanoes of Stromboli, Vulcano, Lipari and Salina. Panarea is the smallest among the Aeolian Islands and represents the subaerial portion of a 2000 m high and 20 km wide submarine stratovolcano, a dormant edifice with a known age range of ca. 150-200 ka (Anzidei et al., 2005; Calanchi et al., 1999; Dolfi et al., 2007).

As a matter of fact, Panarea volcano was generally considered extinct until November 3, 2002, when a low-energy submarine explosion, due to the injection of magmatic fluids in the deep geothermal body (Caracusi et al., 2005), caused an intense and long-lasting submarine gas eruption in the ~2.3 km<sup>2</sup> area rimmed by the islets of Lisca Bianca, Bottaro, Lisca Nera, Dattilo, and Panarelli, about 2.5 km east of Panarea, leading to the opening of a submarine crater 20x8 m wide and 9 m deep (Anzidei and Esposito, 2003; Anzidei et al. 2005; Esposito et al. 2006; Figure 2.1).

The explosion released a huge amount of CO<sub>2</sub> that provoked a drop of seawater pH to a value of 5.6-5.7 and the “degassing crisis” lasted several months (Caracusi et al., 2005; Romano et al., 2019). Several studies conducted in the islet area indicated that, with about 98% CO<sub>2</sub>, the composition of the persistent gaseous emissions is quite stable (Beaubien et al., 2014; Caliro et al., 2004; Espa et al., 2010; Marchini et al., 2021; Sani et al., 2024). Nevertheless, CH<sub>4</sub> concentrations, showed values

up to 900 ppm, are generally not negligible (Romano et al., 2019), making the islet area of Panarea suitable for the MEFISTO project purposes.

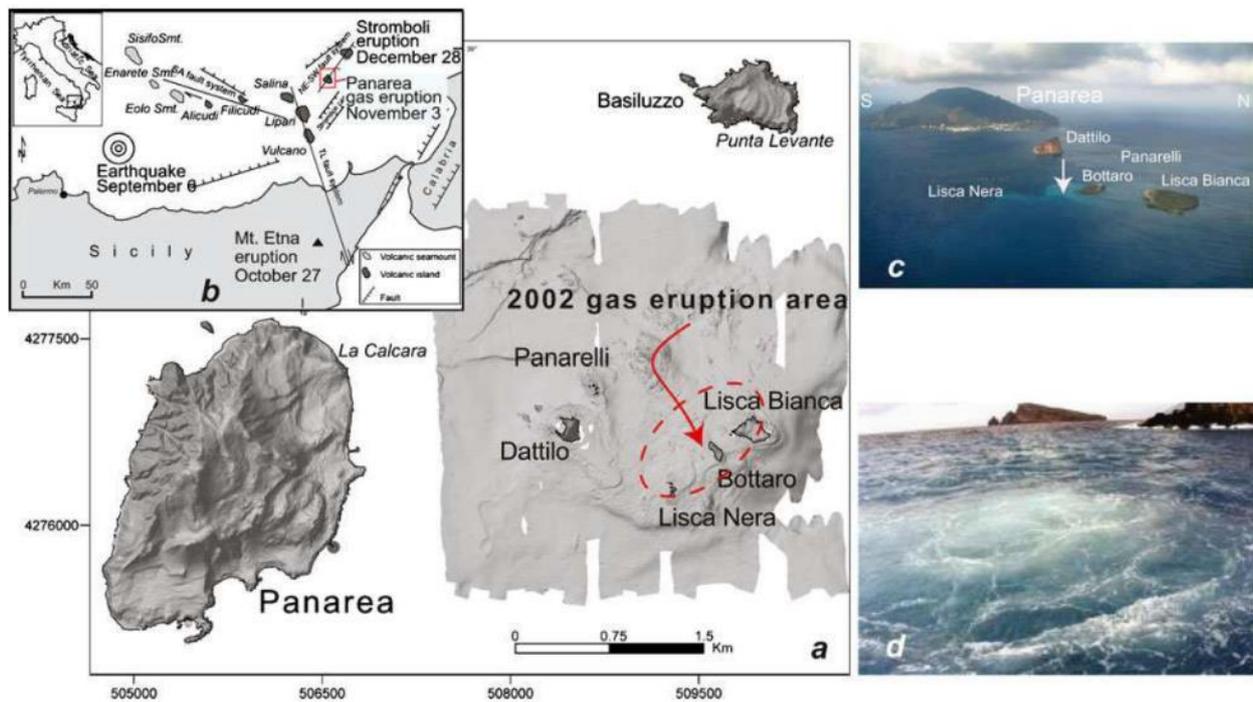


Figure 2.1. a) Location of the 2002 gas eruption. b) Structural sketch map of the Southern Tyrrhenian Sea and Aeolian Islands. c) Aerial view of Panarea Island and islet area with indication of major emission point. d) Gas bubbling in sea surface above the Bottaro crater. From Esposito et al. (2010).

## 2.4 Field research program to accomplish MEFISTO objectives

The field research program originally included the visual detection of bubble streams generated by leaking gases by mean of a remotely operated vehicle (ROV). However, the MEFISTO research team decided to carry out the survey using GoPro cameras mounted on divers' mask. This change to the original approved plan was due to logistical and scientific reasons. In fact, given the complexity of the rocky seabed in several of the areas investigated around the island and the generally shallow water depth (usually no more than 10 metres), the activity was simplified and accelerated up by entrusting the mapping of the hydrothermal vent area and the identification of the emission sites to the divers of the INGV operational unit. It should also be noted that, as previously mentioned, the gases leaking in this area have an extremely high CO<sub>2</sub> content (Beaubien et al., 2014; Caliro et al., 2004; Espa et al., 2010; Marchini et al., 2021; Sani et al., 2024), which means that the mere identification of bubble streams does not per se indicate CH<sub>4</sub> emissions.

Therefore, in each investigated site, the visual survey was conducted by the deployment along the water column of a multi-parametric probe equipped with a CH<sub>4</sub> sensor and by the measurement of the CH<sub>4</sub> efflux at the water-air interface through a floating accumulation chamber.

The evaluation of these preliminary data in real time allowed a quick and correct selection of the target areas, which in turn enabled the MEFISTO research team to carry out the sampling of each CH<sub>4</sub> emission site directly after its identification.

The new work plan included in each investigated site:

- gaseous emission visual detection and video recording (INGV scuba divers);
- casting of the multi-parametric probe along the water column (OGS personnel);
- collection of hydrothermal fluid, pore-water and biofilm/sediment samples (INGV scuba divers);
- deployment of Niskin bottles along the water column (OGS personnel);
- closure of Niskin bottles at discrete water depths above the emission site (INGV scuba divers);
- recovery of Niskin bottles and collection of water samples for chemical and microbiological analyses (OGS and INGV personnel);
- deployment and recovery of hydrophones for passive hydroacoustic measurements (INGV scuba divers).

A total of 8 stations were investigated during the campaign (Figures 2.2 and 2.3).

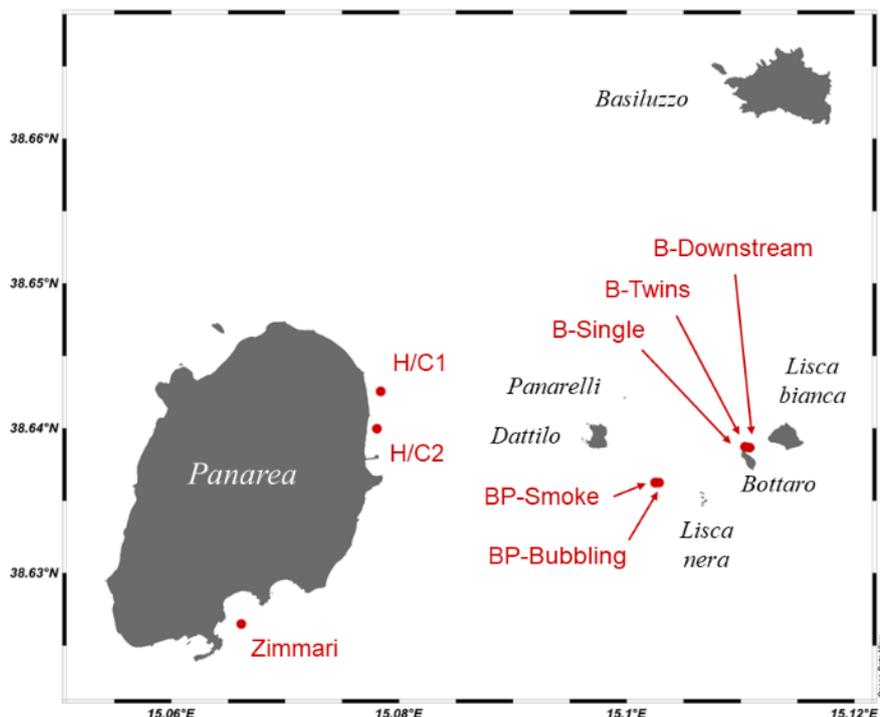


Figure 2.2. Location map of the study area displaying the investigated stations: Hot/Cold1 (H/C1), Hot/Cold2 (H/C2), Zimmari, Black point Smoke (BP-Smoke), Black Point Bubbling (BP-Bubbling) Bottaro Twins (B-Twins), Bottaro Single (B-Single) and Bottaro Downstream (B-Downstream).

Two stations (hereafter named “Black Point Smoke” and “Black Point Bubbling”) were sampled near the INGV meda-observatory system, in correspondence of a black-colored, sulfide-rich hydrothermal vent detected at 23 m depth in 2002 (Tassi et al., 2009).

Two stations (hereafter named “Hot/Cold1” and “Hot/Cold2”) were investigated in an area located NE of Panarea Island at 10–12 m depth and characterized by spots with very different temperatures at the distance of few meters from each other. Unvegetated hot spots, characterized by CO<sub>2</sub> emissions, temperatures up to 60 °C, and pH values ranging from 7 to 5.6, alternates here to cold spots featuring meadows of *Posidonia oceanica* seagrass, reduced venting activity, temperatures of about 26 °C and pH of about 7.9 (Di Bella et al., 2022).

One site (hereafter named “Zimmari”) located in a bay S of Panarea Island, where generally no emissions has been observed, was chosen as reference station.

Eventually, three stations (hereafter named “Bottaro Twins”, “Bottaro Single” and “Bottaro Downstream”) were sampled in the crater produced after the explosion of November 2002 and positioned a few tens of meters NW of Bottaro islet, where three particularly large vents occur (Anzidei et al., 2005; Capaccioni et al., 2005; Caracusi et al., 2005; Esposito et al., 2006).

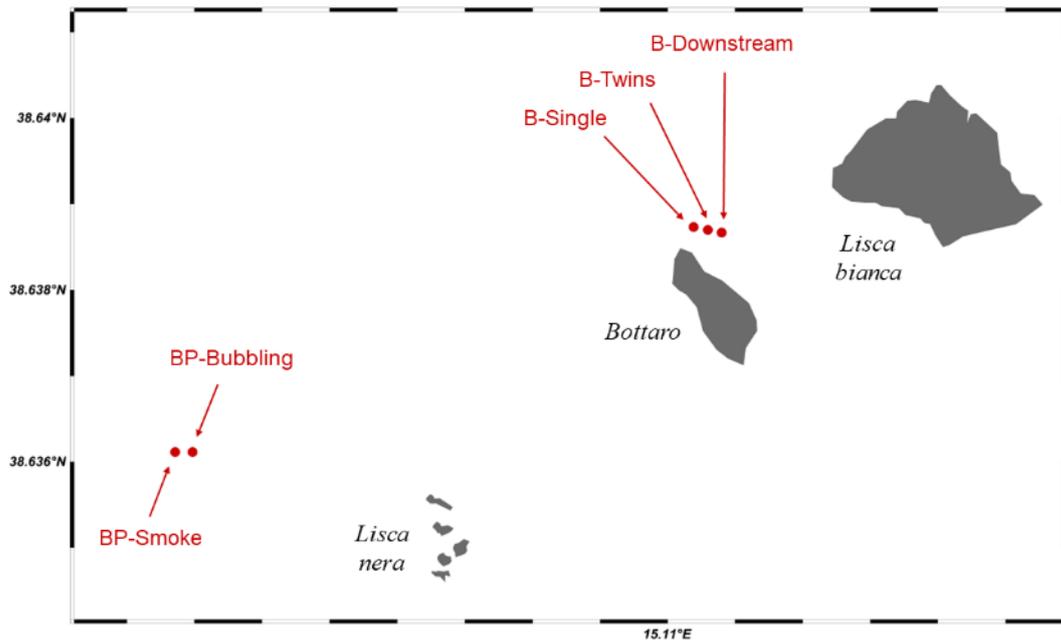


Figure 2.3. Detailed view of the stations in the Panarea islet area, showing the locations of Black point Smoke (BP-Smoke), Black Point Bubbling (BP-Bubbling) Bottaro Twins (B-Twins), Bottaro Single (B-Single) and Bottaro Downstream (B-Downstream).

### 3. NARRATIVE OF THE CAMPAIGN

MEFISTO pre-survey and sampling campaign in the hydrothermal vent area off the Panarea Island (Aeolian Archipelago, Southern Tyrrhenian Sea) was jointly carried out by OGS and INGV operational units in March 21-23, 2024. The activities were conducted thanks to the logistical support provided by the M/N Corvo vessel and crew and by the OGS ECCSEL NatLab-Italy personnel and laboratory of Panarea. This facility is one of the Italian components of ECCSEL, the "European Carbon Dioxide Capture and Storage Laboratory Infrastructure," an initiative that aims to create a network of world-class research laboratories dedicated to developing carbon capture and storage (CCS) techniques and combating global climate change by enabling low to zero CO<sub>2</sub> emissions from industry and power generation. The laboratory, owned by OGS since 2015 and provided with technologically advanced multidisciplinary equipment, offered the MEFISTO research team the possibility to store, preprocess and, in certain cases, immediately analyse the samples collected daily from the Panarea vents.

**Thursday, March 21, 2024** (air temp. 15.05 °C; wind 3.31 m/s; sea temp. at 18.03 m b.s.l. 18.03 °C; wave 0.2 m, 301.5°; data recorded by INGV MEDA at 09:00)

08:30 - Storing of the equipment on the M/N Corvo vessel and briefing on the daily work plan.

09:58 - Departure to the work area.



Figure 3.1. INGV meda-observatory system in Black Point area.

10:09 - Arrival at Black Point site, mooring to the INGV meda-observatory system and preparation of the divers.

10:50 - Divers in water for hydrothermal fluid, pore-water, biofilm and sediment sampling; vessel positioning above the emission point (“Black Point Smoke”) signalled by the buoy released by the divers.

11:38 - Niskin bottles deployment.

11:45 - All Niskin bottles closed by divers.

11:49 - End of scuba diving activity.

12:00 - Niskin bottles onboard and water sample collection.



Figure 3.2. Niskin bottles deployment in “Black Point Smoke”.

12:25 - First multi-parametric probe cast.

12:57 - Multi-parametric probe recovery.

13:00 - Second multi-parametric probe cast.

13:04 - Multi-parametric probe recovery.

13:09 - Accumulation chamber measurements.

13:20 - End of accumulation chamber measurements and departure to Panarea harbour.

13:26 - Arrival at Panarea harbour and delivery of samples for laboratory filtrations.

13:30 - Lunch.

14:30 - End of water sample collection.

15:05 - Departure to the work area.

15:11 - Arrival at Black Point site mooring to the INGV meda-observatory system and preparation of the divers.

15:19 - Vessel positioning above the second emission point (“Black Point Bubbling”).

15:30 - Niskin bottles deployment.

16:00 - Divers in water for sampling of biofilms and deployment of the hydrophone for acoustic measurements.



Figure 3.3. Multi-parametric probe deployment in “Black Point Bubbling”.

16:45 - All Niskin bottles closed by divers; end of scuba diving activity.

16:47 - Niskin bottles onboard and water sample collection.

17:00 - Multi-parametric probe cast.

17:22 - Multi-parametric probe recovery and departure to Panarea harbour.

17:30 - Arrival at Panarea harbour and delivery of samples for laboratory filtrations.

**Friday, March 22, 2024**, (*air temp. 14.35 °C; wind 2.44 m/s; sea temp. at 17.70 m b.s.l. 18.02 °C; wave 0.2 m, 303.7°; data recorded by INGV MEDA at 09:00*)

08:50 - Storing of the equipment on the M/N Corvo vessel and briefing on the daily work plan.

08:52 - Departure to Black Point area for hydrophone recovery.

09:05 - Arrival at INGV meda-observatory system; hydrophone successfully retrieved.

09:06 - Departure to Hot/Cold area.

09:27 - Arrival on work area and preparation of the divers.

10:02 - Divers in water for hydrothermal fluid, pore-water, biofilm and sediment sampling.

10:10 - Vessel positioning above the emission point (“Hot/Cold1”) signalled by the buoy released by the divers.

10:19 - Niskin bottles deployment.

10:48 - All Niskin bottles closed by divers; end of scuba diving activity.

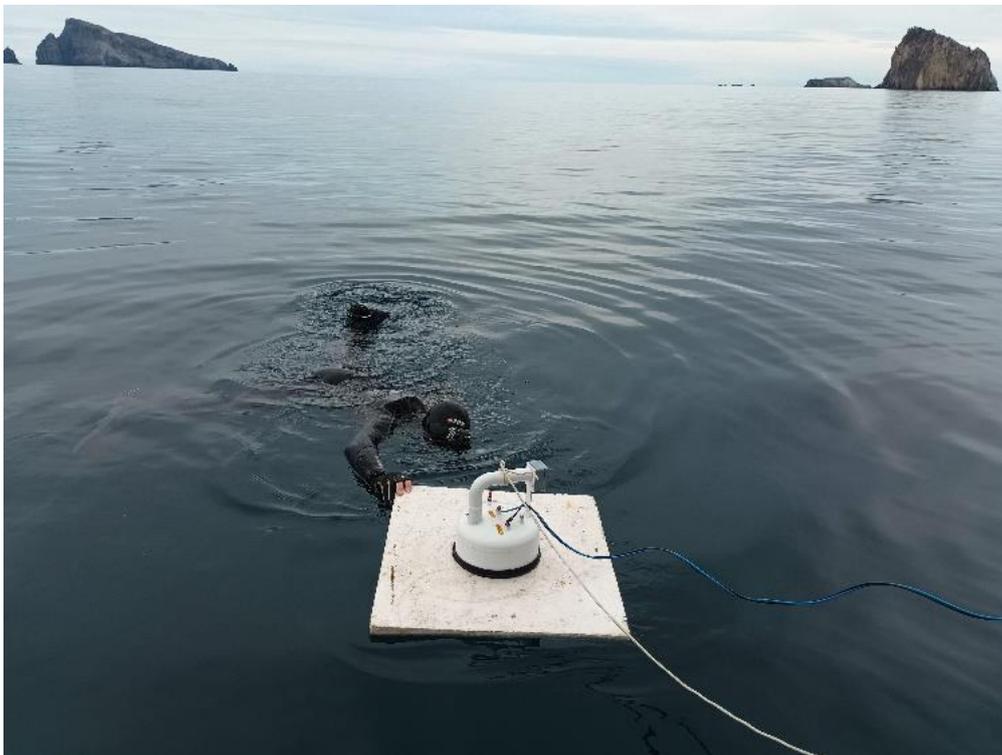


Figure 3.4. Accumulation chamber operated by INGV diver in “Hot/Cold1”.

- 10:50 - Niskin bottles onboard and water sample collection.
- 10:49 - Accumulation chamber measurements.
- 11:04 - End of accumulation chamber measurements.
- 11:05 - Multi-parametric probe cast.
- 11:26 - Multi-parametric probe recovery and departure to Panarea harbour.
- 11:30 - Arrival at Panarea harbour and delivery of samples for laboratory filtrations.
- 12:14 - End of water sample collection and departure to the reference station (“Zimmari”).
- 12:40 - Arrival on work area and Niskin bottles deployment (bottle closure mechanisms were activated by drop messengers).
- 13:07 - Niskin bottles onboard and water sample collection.
- 13:37 - End of water sample collection.
- 13:40 - Lunch.



Figure 3.5. Hydrophone for acoustic measurements of noise radiated by the gas bubble oscillating walls.

- 14:07 - Multi-parametric probe cast.
- 14:26 - Multi-parametric probe recovery.
- 14:47 - Accumulation chamber measurements.
- 15:00 - End of accumulation chamber measurements.

15:04 - Van Veen grab deployment and sediment sampling.

15:22 - Departure to Hot/Cold area.

15:54 - Arrival on work area and preparation of the divers.

16:30 - Divers in water for sampling of hydrothermal fluids, pore-waters, biofilm and sediment and deployment of the hydrophone for acoustic measurements.

16:45 - Vessel positioning above the study site (“Hot/Cold2”) signalled by the buoy released by the divers and located about 100 meters to the S with respect to “Hot/Cold1”.

16:52 - Niskin bottles deployment.

17:16 - All Niskin bottles closed by divers and brought onboard for water sampling.

17:21 - Buoy lost due to strong current; scuba divers looked for a new ideal location for hydroacoustic measurements.

17:30 - Multi-parametric probe cast.

18:00 - Multi-parametric probe recovery; hydrophone deployed; end of scuba diving activity.

19:00 - Departure to Panarea harbour; end of water sample collection.

**Saturday, March 23, 2024**, (*air temp. 15.45 °C; wind 2.90 m/s; sea temp. at 18 m b.s.l. 18.03 °C; wave 0.2 m, 302.9°; data recorded by INGV MEDA at 09:00*)

08:20 - Storing of the equipment on the M/N Corvo vessel and briefing on the daily work plan.

08:40 - Departure to Hot/Cold area for hydrophone recovery.

08:59 - Buoy detached from the hydrophone; scuba divers in water to retrieve it.

09:04 - Hydrophone successfully retrieved.

09:30 - Departure to Bottaro crater.

09:41 - Arrival in the work area and preparation of divers; three main vents were detected near the Bottaro islet, two of which were less than a meter apart from each other (“Bottaro Twins”), while the third (“Bottaro Single”) was about 10 meters to the W;

10:04 - Divers in water for sampling of hydrothermal fluids, pore-waters, biofilm and sediment and deployment of the hydrophone for acoustic measurements; vessel positioning with the bow above “Bottaro Single” and the stern on “Bottaro Twins”.

10:18 - Niskin bottles deployment.

11:00 - All Niskin bottles closed by divers and brought onboard for water sampling; end of scuba diving activity.

11:30 - Multi-parametric probe cast in “Bottaro Twins”.

11:57 - Multi-parametric probe recovery.

13:08 - Multi-parametric probe cast in “Bottaro Single”.

13:28 - Multi-parametric probe recovery.

13:35 - Accumulation chamber measurements.

13:38 - End of accumulation chamber measurements and departure to Panarea harbour.

14:00 - Arrival at Panarea harbour, end of water sampling and delivery of samples for laboratory filtrations.

14:10 - Lunch.



Figure 3.5. Bubble formation on the water surface due to hydrothermal vents in “Bottaro Twins”.

14:40 - Departure to Bottaro crater.

14:58 - Arrival in the work area and preparation of divers; vessel positioning on “Bottaro Downstream”, about 10 meters to the E (main current direction) in relation to “Bottaro Twins”.

15:13 - Niskin bottles deployment.

15:18 - Divers in water for sampling of pore-waters, biofilm and sediment and retrieval of the hydrophone for acoustic measurements.

15:24 - All Niskin bottles closed by divers and brought onboard for water sampling.

15:25 - End of scuba diving activity.

16:42 - Accumulation chamber measurements.

16:48 - End of accumulation chamber measurements and departure to Panarea harbour.

17:04 - Arrival at Panarea harbour and docking; end of the operations.

## 4. PRELIMINARY RESULTS

Preliminary results of the CH<sub>4</sub> and CO<sub>2</sub> concentrations measured along the water column and at the air-sea interface, as well as the most informative images taken by divers during the investigations of each emission site, are presented below.

Water column profiling was performed by a multi-parametric system consisting of a RBR*maestro*<sup>3</sup> multi-channel logger (for conductivity, temperature, pressure, dissolved oxygen and pH detection), a CONTROS HydroC CO<sub>2</sub> sensor (for CO<sub>2</sub> partial pressure measurement) and a CONTROS HydroC CH<sub>4</sub> sensor (for CH<sub>4</sub> partial pressure measurement).

Concentrations of CH<sub>4</sub> and CO<sub>2</sub> outgassing to the atmosphere were determined using a closed-chamber mounted on a floating platform, an innovative, ad hoc instrument for determining air-water gas exchange rates. Tools for gas flux measurements based on static closed-chamber methods have been developed and used by several scientists in most terrestrial, wetland and aquatic ecosystems. The system used during this campaign was inspired by that employed for CO<sub>2</sub> flux measurements in volcanic and geothermal areas, that are based on the accumulation chamber method. It consisted of two main parts: an inverted chamber and a portable device with CO<sub>2</sub> and CH<sub>4</sub> detectors equipped with an air pump and an analog-digital converter.

Underwater photos were taken by scuba divers using GoPro cameras mounted on the masks.

### 4.2 Black Point sites

In “Black Point Smoke” station CH<sub>4</sub> concentrations showed a negative trend with depth along the water column, with higher values at the surface (4.60±0.09 ppm) and lower at the bottom (3.75±0.54 ppm). An opposite trend was observed for CO<sub>2</sub>, with lower values at the surface (380.84±1.55 ppm) and higher at the bottom (428.75±0.54 ppm). Similar concentrations and trends of CH<sub>4</sub> (3.61±0.08 ppm in surface and 2.88±0.32 ppm at the bottom) and CO<sub>2</sub> (386.89±8.66 ppm in surface and 486.71±7.04 ppm at the bottom) were detected in “Black Point Bubbling” station.

Gas flux measurements at the air-sea interface were carried out at the “Black Point Bubbling” station. The CH<sub>4</sub> flux reached a value of 0.194 g m<sup>-2</sup> d<sup>-1</sup>, whereas a maximum CO<sub>2</sub> flux of 15.04 g m<sup>-2</sup> d<sup>-1</sup> was measured.



Figure 4.1. Biofilm collection in “Black Point Smoke” station. The black vent fumarole can be seen pouring out of the hole between the rocks.



Figure 4.2. Hydrophone recording the noise radiated by the gas bubble oscillating walls in “Black Point Bubbling” station.

### 4.3 Hot/Cold sites

In “Hot/Cold1” station both CH<sub>4</sub> (7.25±0.12 ppm) and CO<sub>2</sub> (502.83±1.12 ppm) showed quite homogeneous distributions along the water column. Similarly, CH<sub>4</sub> concentrations (4.34±0.12 ppm) poorly varied with depth in “Hot/Cold2” site, while CO<sub>2</sub> values, ranging between 426.24 ppm measured at the surface and 613.55 ppm detected at the bottom, showed a strong positive trend along the water column.

Gas flux measurements were carried out both in “Hot/Cold1” and “Hot/Cold2” stations, but ideal gas concentrations inside the accumulation chamber were obtained only for CH<sub>4</sub> in “Hot/Cold1” station, where a maximum CH<sub>4</sub> flux of 0.103 g m<sup>-2</sup> d<sup>-1</sup> was measured.



Figure 4.3. INGV diver collecting biofilm and sediment samples in “Hot/Cold1”.

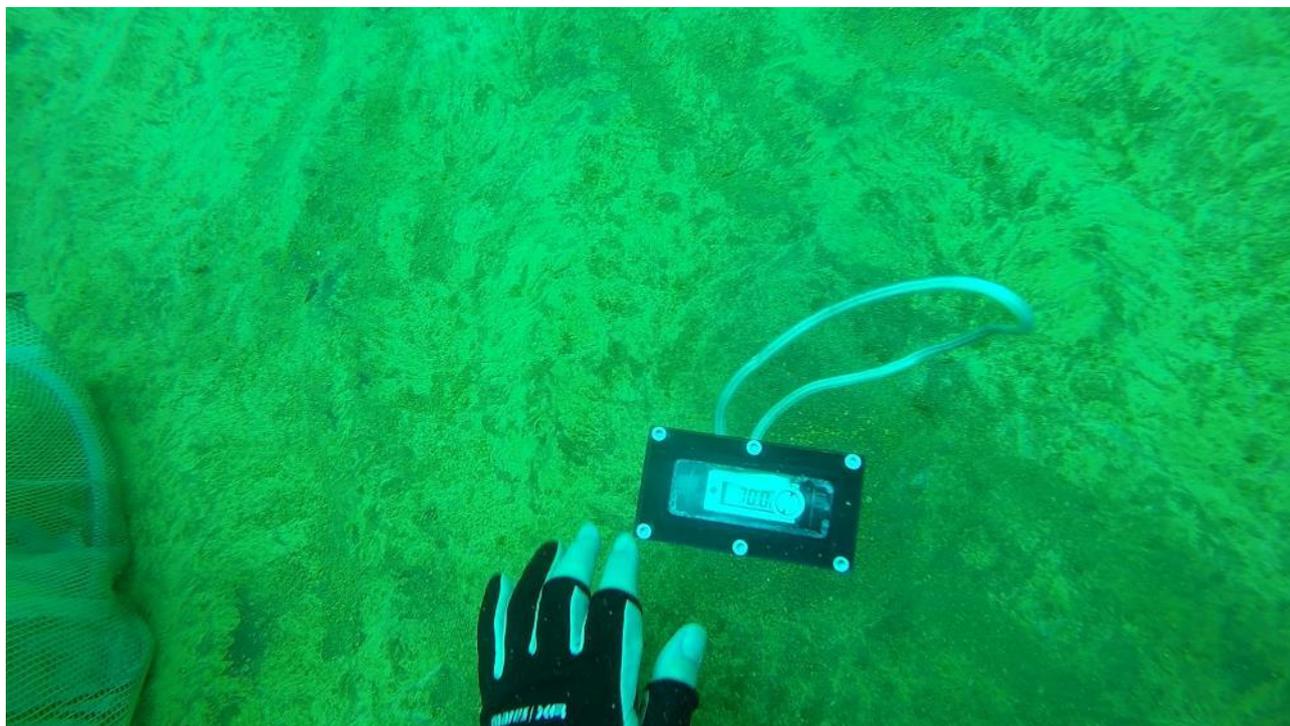


Figure 4.4. INGV diver measuring surface sediment temperature in a hot patch detected in “Hot/Cold1”. The digital thermometer display indicated 70.0 °C.



Figure 4.5. INGV diver carrying operating in “Hot/Cold1” station.



Figure 4.6. “Hot/Cold2” site.

#### 4.4 Zimmari

A quite homogeneous distribution of CH<sub>4</sub> along the water column was observed in “Zimmari” station, in which an average value of  $4.42 \pm 0.06$  ppm was measured. CO<sub>2</sub> concentrations, ranging between 449.82 ppm and 463.52 ppm, showed a positive trend with depth along the water column, with lower values at the surface and higher at the bottom

Gas flux measurements at the air-sea interface were carried out also in this site but neither CH<sub>4</sub> or CO<sub>2</sub> reached ideal concentration values inside the accumulation chamber.

#### 4.5 Bottaro sites

CH<sub>4</sub> concentrations showed a quite homogeneous distribution along the water column of “Bottaro Twins” station, with a mean value of  $2.45 \pm 0.09$  ppm. The comparison between bottom and surface waters indicated that CH<sub>4</sub> concentrations detected at 7 m b.s.l. ( $2.29 \pm 0.63$  ppm) were on average slightly lower than those observed at 1 m b.s.l. ( $2.65 \pm 0.22$  ppm). CO<sub>2</sub> concentrations, ranging between 5675.53 ppm and 6122.94 ppm, had a negative trend with depth along the water column, with higher values at the surface and lower at the bottom.

A quite homogeneous distribution of CH<sub>4</sub> along the water column was also observed in “Bottaro Single” and “Bottaro Downstream” stations ( $2.14 \pm 0.10$  ppm and  $2.04 \pm 0.12$  ppm, respectively), while CO<sub>2</sub> concentrations, ranging between 617.89 ppm and 642.96 ppm in “Bottaro Single” and between 440.56 ppm and 442.61 ppm in “Bottaro Downstream”, were one order of magnitude lower than those measured in “Bottaro Twins” but showed the same negative trend with depth.

Gas flux measurements at the air-sea interface were carried out between “Bottaro Twins” and “Bottaro Single” emission sites. The CH<sub>4</sub> flux reached a value of  $0.030 \text{ g m}^{-2} \text{ d}^{-1}$ , whereas a maximum CO<sub>2</sub> flux of  $11910 \text{ g m}^{-2} \text{ d}^{-1}$  was detected. A similar CH<sub>4</sub> value of  $0.034 \text{ g m}^{-2} \text{ d}^{-1}$  was observed in “Bottaro Downstream” station, in which ideal gas concentrations inside the accumulation chamber were not obtained for CO<sub>2</sub>.

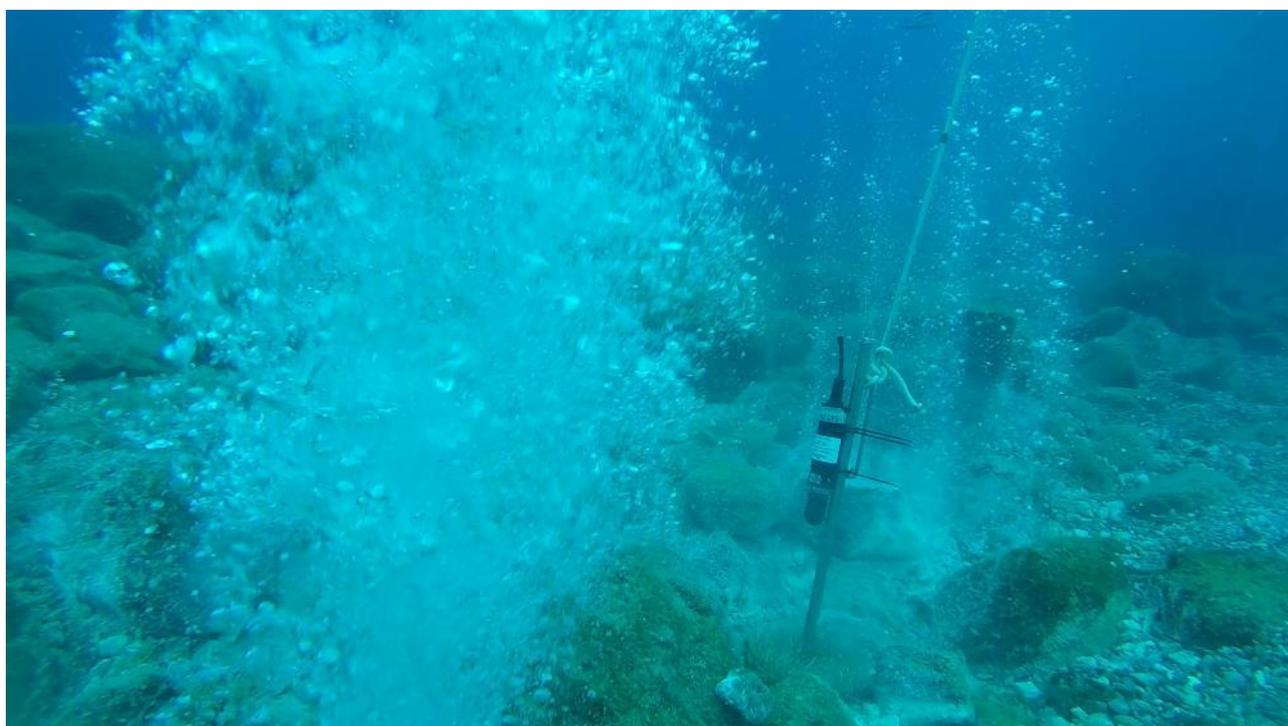


Figure 4.7. Hydrophone recording the noise radiated by the gas bubble oscillating walls in “Bottaro Twins” station.

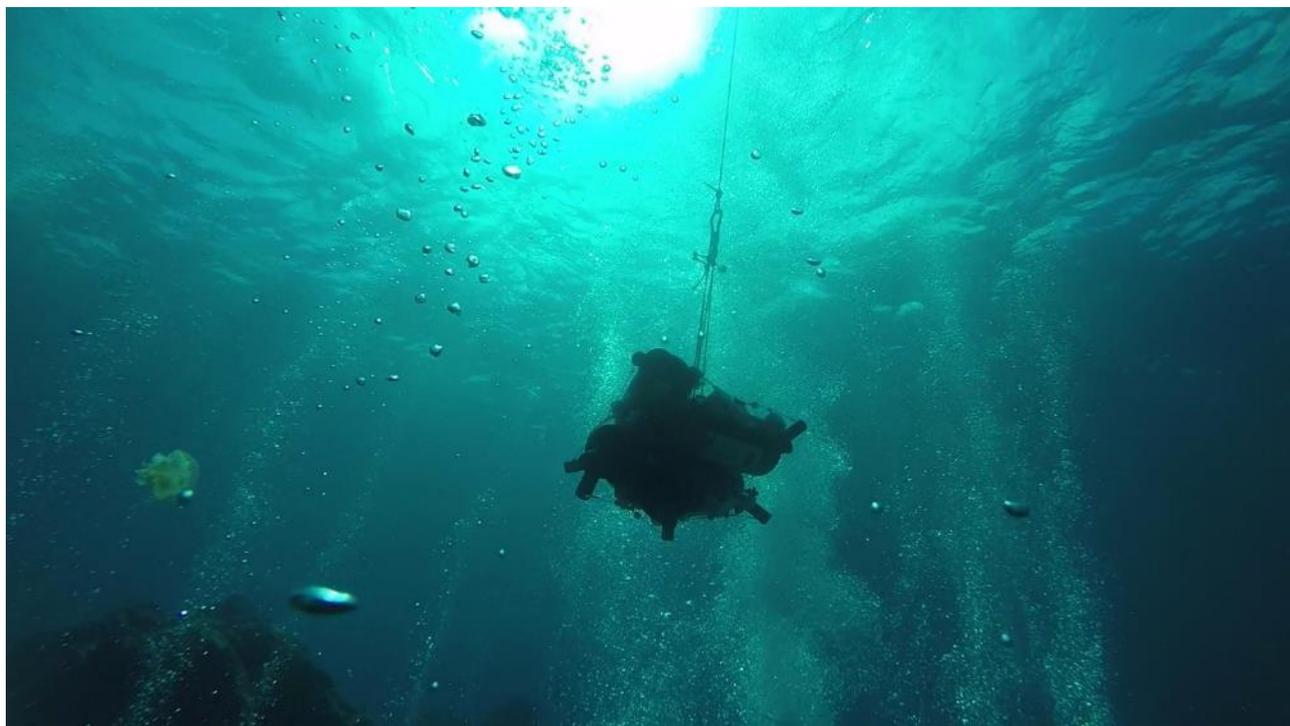


Figure 4.8. Deployment of Niskin bottles in “Bottaro Twins”.



Figure 4.9. Deployment of Niskin bottles in “Bottaro Single”.

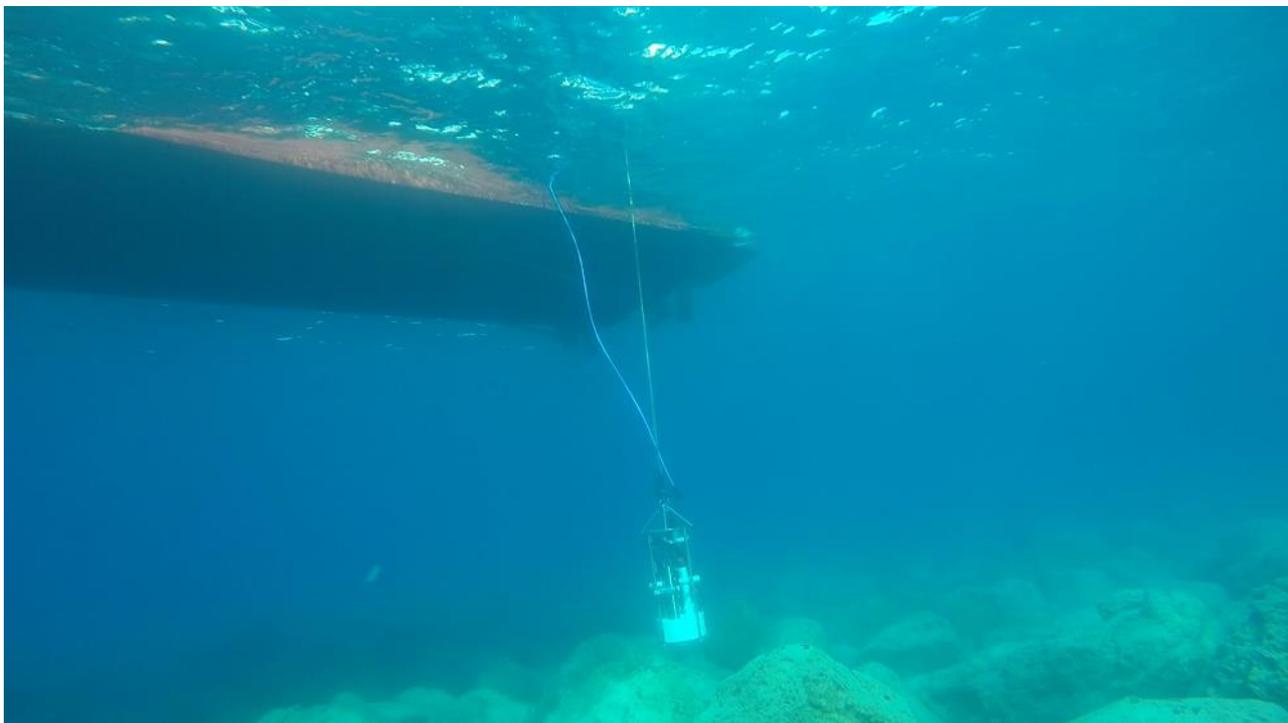


Figure 4.10. Multi-parametric probe cast in “Bottaro Downstream”.



Figure 4.11. Niskin closure and sediment retrieval from “Bottaro Downstream” rocky seabed.

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