ECO2

Sub-seabed CO_2 Storage:
Impact on Marine Ecosystems

Citation: De Vittor C.[1], Beaubien S.E.[2], Franzo A.[1] and Comici C.[1] (2014) Physical, chemical and biological survey at submarine CO_2 vents off Panarea Island (Italy): cruise report ECO_2-9. [1]OGS (Istituto Nazionale di Oceanografia e Geofisica Sperimentale), Trieste, Italy/[2]Università di Roma La Sapienza, Roma, Italy, 26 pp.

Summary

1 INTRODUCTION

Carbon capture and storage (CCS) is expected to provide an important, short-term approach for mitigating potential global climate change due to anthropogenic emissions of carbon dioxide (CO_2). This technology involves the capture of CO_2 emitted from large point sources and its injection into deep geological reservoirs, such as depleted hydrocarbon reservoirs and deep saline aquifers, both on land and off-shore. Offshore reservoirs are particularly favourable due to potentially high storage capacities, the extra barrier provided by the overlying water, and the physical separation between injection sites and populated centres.

Concerns have been raised amongst various stakeholders regarding the long term safety of sub-seabed CO_2 storage, however, including the potential for leakage of CO_2 and associated gases/compounds into the water column (with potential impacts on the marine ecosystem) and possible migration to the atmosphere.

Although laboratory experiments and modelling can be performed to address these concerns, the study of natural, analogous systems is particularly useful as they can address issues related to scale and site complexity. The Università di Roma "La Sapienza" and OGS first proposed the inclusion (within the ECO_2 project) of the natural, shallow analogue site near the island of Panarea (Aeolian Islands, Italy; Fig. 1), where natural, thermo-magmatic CO_2 is leaking from the seafloor. Based on the range of depths and relatively high and persistent gas flow rates, the occurrence of both gas only and gas-water seepage, and its close proximity to shore (Fig. 1), Panarea represents an exceptional location to study natural processes and impacts related to shallow seabed CO_2 leakage.

This CO_2 is released most strongly in the area surrounding two of islets located 3 km to the east of Panarea (Lisca Bianca and Bottaro). This natural CO_2-release field (c. 3 km^2) has been active for centuries, with gas emanating from a series of NW-SE and NE-SW trending fractures (Esposito et al., 2006). In the early 1980's researchers began to conduct gas geochemistry surveys of the area (Caliro et al., 2004), showing that the system was relatively stable in both gas chemistry (e.g. 98% CO_2, 1.7% H_2S plus other trace gases) and flux rates (7-9 x 10^6 L/d). On November 2 and 3, 2002, a gas outburst event increased the total gas flow rate by about 2 orders of magnitude (4 x 10^8 L/d) (Caliro et al., 2004), with large volumes of gas reaching the water surface. Flux rates began to decrease towards pre-outburst conditions about 3 months after the event. Most release points are gas only, although various points also release water of different origin, ranging from geothermal to seawater end-members that are mixed to variable degrees (Tassi et al., 2009).

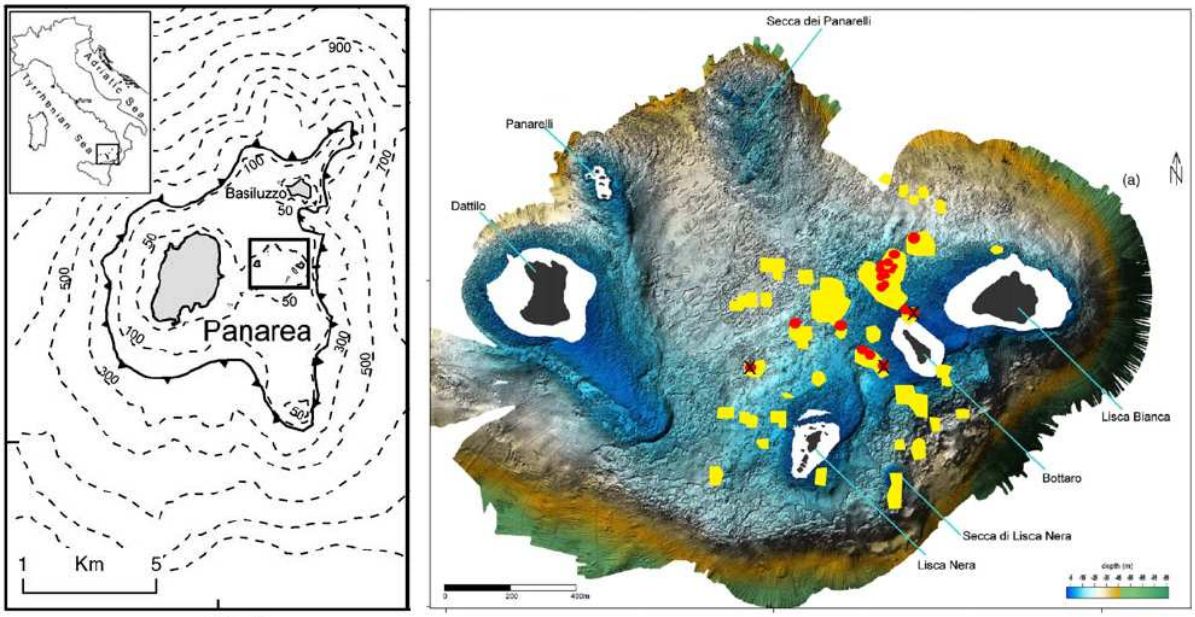


Figure 1. Map (left) showing Panarea Island and associated islets to the east (boxed area). Bathymetric map (right) showing the location of the gas leaks in December 2002 (yellow) soon after the outburst, the three strongest gas release points during the outburst (x), and the gas leak locations one year later (red circles). Modified after Esposito et al. (2006).

2 OBJECTIVES

Research conducted at the Panarea site by UniRoma1 and OGS within the ECO$_2$ project occurs within three separate work packages: WP2, WP3, and WP4. The following lists the original goals of this cruise.

WP2 ("Fluid and Gas Fluxes across the Seabed at Storage Sites and Natural CO_2 Seeps"):

- Conduct gas bubble flux measurements using the accumulation chamber method. Work focused on the new deeper water site called "point 21".
- Perform benthic chamber measurements at sites where there is a flux of deep water which only contains dissolved CO_2 but no gas bubbles. The chamber was sampled for major and trace elements, inorganic nutrients and carbonate system parameters. A pCO_2 probe and a new multi-parameter probe (pH, temperature, salinity and Eh) were deployed within the chamber for continuous monitoring.

WP3 ("Fate of CO_2 and other Gases emitted at the Seabed"):

- Study gas exchange processes between an ascending CO_2 bubble and the surrounding water column through the use of video filming, gas bubble chemistry analyses, and water column chemistry analyses.
- Deployment of a total of 20 GasPro-pCO_2 probes (developed by the University of Rome) along two 2D water-column transects to monitor the spatial-temporal behaviour of dissolved CO_2. The first site was a repeat monitoring of a site a few metres SE of the pockmark "crater" near Bottaro Island, while the second was to study the migration of dissolved CO_2 in the near field around a single, moderately strong bubble flare located at a new site called "point 21".

WP4 ("Impact of Leakage on Benthic Organisms and the Marine Ecosystems"):

- Water sampling to examine the effect of increasing pCO_2 on the planktonic ecosystem by analysing water samples at two station (control and impacted) near Basiluzzo islet and along a transect which encompasses a set of scenarios, ranging from highly impacted to unaffected sites. Qualitative and quantitative

estimates of the planktonic communities from picoplankton to zooplankton along the water column will be used to determine the effect of increasing pCO_2 on natural marine communities.

- Sediment sampling to determine the potential impacts of CO_2 and fluid leakage on microphytobenthos.
- Primary and secondary benthic production experiments in areas of both CO_2 and fluid leakage. The integration of these functional parameters with the structure of benthic communities could provide some indications about the C flux within the benthic domain and if it could be affected by CO_2.

3 SUMMARY OF WORK

3.1 Participants

Family name	Name	Background	Institute
Beaubien	Stan	Geochemist	UniRoma1
De Vittor	Cinzia	Biologist	OGS
Comici	Cinzia	Geologist	OGS
Franzo	Annalisa	Biologist	OGS

3.2 Narrative

Tuesday, May 6th

- 18:00 UTC: Departure from Naples with the ferry boat for the Aeolian Islands of OGS researchers

Wednesday, May 7th

- 06:00 UTC: Arrival on Panarea Island of OGS researchers
- 07:00 UTC: Unpacking and set-up of the on-land laboratory
- 08:00 UTC: Briefing with the diving- and boat- support staff from 'Amphibia' diving center, Panarea
- 09:34 UTC: The water column profile was measured at Basiluzzo Island (B1 and B2) by means of a CTD (Seabird 19 Plus) and the sampling of water was performed at discrete depths (0.2 m, 7 m and 11 or 13 m) using Niskin bottles
- 13:00 UTC: Laboratory analysis

Thursday, May 8th

- 07:35 UTC: The water column profile was measured at three stations (LB6-LB4-LB1) along the transect between Bottaro and Lisca Bianca (LB transect) by means of a CTD (Seabird 19 Plus) and the sampling of water was performed at discrete depths (between 0.2-0.4m and 4-8m) using Niskin bottles
- 14:30 UTC: Laboratory analysis

Friday, May 9th

- 07:20 UTC: The water column profile was measured in four stations (LB2-LB3-LB5-LB7) along the LB transect by means of a CTD (Seabird 19 Plus) and the sampling of water was performed at 2 (between 0.4m and 3-5-6.5m) or 3 (LB7, 0.4m, 7m and 11m) discrete depths using Niskin bottles
- 11:00 UTC: Laboratory analysis

Saturday, May 10th

- 06:00 UTC: Arrival on Panarea Island of UniRoma1 researcher
- 06:30 UTC: Laboratory analysis

- 07:00 UTC: Briefing with the diving- and boat- support staff from 'Amphibia' diving center, Panarea
- 08:00 UTC: Laboratory analysis
- 11.40 UTC: Block deployment of GasPro-pCO_2 sensors within the "crater" south of Bottaro Island
- Sediment sampling off Panarea Island (the "Corpi Morti" or Hot-Cold station, HC)

Sunday, May 11th
- 08:00 UTC: Sediment sampling off Panarea Island (the "Corpi Morti" or Hot-Cold station, HC)
- 09:50 UTC: Primary and secondary benthic productions experiments off Panarea Island (the Hot-Cold station, HC)
- 10:05 UTC: Photosynthetically Available Radiation profile by means of a PAR device (Biospherical PNF 300) during the incubation of Primary and Secondary Productions
- 11:45 UTC: Water column profile by means of a CTD (Seabird 19 Plus)
- 15:40 UTC: Recovery of block deployed GasPro-pCO_2 sensors

Monday, May 12th
- 7:00 UTC: Laboratory analysis
- 12:40 UTC: Deployment of ADCP and GasPro-pCO_2 sensors along water column transect near the "crater" site

Tuesday, May 13th
- 12:15 UTC: Bubble rise structure deployment at the "Crater" station and testing

Wednesday, May 14th
- Rough seas
- New YSI probe calibration and testing

Thursday, May 15th
- 08:40 UTC: Sediment sampling at Basiluzzo Island (B1)
- 09:40 UTC: Primary and secondary benthic productions experiments at Basiluzzo Island (B1)
- 12:40 UTC: Water column profile by means of a CTD (Seabird 19 Plus)
- 12:50 UTC: Photosynthetically Available Radiation profile by means of a PAR device (Biospherical PNF 300) during the incubation of primary and secondary productions
- 11:05 UTC: Primary and secondary benthic productions experiments at Basiluzzo Island (B2)
- 13:05 UTC: Photosynthetically Available Radiation profile by means of a PAR device (Biospherical PNF 300) during the incubation of primary and secondary productions
- 13:13 UTC: Water column profile by means of a CTD (Seabird 19 Plus)

Friday, May 16th
- Rough seas

Saturday, May 17th

- 07:25 UTC: Sediment sampling at Basiluzzo Island (B3)
- 08:55 UTC: Primary and secondary benthic productions experiments at Basiluzzo Island (B3)
- 09:48 UTC: Water column profile by means of a CTD (Seabird 19 Plus)
- 10:36 UTC: Photosynthetically Available Radiation profile by means of a PAR device (Biospherical PNF 300) during the incubation of primary and secondary productions
- 14:22 UTC: Recovery of ADCP and the GasPro-pCO_2 sensor transect deployed near the "crater" site

Sunday, May 18th

- 7:00 UTC: Briefing with the diving- and boat- support staff from 'Amphibia' diving center, Panarea
- 10:30 UTC: Bubble rise experiment at the "Crater" station (Bottaro Island west)
- 17:00 UTC: Bubble rise experiment at the "Crater" station (Bottaro Island west)

Monday, May 19th

- 09:00 UTC: new site inspection for GasPro-pCO_2 sensors transect
- 14:20 UTC: Diver mapping at Point 21
- New YSI probe calibration and testing

Tuesday, May 20th

- 10:42 UTC: Deployment of ADCP and GasPro-pCO_2 sensors along water column transect at the "Point 21" site

Wednesday, May 21st

- 09:28 UTC: Benthic chamber experiments off Panarea Island (the "Corpi Morti" or Hot-Cold station, HC)
- 13:48 UTC: Water column profile by means of a CTD (Seabird 19 Plus) off Panarea Island (the "Corpi Morti" or Hot-Cold station, HC)
- 15:20 UTC: Water column profile by means of a CTD (Seabird 19 Plus) at the "Crater" station (Bottaro Island west)
- 15:30 UTC: Water sampling at discrete depths (10.7 m, 10.2 m, 9.7 m, 9.2 m and 8.7 m) using Niskin bottles at the "Crater" station (Bottaro Island west)

Thursday, May 22nd

- 09:30 UTC: Laboratory analyses, cleaning and packing of equipment for OGS researchers
- 09:39 UTC: ADCP deployment adjustment. Accumulation chamber experiment for gas bubble collection and estimation of gas bubble fluxes at point 21
- 18:00 UTC: Embark on ferry to Naples for OGS researchers

Friday, May 23rd

- 06:00 UTC: Arrival at the Port of Naples for OGS researchers

- 09:45 UTC: Bubble rise experiment at the "Crater" station (Bottaro Island west)
- 13:20 UTC: Bubble rise experiment at the "Crater" station (Bottaro Island west)

Saturday, May 24th
- 12:15 UTC: Recovery of ADCP and GasPro-pCO_2 sensors from the water column transect at the "Point 21" site
- 12:30 UTC: Accumulation chamber experiment for gas bubble collection and estimation of gas bubble fluxes at point 21

Sunday May 25th
- 09:25 UTC: Bubble rise experiment at the "Crater" station (Bottaro Island west)
- 12:40 UTC: Bubble rise experiment at the "Crater" station (Bottaro Island west)

Monday May 26th
- 12:00 UTC: Recovery of bubble rise experiment structure
- 18:00 UTC: Embark on ferry to Naples for UniRoma1 researcher

Tuesday May 27th
- 06:00 UTC: Arrival at the Port of Naples for UniRoma1 researcher

4 DESCRIPTION OF WORK

Note that all work was conducted from a 8.5 m long inflatable Zodiac boat.

4.1 Water column sampling

Water was sampled at two stations, located just off the eastern tip of Basiluzzo Island and defined during the ECO_2-4, ECO_2-6 and ECO_2-7 cruises (June 2012, October 2012 and May 2013, respectively):

- station B1 (38°39.749' N, 15°07.132' E), characterized by gas emission
- station B2 (38°39.827' N, 15°07.118' E) without gas emission, referred to as the control site

Water was sampled at 0.2 m, 7 m and 13 m (B1) and at 0.2 m, 7 m and 11 m (B2).

In addition, water was sampled at seven stations located along a transect (LB transect) that follows the main current direction and that has been defined during the ECO_2-4 campaign (June 2012):

- station LB1 (38°38.333' N, 15° 06.608' E), at 0.4 m and 6 m.
- station LB2 (38°38.322' N, 15° 06.616' E), at 0.4 m and 6.5 m.
- station LB3 (38°38.321' N, 15° 06.626' E), at 0.4 m and at 5 m.
- station LB4 (38°38.321' N, 15° 06.643' E), at 0.2 m and 3.5 m.
- station LB5 (38°38.315' N, 15° 06.666' E), at 0.4 m and 3 m.
- station LB6 (38°38.267' N, 15° 06.745' E), at 0.4 m and 8 m.
- station LB7 (38°38.246' N, 15° 06.786' E), at 0.4 m, 7 m and 11 m.

The physical characterization of the water column was performed using a CTD (SeaBird 19 plus) equipped with the sensors described in Table 1. These sensors are calibrated on a regular basis in the OGS calibration laboratory.

Table 1. Technical characteristics of the sensors mounted on the CTD probe.

PARAMETER	RANGE	ACCURACY	RESOLUTION
Temperature (°C)	-5 to 35	0.005	0.0001
Conductivity (S/m)	0 to 9	0.0005	0.00007 S/m (resolves 0.4 ppm in salinity)
Pressure (strain gauge)	0 to 100	0.1% of full scale range	0.002% of full scale range
Fluorescence (Scufa submersible fluorimeter)	4 orders of magnitude		12 bit
pH (SBE18)	0-14 pH	0.1 pH	
Dissolved Oxygen (SBE43)	120% of surface saturation	2% of saturation	

The resultant CTD data, which defines water column stratification and pH distribution, were used to choose the depth of discrete water samples (at two or three levels) for various chemical and biological analyses. The following parameters were analysed: dissolved oxygen, pH, alkalinity, dissolved inorganic nutrients, dissolved organic phosphorous and nitrogen, dissolved inorganic and organic carbon, particulate total carbon, particulate organic carbon, dissolved gasses and H_2S concentration, phytoplankton abundance and diversity, microzooplankton abundance and diversity and prokaryotes abundance. The rates of prokaryotic carbon production and of the main exoenzymatic activities have also been estimated.

Furthermore, along the LB transect, water samples were collected at stations LB1, LB2 and LB7 at surface and bottom, LB4 at surface and LB3 at bottom to investigate the coccolithophore assemblages. This research follows results obtained in the framework of the OGS Italian project CO_2Monitor (http://co2monitor.inogs.it/). In the task 4.1 - *Study of fatigue effects induced on micro-organisms by pH variations due to CO_2 emissions* - two culture experiments (with two different CO_2 concentrations, 1 and 2%) were carried out in vertical closed photobioreactors with *Pleurochrysis* cf. *pseudoroscoffensis*, a coccolithophore isolated from the Gulf of Trieste (North Adriatic Sea). The aim of this study was to investigate the effects induced by pH variations due to CO_2 emissions on growth and morphology of the microalga. Slight changes in morphology of coccoliths resulted from analysis of scanning electron micrographs. Coccoliths particularly showed thinner inner tubes and a lower number of nodes compared to the control in the experiment with 1% CO_2. These results prompted us to

investigate the coccolithophore assemblages at Panarea site. Samples collected along the LB transect will be analyzed at scanning electron microscope to asses possible coccolith morphological alterations induced by the natural CO_2 gas seeps.

All samples were placed in coolers with ice packs on the boat until transfer to the land laboratory on Panarea Island. Samples for oxygen and pH were immediately analysed, while those for particulate organic and inorganic matter were filtered and filters were frozen until return to the laboratories at OGS. Samples for prokaryotic abundance were fixed with formalin (4% final concentration) and stored at 4°C until the return at OGS laboratories. For prokaryotic carbon production and exoenzymatic activities samples were immediately processed.

4.2 Sediment sampling (Basiluzzo and Panarea Islands)

Sediment samples were collected for the analyses of both physico-chemical (sediment grain-size, Total Organic Carbon, Biopolymeric Carbon, pigments) and biological parameters (Primary Production, Prokaryotic C Production and microphytobenthos). A total of five stations were sampled: three near Basiluzzo Island previously identified with our ECO_2 colleagues MPI/Hydra (station B1, "Red with Gas" - 38°39.749'N, 15°07.132'E; station B2, "Grey no Gas" - 38°39.827'N, 15°07.118'E; and station B3, "Grey with Gas" - 38°39.820'N, 15°07.137'E), and two just NE of Panarea Island (38°38.536'N, 15°04.714'E) where the sediments are characterized by very different temperatures at a distance of approximately 1 m one from another. This last site is referred here as "Hot-Cold" (HC) and by partners MPI-Hydra as "Corpi Morti" site.


a)

b)

Figure 2. Sampling of sediment by scuba diver (a); extrusion of sediment cores and surface layer subsampling (b).

Virtually undisturbed sediment cores were collected by scuba divers using cut-off plastic syringes (2.7 cm i.d., length 11.4 cm) and then the lowermost side was closed with a plastic cap (Figure 2a). For chemical analyses, sediment cores were partially extruded and only the surface layer (1 cm thick) was collected (Figure 2b). Subsamples were placed in coolers with ice packs on the boat until transfer to the land laboratory on Panarea Island where they were immediately stored at –20°C until their subsequent processing at OGS laboratories. For microphytobenthos the surface sediment layer was collected in triplicates, fixed with 4% formaldehyde/filtered sea water and stored at 4 °C.

4.3 Benthic primary and secondary productions

During this campaign, functional parameters, i.e. benthic primary and secondary productions, were estimated at the three sites near Basiluzzo Island (Sts B1, B2 and B3) and at both counterparts of the Hot-Cold station.

Primary Production (PP) was estimated using the ^{14}C incubation method (Cibic et al., 2008, modified for coarse sediments). Two sediment cores were collected at each site by scuba divers using cut-off plastic syringes (2.7 cm i.d., length 11.4 cm). The surface layer (0.5 cm thick) was extruded and re-suspended in 100 mL of previously filtered (0.2 µm) *in situ* sea water. After inoculation of 500 µL of $NaH^{14}CO_3$ (10 µCi), 9 mL of the slurry was transferred into 9 glass vials divided as follows: 3 replicates to assess

the sediment matrix effect, 2 dark replicates and 4 light replicates. Carbon incorporation was immediately stopped in the first 3 vials adding 100 µL of HCl (5N). The other vials were incubated *in situ* for 1 hour. At the end of the incubation period, carbon incorporation was stopped in all vials.

Secondary benthic production (PCP, Prokaryotic C Production) was measured using the ^{3}H-Leucine (Leu) incorporation method (van Duyl and Kop, 1994 as detailed by Manini et al., 2004). As for PP, two sediment cores were collected at each site by scuba divers using cut-off plastic syringes. The surface layer (0.5 cm thick) was extruded and homogenized. Aliquots of 200 µL were subsampled in 5 plastic vials (2 controls and 3 replicates). After the addition of ^{3}H-Leu (6 µCi) to all the subsamples, the radiotracer incorporation in the controls was stopped by adding 80% ethanol (1.7 mL) while the other vials were incubated in the dark and *in situ* for 1 h together with samples of PP. After incubation, 1.7 mL of 80% ethanol was added to the incubated vials.

The samples of PP and PCP were stored at 4°C until the subsequent processing at the OGS laboratories.

4.4 Dissolved constituents flux (Panarea Island)

Three benthic chamber experiments were conducted at the hot counterpart of the Hot-Cold station (38°38.536'N, 15°04.714'E), where small areas (c. 1-2m in diameter) of hot sand are surrounded by normal temperature sediments. The benthic chamber was used to measure the flux of dissolved CO_2, heat, various carbonate system parameters, and major elements from the sediments to the overlying seawater. Measurements were made on the assumption that the hot sediments are an indication of deep, hydrothermal waters that are migrating to the surface via preferential pathways.

The experiment was conducted as follows. First a GasPro-pCO_2 probe was placed on the hot measurement point and left for 10 minutes to equilibrate with the surrounding conditions. After this period, water samples were collected from right beside the probe, just above the sediments, and then the benthic chamber was placed over probe (Figure

3). Different from previous work, a new multiparametric probe (YSI professional plus), that measures pH, Eh, conductivity, temperature and Dissolved Oxygen, was also mounted inside the chamber near the gas permeable membrane of the GasPro probe (see vertical black cylinder with cable located in the left corner of the chamber in Figure 3). Samples were then collected from the chamber 3 times (once every 10 minutes) from a tube positioned near the two probes. Water samples will be analysed for dissolved inorganic carbon (DIC), dissolved oxygen, hydrosulfide, pH, inorganic nutrients, dissolves gasses, anions and cations.

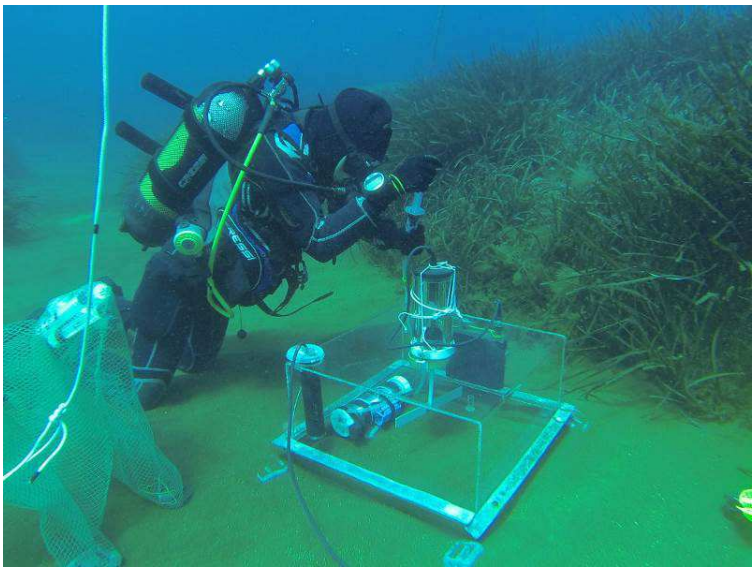


Figure 3. Benthic chamber being sampled by the diver at the hot sand site at the Corpi Morti, with the pCO_2 and multiparametric sensors deployed within the chamber.

4.5 GasPro-pCO_2 probe transects (Bottaro Island, Point 21)

A total of 20 pCO_2 probes, developed by the University of Rome La Sapienza, were built, tested, and calibrated in the laboratory prior to the present cruise, with the goal of deploying all units along 2D transects in the water column to study temporal and spatial variations of dissolved CO_2. In addition an ADCP was deployed during this work to monitor marine currents, however unfortunately this instrument did not collect useable data.

Initial work involved deployment of all units together as a single block within the studied leakage area (i.e. the "crater") for a single day to test the individual units (e.g. water tightness) and to compare measured concentrations in the study environment to ensure an accurate inter-calibration of the probes. This phase was crucial to allow for small corrections in measured values during the experiment, especially at the low concentration range, to ensure an accurate representation of the system. The block of probes was deployed for a period of about 28 hours, with a measurement frequency of once every 10 minutes.

After completion of the block deployment the probes were mounted on two different water column transects, one near the pockmark ("crater") beside Bottaro Island and one in deeper water at the so called "point 21". All probes logged pCO_2 and water temperature data, while one unit was also equipped with a pressure sensor to monitor tidal fluctuations. Measurement frequency was set at once every 10 minutes. Note that one probe (no. 4) malfunctioned and had to be substituted.

The transect near Bottaro was a duplicate of that conducted in May 2013, with the goal being to compare the temporal evolution of pCO_2 data with that of the ADCP current meter to better understand the origin of the previously observed anomalies. As mentioned the ADCP did not function properly and thus a major goal of this work cannot be attained. Regardless, this duplicate will allow us to determine the reproducibility of the previous results, collected during the same season but one year earlier. This deployment took place from May 12 to 17 over a 5 day period.

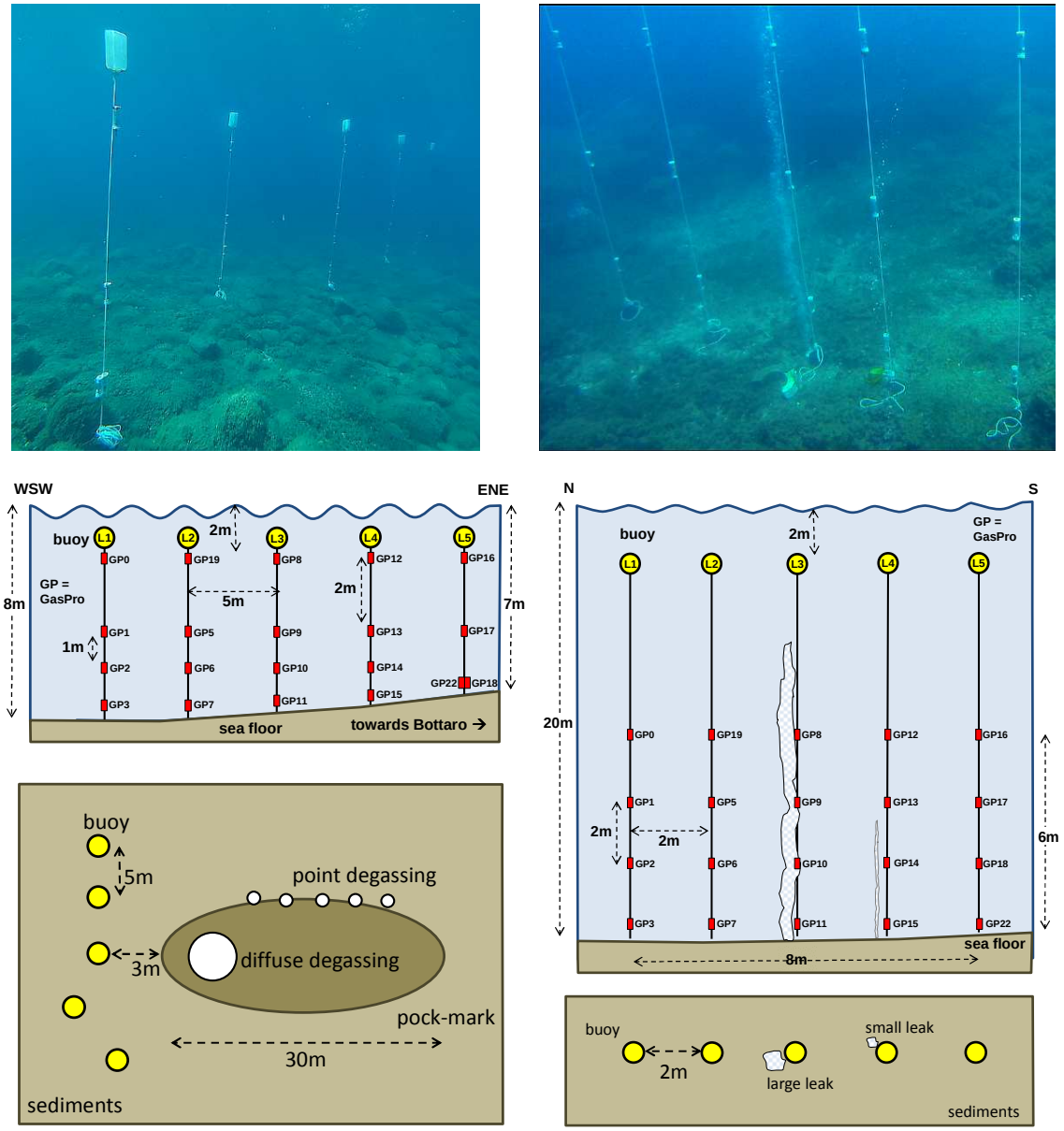


Figure 5. Left column: photograph and schematic drawings of the GasPro sensor transect near Bottaro island. Right column: photograph and schematic drawings of the GasPro sensor transect at "point 21" that straddles a bubble flare.

The spatial distribution of the probes are shown in the photo and schematic drawings in the left column of Figure 5. The probes were mounted on 5 cords held vertically using c. 20L buoys and held in place using 20 kg of ballast each. The points of ballast deployment were located about 5 m from each other and about 3 m from the edge of the crater, along a line perpendicular to the main current direction and to the long axis of the crater itself. Note that the last two ropes are not perfectly in line with the

others due to slight adjustments needed to obtained the required water depth; these data will be projected on a central line to obtain the 2D transect. Note also that the bottom three probes on each line were deployed about 1 m apart to give more resolution in deeper waters where the strongest anomalies were observed, as opposed to the previous deployment at this site where all probes were evenly spaced at 2 m apart.

During this deployment a new GasPro prototype was also tested beside a standard unit (Figure 6). This new unit integrates a pH sensor immediately beside the gas permeable membrane, and will be used to assess the response time of the pCO_2 sensor and the combined pCO_2 and pH data will be used to make an estimate of total DIC at that point in the water column.

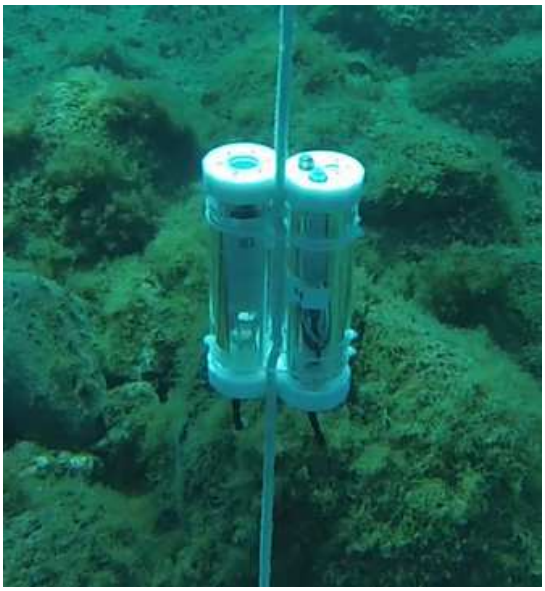


Figure 6. Photograph of the side-by-side deployment of two GasPro sensors, one standard unit for pCO_2 analysis only (left) and a new prototype with a small membrane, a temperature sensor, and a pH sensor mounted together on the front face (right).

The second GasPro transect at "point 21" (38° 38.302' N; 15° 06.407' E) was a completely new experiment, conducted to look at the movement of dissolved CO_2 around a single, moderately strong gas leakage point. The transect was laid-out with the central rope (line 3) just beside the leak, with the four probes of this line often occurring directly within the bubble flare (right column in Figure 5). The probes were

placed on a regular grid, with 2 m spacing both vertically along the ropes and horizontally between the ropes. Note that a second leak was located just beside line 4, however as its flux rate was much smaller than the one at line 3 it is assumed that it will have little impact on the results. The fact that this site occurs in deeper waters (c. 20 m) made the work of the divers more difficult, as the time of each dive had to be limited for safety considerations. This deployment took place from May 20 to 24 over a 4 day period, and once again the ADCP did not function properly.

4.6 Gas bubble flux measurements (Point 21)

Considering the good results obtained at the "crater" site near Bottaro Island during the previous campaign, bubble flux measurements were not repeated at this location. Instead a limited number of flux measurements were conducted at the new site of "point 21" (38° 38.302' N; 15° 06.407' E). After a general mapping of the area to define the distribution of the major leakage points, measurements were made of the main leak occurring at line 3 of the GasPro transect described above (Figure 7a), at the small leakage point at line 4 of the same transect, and at a very high flux point located about 30 m away from the transect (Figure 7b).

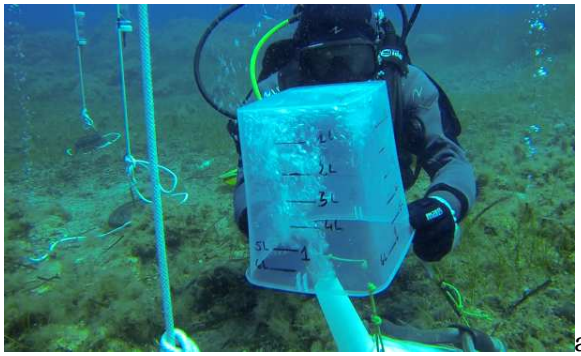
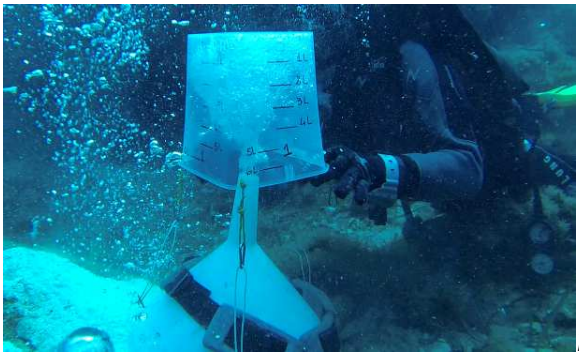

a)

b)

Figure 7. Gas bubble flux measurements at two locations at the site "point 21", including the leakage point at line 3 on the GasPro transect (a) and a very high flux point nearby (b).

4.7 Gas bubble video experiments (Bottaro Island)

An important goal within the ECO_2 project is to better understand the fate of CO_2 in the water column after it has migrated out of the sediments. As a CO_2 bubble rises it will exchange gases such that CO_2 dissolves into the water and N2 and O2 are stripped out of the water into the bubble. These processes, combined with such factors as depth (i.e. confining pressure), temperature, and salinity, will control the life of the bubble and how it evolves in size and composition during its ascent. Once dissolved in the water, the CO_2 can then be transported via currents, react chemically or biologically, or can eventually be released to the atmosphere.

Experiments were conducted during the present cruise to address such issues, building on the experience gained during a previous campaign (ECO_2-6). As the methods used are detailed in the ECO_2-6 cruise report (Beaubien, De Vittor, and Franzo, 2012), only a brief summary will be given here.

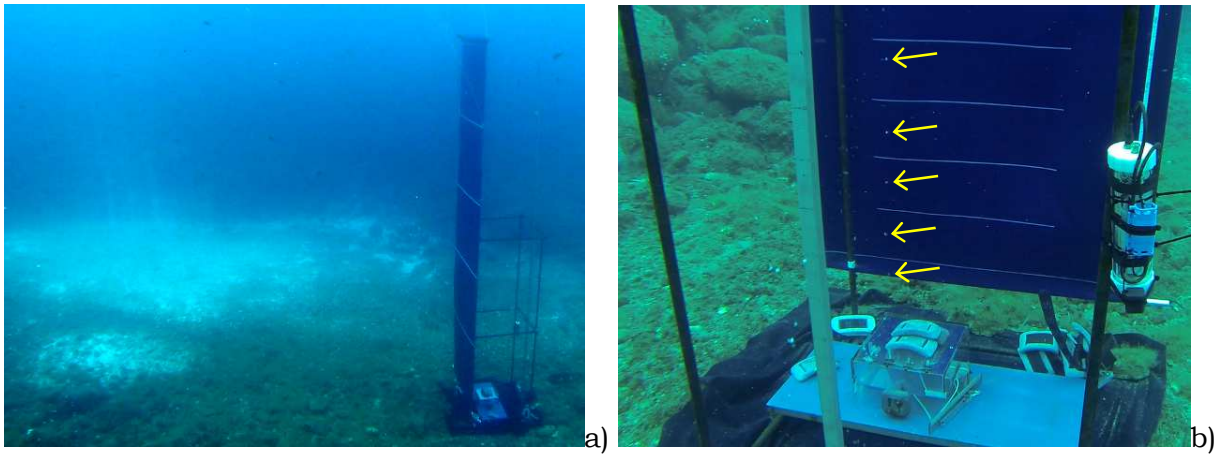


Figure 8. (a) Experimental frame deployed on the floor of the pockmark "crater", close to the area of diffuse degassing. In the photo the backdrop cloth and guide are deployed to a height of 5 m. (b) detail of the base of the experimental frame, showing the aluminum guide at the front, the dark blue backdrop with 20 cm gradations, the GasPro sensor on the right of the frame, and the Plexiglas box at the base from which are being released a stream of bubbles (marked by the yellow arrows.

The 3x1x1 m, hollow-tube frame used for the experiments was mounted on the floor of the pockmark "crater" (Figure 8a), which is located just to the south of Bottaro Island. On the back of the structure a dark cloth was mounted to provide contrast for the filmed bubbles, while an aluminum track was mounted on the front along which the

video camera and other equipment can slide or be fixed. A Plexiglas box holding gas from one of the near-by strong leakage points was positioned at the base of the structure, with different sized tubes on its upper surface being used to make bubbles of various diameters. A floating barrier was placed in the box to minimize exchange between the gas and water, to maintain a constant gas composition for the duration of the experiment. Measurements and sampling performed during the various experiments included:

- Bubble rise velocity measurements, performed by following individual bubbles during their vertical ascent and then using the graduated backdrop to calculate the velocity over each 20 cm interval.
- Bubble size at different heights, performed by filming bubbles as they strike a Plexiglas sheet suspended above the bubble release point. Diameter is calculated by comparing the bubble size just before impact to graduated 1 cm marks on the Plexiglas.
- Bubble composition at different heights, performed by collecting bubbles in VOA glass vials and transferring them on board to pre-evacuated stainless steel canisters for subsequent laboratory gas chromatograph analysis.
- Water column chemistry at different heights, performed by collecting water samples by divers using hand-held Niskin bottles and analyzing them for the complete carbonate system parameters and for dissolved gases. In addition a CTD cast was made near the structure to obtain salinity, temperature, and DO profiles. A GasPro-pCO_2 sensor was also mounted on the frame to monitor pCO_2 levels during the various experiments.

One experiment was conducted using air from the diver's tank, while three experiments were performed using the gas (mainly CO_2) leaking from the sea floor. Three different tubes (i.e., three different bubble sizes) were used for the three CO_2 experiments, while the air experiment was performed with one of these tubes.

Results from these experiments will be modelled to test the predictive capabilities of the model and to test the quality of the experimental data.

5 SUMMARY

Work was performed at the Panarea natural laboratory by personnel from the Università di Roma La Sapienza and OGS during the period May 6 to 22, 2014 within the framework of Work Packages 2, 3, and 4 for the EC-funded research project ECO_2. As for the previous field campaigns, research was divided into three main themes focussing on: i) chemical and biological processes in the sediments and along the water column; ii) the flux of gas bubbles and deep-origin brines from the sediments to the water column; and iii) the fate of gas bubbles within the water column.

Water sampling was conducted successfully at the two stations close to Basiluzzo Island (B1 and B2) and along the transect, continuing the previous work done during the field campaigns of 2012 and 2013.

Sediment-focused research was concentrated on two areas, one off the east coast of Basiluzzo Island and another just to the NE of Panarea Island itself (Corpi Morti). This work was conducted at the same sites as the previous campaign in October 2012 and in May 2013. Primary and secondary production experiments have been performed both near Basiluzzo Island and at the station Corpi Morti. All planned measurements were successfully performed for this task.

The measurement of dissolved constituent flux rates was again successfully repeated, with benthic chamber deployments near Panarea Island at a site where CO_2-rich, warm water is being discharged from the sediments into the overlying water column. Samples were collected at 10 minute intervals for the analysis of a full suite of chemical parameters, including all carbonate system variables, nutrients, and major ions. In addition, a GasPro-pCO_2 sensor and a multi-parameter probe (with sensors for temperature, pH, salinity, and DO) were deployed in the chamber for continuous monitoring during the experiment. The data will be used to calculate the flux rates of the various parameters, and the discrete and continuous data will be compared in an effort to develop new, automated benthic chamber systems.

Experiments were conducted with the deployment of 20 GasPro-pCO_2 sensors along two different water column transects, the first near Bottaro Island to verify results collected the previous year and the second around a single bubble flare in deeper

water at the new site “point 21”. The probes were programmed to measure dissolved CO_2 and temperature (as well as pressure in one probes) once every 10 minutes for the entire deployment time of about 5 days at the first site and 3 days at the second. These deployments will be used to better understand the temporal-spatial behaviour of dissolved CO_2 in the water column, information that will aid in better understanding (and modelling) fate and transport mechanisms.

Due to extensive work in previous campaigns, only limited bubble flux measurements were conducted at the new site of “point 21”, primarily as support for interpreting the results of the GasPro-pCO_2 water column transect at that location.

Building on the Panarea campaign of October 2012, more experiments were conducted into bubble behaviour and migration. Multiple experiments were performed, including three different bubble sizes using the CO_2 gas leaking from the sea floor and one bubble size using compressed air from the diver’s canister. Samples were collected for the chemical analyses of the gas bubbles and surrounding water, while video measurements were made of bubble rise velocity and bubble diameter; this work was performed to characterize the system and the produced data will be modelled.

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7 REFERENCES

Beaubien S.E., De Vittor C., and Franzo A. (2012) Study of CO_2 flux, bubble behaviour and planktonic and benthic communities off Panarea Island (Italy): cruise report ECO_2-6. Università di Roma La Sapienza, Roma, Italy / Istituto Nazionale di Oceanografia e Geofisica Sperimentale, Trieste, Italy 23 pp.

Caliro S., Caracausi A., Chiodini G., Ditta M., Italiano F., Longo M., Minopoli C., Nuccio P.M., Paonita A. and Rizzo A. (2004) Evidence of a recent input of magmatic gases into the quiescent volcanic edifice of Panarea, Aeolian Islands, Italy. Geophys. Res. Lett., 31(7): L07619.

Cibic T., Blasutto O., Burba N., Fonda Umani S. (2008) Microphytobenthic primari production as ^{14}C uptake in sublittoral sediments of the Gulf of Trieste (northren Adriatic Sea): methodological aspects and data analyses. Estuar. Coast. Shelf Sci. 77: 113-122.

Esposito A., Giordano G., Anzidei M. (2006) The 2002-2003 submarine gas eruption at Panarea volcano (Aeolian Islands, Italy): Volcanology of the seafloor and implications for the hazard scenario. Mar. Geol., 227(1-2): 119-134.

Manini E., Luna G.M., Danovaro R. (2004) Benthic bacterial response to variable estuarine water inputs. FEMS Microbiol. Ecol., 50: 185-194.

Tassi F., Capaccioni B., Caramanna G., Cinti D., Montegrossi G., Pizzino L., Quattrocchi F., Vaselli O. (2009). Low-pH waters discharging from submarine vents at Panarea Island (Aeolian Islands, southern Italy) after the 2002 gas blast: Origin of hydrothermal fluids and implications for volcanic surveillance. Appl. Geochem., 24(2): 246-254.

Van Duyl F.C., Kop A.J. (1994) Bacterial production in North Sea sediments: clues to seasonal and spatial variations. Mar. Biol., 120: 323-337.