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ScienceDirect

Energy Procedia 4 (2011) 3262–3268

Energy Procedia

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GHGT-10

Monitoring techniques of a natural analogue for sub-seabed CO_2 leakages

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Abstract

Carbon dioxide sequestration in sub-seafloor aims to store CO_2 inside geological trapping structures below the seafloor. However there are concerns related to the possibility of leakage from the storage sites and potential consequences on the marine environment.

In order to develop safe and reliable methods for CO_2 monitoring, field studies were conducted in a natural analogue – an area where there is a natural release of CO_2 from the seafloor.

Due to the very high volume of gas emitted, this natural analogue could be considered as the worst-case scenario for a possible leakage from a sub-seabed storage site.

Sampling procedures for free and dissolved gas and measuring techniques of the main physical and chemical parameters were developed for use both from the surface and directly underwater by scientific scuba divers.

The first results of the research indicate that high levels of CO_2 released in the marine realm strongly affect the local environmental conditions with a generalized acidification of the seawater.

The experience gained in this study allows further development of a more accurate and suitable monitoring suite that will integrate sensors for measuring pH, dissolved CO_2, and eventually, acoustic systems for the detection, monitoring and quantification of gas bubbles. The monitoring system could be deployed on the seafloor for long-term monitoring or could be carried onboard movable platforms such as ROV's (Remote Operated Vehicles) or AUV's (Autonomous Underwater Vehicles) for systematic surveys of the sub-seabed storage areas.

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Keywords: CO_2 geological storage; Dissolved CO_2 ; Sub-seabed; Natural analogue; Panarea

1. Introduction

Sub-seabed storage allows the storage of large volumes of anthropogenic CO_2 in reservoirs under the seafloor with technologies very similar to the ones used in continental geological storage.

doi:10.1016/j.egypro.2011.02.245

Even if sub-seabed storage methods are considered reliable, the risk of a potential lekage is to be contemplated. In order to develop appropriate detection techniques for any leakage and to monitor the impact of CO_2 on the marine realm it is possible to study areas where, for natural reasons, seepage of CO_2 is present [1].
One of these "natural analogues" is located in the Southern Tyrrhenian Sea and close to the volcanic island of Panarea (Aeolian Islands, Italy). The degassing area lies 2 nautical miles east of the main island and is surrounded by several islets and shoals (Fig. 1). Here CO_2 flows steadily from the seafloor in shallow water (10 to 40 metres deep) originating areas of diffuse seepage plus several spots of higher gas flow with formation of bubbles plumes. The area, even not suitable for any CO_2 storage, can be considered as a field-lab where it is possible to study the effects of high levels of CO_2 on the marine realm and validate measuring, monitoring and verification (MMV) techniques for sub-seabed CO_2 leakages. This is one of the few areas which environmental conditions allow a year-around field-work, a very safe utilization of scientific divers for the research and a simplified logistic with excellent ratio costs/benefits [2-4].

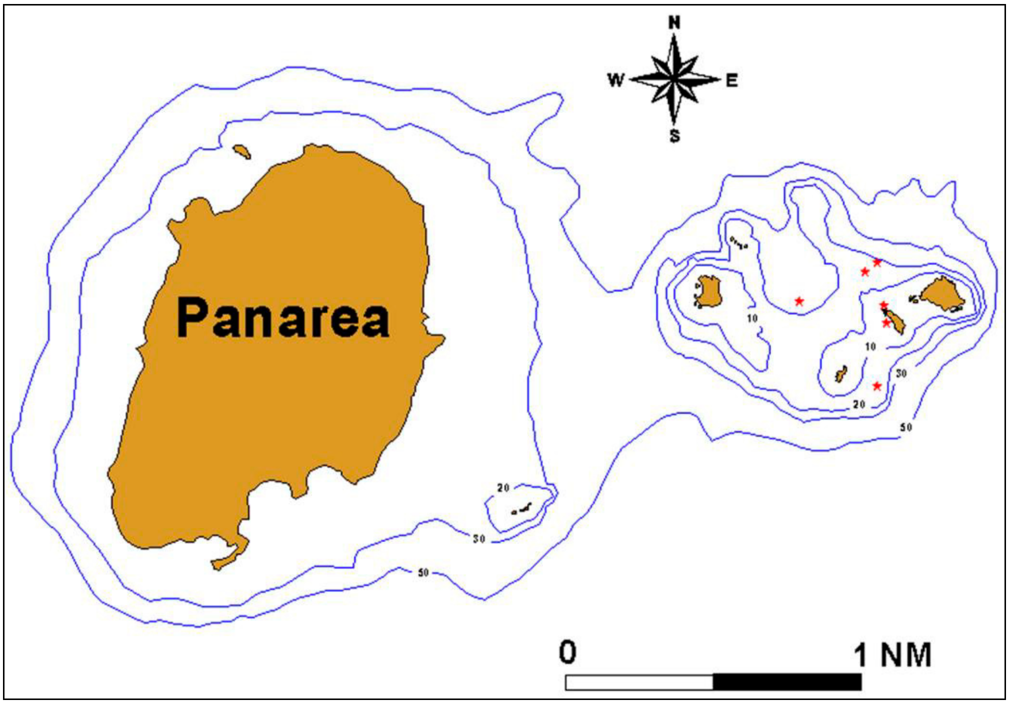


Figure 1 Map of Panarea Island and the surrounding islets with the positions (red stars) of the main gas vents (modified from the official nautical map 249 "Isole di Panarea e Stromboli" 1:30.000 Ufficio Idrografico della Marina - Gennaio 2006).

2. Methodology

For the study of the Panarea natural analogue, some special sampling techniques have been developed in order to operate underwater.
These techniques are mainly sampling methods for free and dissolved gases and the use of a multi-parametric probe to make vertical logs from a boat and also directly underwater by means of scuba divers.

2.1. Free and dissolved gas

To collect free gas samples, a plastic funnel was placed upside-down directly on the gas vent to be sampled. This funnel has ballast on the lower ring to avoid lifting or tilting once it is filled by the gas. The funnel is connected to a Pyrex glass flask with twin valves by a silicon hose. This flask has been previously filled with air at a pressure

above that than the hydrostatic pressure expected at the sampling depth to prevent seawater from entering into the sampler. With this system, it is possible to change the flasks underwater to collect several samples from each vent.
The free gases have been analyzed by two Carlo Erba 8000 Series gas chromatographs (GCs), one equipped with a CarboBlack packed column for the analysis of CH_4 and the second with a packed Moleseive column for N2 and O2 and a PoraPak column for CO_2.
An easy and inexpensive system to measure gas flow is to connect the funnel to a tank of known volume. By counting the filling time, it is possible to know the flow rate (litres per minute) at any given depth. The flow rate of the vent can be determined by reporting this measure to SPT. The funnel used for this work ad a diameter (35 cm) large enough to avoid gas leakage from the rim during the flow measurement procedure. In order to determine a reliable value, several measurements of the same vent were performed and the average value was considered.
Dissolved gas sampling was performed by the use of a vial glass sampler that has a screw cap. The vials are carried capped underwater and are previously filled with deionised water to avoid its implosion. Once the vials are on the sampling point, they are placed upside-down on the funnel discharge hose to be purged and are then refilled with seawater close to the gas vent and capped. The underwater environment prevents any atmospheric air contamination of the samples.
Dissolved gases were measured using a slightly modified version of the head-space technique proposed by [5].

2.2. Vertical logs

In order to collect data on the water chemistry (pH, redox potentials) a multi-parametric probe was used from a small boat and then taken directly underwater by scuba divers. Divers operated the probe underwater with a lifting bag to maintain the instrument in almost neutral buoyancy. The probe used was a “Sea-Bird SBE 19 – Seacat profiler”. It was set as data-logger and being self-powered it was possible to be used by the divers without any link with the surface. During the underwater operations a wireless system was used by the diver team to communicate with the surface crew enhancing the safety of the dives and facilitating the exchange of information.
The divers were able to place the probe on the selected vents with a level of precision that is not possible operating from the surface.

3. Results and discussion

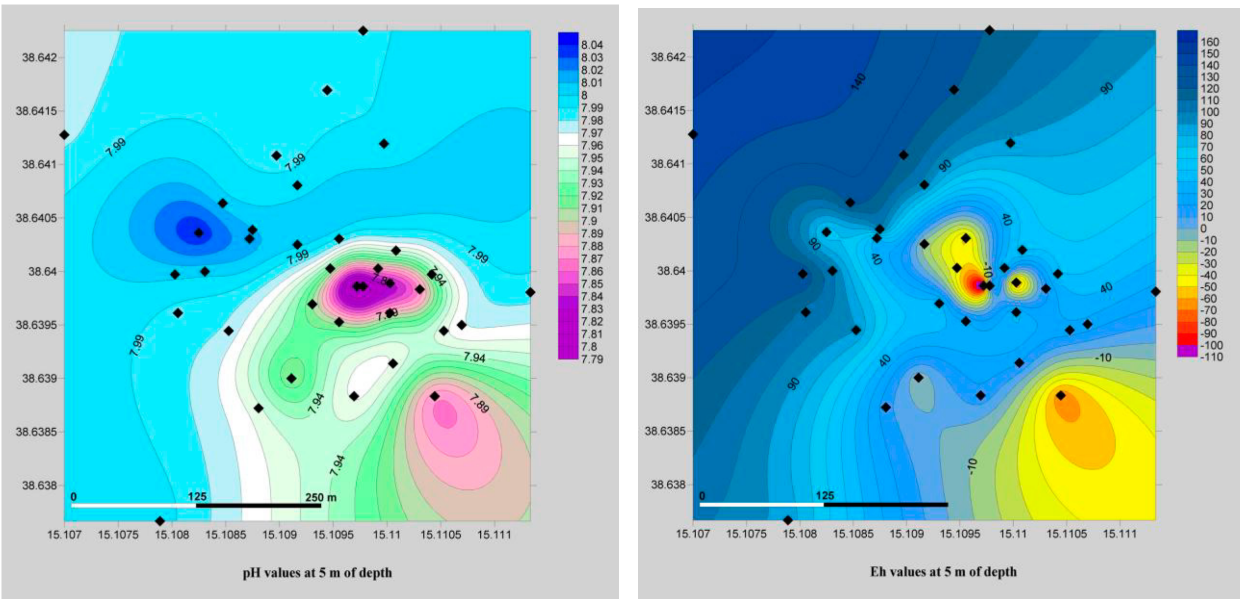
In the Panarea area the vents on the seafloor emit fluids whose origin is linked to the volcanic setting of the island [6-7]. High concentrations of CO_2 were detected as free and dissolved gas, and small amounts of H_2S are also present in the fluids [3]. The presence of these fluids affected the chemistry of the seawater in the whole area modifying some of the main parameters, such as pH and redox, with strong influences on the local environment and the biota [8].
Five different vents were investigated collecting over 100 samples of free and dissolved gas; the values were averaged to obtain a general picture of the fluids composition.
Table 1 shows that the main component of the free gas is CO_2; H_2S is also detected in low concentration. Nitrogen and oxygen are present in small concentrations.
The principal component of the dissolved gas is CO_2 followed by nitrogen and oxygen (Tab. 1). These values strongly differ from the values of the dissolved gases in the seawater that are detected in areas not affected by any anomalous presence of CO_2 [9]. The presence of CO_2 seepage can therefore be identified from anomalous values of dissolved gases even without the presence of bubbles.

Table 1Gas composition averaged on all the sampled vents

Average values	CO_2	H_2S	N_2	O_2
Free gas (%)	93.98	2.20	3.88	0.93
Dissolved gas (cc/l at SPT)	183.55	n.d.	17.64	2.00

The detection and measurement of dissolved gases is a mature but still continuously developing field with commercial instruments available. A comprehensive overview over various optical sensors is given in [10]. The advantages of using sensors over taking only discrete samples are an increased number of data points per time leading to an improved spatial and temporal coverage of the point values of interest. Scientific investigations often

benefit from this enhanced data availability as well as time and hence money is saved during operation. In addition measuring data from a sensor can be made available in real time and by that mission accomplishment can be optimized; places of interest can be easily indentified or installed sensors can provide valuable time series.
Sensors for the measurement of dissolved O_2 are nowadays common small-sized oceanographic instruments being installed on various platforms during diverse missions and sensors for the measurement of dissolved CO_2 are following this direction [11-12]. The measuring principle of the latter is mostly based on partial pressure equilibration of the dissolved gas matrix across a semi-permeable membrane with either a gaseous headspace inside the sensor or with a pH-dye test solution. In the headspace the CO_2 concentration is commonly measured by means of infrared absorption [13] and spectrophotometric measurements are used within sensors employing equilibrated artificial liquids [12].
Sensors for dissolved CO_2 are promising candidates for and key components within different MMV strategies. Their platform and deployment versatility, accuracy and long-term stability make them good tools for emission detection at CCS sites or for strategy developments endeavours as well as scientific investigations at sequestration site natural analogues like the one described in this paper.
An area characterized by diffuse degassing from the seafloor in shallow water (maximum depth 15 m) was chosen to perform a series of 38 vertical logs of pH and redox values. Due to the high values of dissolved CO_2 measured over these vents a general acidification of the water is to be expected.
The logs, arranged in grid centred on the degassing area, show a clear “low-pH signal” in proximity of the gas emissions (Fig. 2a). The minimum value measured was 7.20 highlighting a reduction of about 11% in respect to the 8.07 value of the water column not affected by the gas release.



a **b**

Figure 2 Map of the pH values (a) and Eh values (b) at 0.5 m of depth. The black dots represent the logs position. In the centre of the map there is the main gas emission.

The redox values highlighted reducing conditions in the water column close to the gas emissions (Fig. 2 b) These are caused by the reduction of CO_2 and, mainly, by the reduction of sulphur that is present in the gas seeping from the seafloor.
To verify the real extent of the water volume affected by the presence of the CO_2 leakage, vertical logs were performed by scientific divers at different distances from one selected degassing spot. This is characterized by a steady emission of high concentration of CO_2 as free and dissolved gas. The pH trend shows a direct relation between proximity to the gas emission and increased acidification. An important feature of this trend is a threshold depth of the values that corresponds to the thermocline (Fig. 3).

The diffusion of the water driven by the rising plume and therefore more affected by the presence of the CO_2 is limited by this density border. This behaviour can play an important role in controlling the extent of the area potentially affected by a CO_2 leakage from a sub-seafloor storage site.

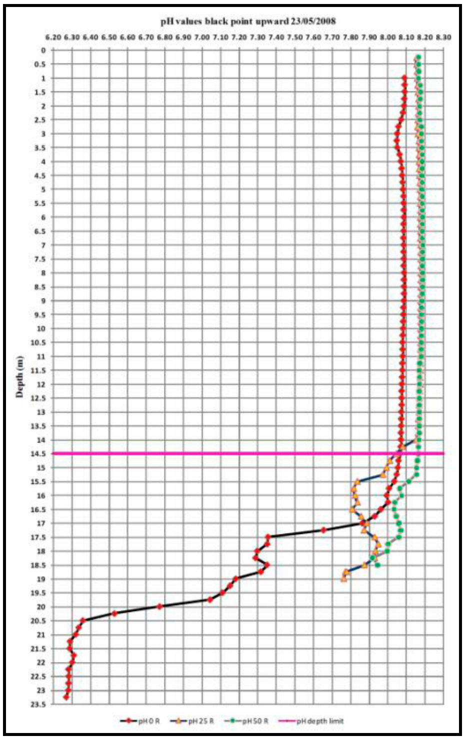


Figure 3 pH measured in the Black Point area. Violet represents the threshold depth of the values.

The measured gas flow ranges from about 7 l/min to about 80 l/min at SPT in the different vents, the higher flows originate plumes of bubbles, the lower just a diffuse bubbling.
The gas plumes, in the shallowest spots, reach the surface where they form blowouts surrounded by pseudo-convective cells (Fig. 4). Similar effects were observed in a bubble plume generated in lab experiment and can strongly influence the mixing between the inner water more affected by the presence of CO_2 and the surrounding one [14].
The impact of the leakages on the marine environments is clearly visible in the area but with very local effects. More investigations are needed to better define these effects caused by acidification.

a b

Figure 4 Gas plume (a) and its surface blowout (b). The flow is around 80 l/min at SPT

4. Conclusions and future developments

The studied site shows excellent characteristics to be used as natural field-lab for the development and testing of monitoring techniques for sub-seabed CO_2 seepage both during short-term as well as long-term deployments. There is a widespread presence of vents that mimic several different scenarios of potential leakages, from small seepage to gas eruption.
These first results can be used as basic input for the development of reliable monitoring systems for CO_2 leakages. These systems should include dissolved gas sensors as well as pH probes and active and passive acoustic instruments for bubbles detection. The gas plumes are in fact very good acoustic reflectors as highlighted during a multi-beam survey of the Panarea area [15-16]. A transfer of the obtained knowledge in these shallow water areas towards other sites still needs to be thoroughly analyzed due to temperature and pressure effects on the CO_2 leakages in the form of gas hydrate formation/decomposition, gas expansion and dissolution into water [17]. Due to the given reasons, especially the high solubility of CO_2, acoustical methods cannot form the only basis of CO_2 emission monitoring tasks in deeper waters. Dissolved gas concentration, pCO_2 and seawater pH modifications are the most reliable indicators for CO_2 leakages when bubbles are not detectable. The high resolution, fast response and accuracy of commercial pCO_2 dissolved gas sensors (~ppm/μatm) allow finding low emission areas of diffuse seepage.
The positioning of dissolved gas sensors around emission plumes should allow an experimental determination of their practical reach for the detection of leakages dependent on local currents and other conditions. By the combination of pCO_2 and pH sensor data the carbonate system can be fully and continuously characterized at the same time.
Zero-Emission power-plant cycles incorporate sequestration and the subsequent storage of CO_2 [18]. Zero net CO_2 emission for the overall process of power-generation can only be achieved through emission free, zero-tolerance CO_2 storage. Hence the instrumentation to be used for monitoring at sequestration sites are required to perform low emission measurements of dissolved CO_2 slightly above background concentrations. Nonetheless partial pressures of up to several bars should be expected in Panarea and elsewhere. This presents new challenges to the application and measuring ranges of the sensors.
It will be possible to use and evaluate mobile platforms, such as ROVs and AUVs to host the new sensor systems. Beside the strategy development the scientific datasets of the Panarea area could be enriched by detailed horizontal and vertical maps and profiles of pCO_2 and pH.

Acknowledgments

The authors acknowledge the Italian National Institute of Volcanology (INGV), the Norwegian Institute of Water research (NIVA) and the National Institute of Oceanography and Experimental Geophysics (OGS) for the scientific support. and the CO_2GeoNet. A very warm acknowledgement for the sea-operation support to the Italian Coast Guard, the Italian Fire Brigade Scuba Team and to the volunteers divers Riccardo Malatesta and Marco Giordani. We would like also to thank the colleagues Dr. Nunzia Voltattorni, Dr. Arild Sundfjord and Dr, Fabio Voltolina for helping in the field-data collection and lab analysis. Last but not least we thank the Aeolian Islands Authorities.

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