Water column monitoring at CO_2 leaking sites near Panarea Island

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Abstract

The fate and transport of geologically produced CO_2 that leaks from the sea floor into the overlying water column has numerous important implications related to large scale carbon cycling and potential impact on marine organisms, and is of interest for the development of improved monitoring techniques and strategies for offshore Carbon Capture and Storage (CCS) sites. The CO_2 leakage areas off the east coast of Panarea Island, Italy provides an excellent environment to study these processes given the wide range of different flux rates in relatively shallow water. The water column at this site was monitored using two completely different but complementary approaches, continuous monitoring along short 2D transects using GasPro pCO_2 sensors and discrete seasonal sampling along a 700 m transect crossing multiple leakage areas. Results are discussed in terms of the movement of CO_2, and associated tracers, in the water column.

Introduction

The release of large volumes of magmatic, mantle and/or thermometamorphic CO_2 from the seafloor into the overlying marine water column is relatively common in volcanic and tectonically active regions world-wide. While direct sampling and analysis of the gas at the release points gives critical information regarding the geological processes in the subsurface, related to genesis and subsequent changes along the flow path, issues related to the fate of the CO_2 once it dissolved and enters the water column is less well studied due to the significant logistical problems associated with monitoring in a harsh and poorly accessible environment.

Instead, the degassing area near Panarea Island, Italy, presents conditions that facilitate this type of study, given that the CO_2 leaks tend to occur in shallow, accessible waters. This area is located 3 km to the east of Panarea on a submerged volcanic platform in 5-30 m deep water. Gas leaks from two main gas-permeable fracture systems (NE-SW and NW-SE) [Esposito et al., 2006], with flux styles and rates ranging from diffuse, gentle bubbling to intense point vents. Most fluid release points are gas only, although some points also release mixed geothermal water / seawater [Tassi et al., 2009]. Aside from occasional gas burst events linked to deep magma activity, the overall flux is relatively stable in both gas chemistry (e.g. 98% CO_2, 1.7% H_2S plus other trace gases) and rates ($7\text{-}9 \times 10^6$ L/d) [Caliro et al., 2004]. In addition to the extensive volcanic, tectonic, and geochemical research conducted at Panarea, this site has also been used as a natural laboratory to understand potential risks and improve safety of offshore Carbon Capture and Storage (CCS) sites. This included work conducted within two projects funded by the European Community, RISCS and ECO_2. In the following we present results from both projects, including small-scale continuous and large-scale discrete monitoring of the water column in gas leakage areas.

Small-Scale Temporal Monitoring

Temporal Monitoring Methods

Small, low-power-consuming, and low-cost pCO_2 gas probes ("GasPro") developed by the authors were used for continuous monitoring of the water column [Graziani et al., 2014]. Each GasPro unit is housed in a 200 mm long, 78 mm diameter Plexiglas cylinder. Measurement is based on equilibration of a small-volume headspace, containing a miniature NDIR detector, with the surrounding water via diffusion through a gas permeable membrane. A second, isolated chamber contains control electronics, memory, and batteries. All probes are equipped with a water temperature sensor, while a pressure sensor was mounted on one probe to monitor tidal fluctuations. All probes were programmed to make measurements every 10 minutes. Two experiments were conducted via the deployment of 20 sensors along cross-sections through the Panarea water column. At the first site the units were placed across a 20 m long and 4 m high, vertical water-column transect in 7 m deep water for 5 days. The transect was perpendicular to the main current and to the long-axis of a near-by CO_2-leaking pockmark. At the second site the same units were deployed for 2.5 days along an 8 m long and 6 m high, vertical water-column transect in 20 m deep water. The transect was positioned parallel to the main current direction with the central vertical line located within a strong single bubble flare.

Temporal Monitoring Results

The first monitoring site was chosen due to its vicinity to a well-known pockmark near Bottaro Island, which at present has constant, diffuse degassing from its base but which was originally formed during a strong blow-out event in 2002. The goal of this deployment was to try to image the movement of the dissolved CO_2 plume associated with this pockmark, which, for spatial reference, is located "behind" the plot shown in Figure 1a.

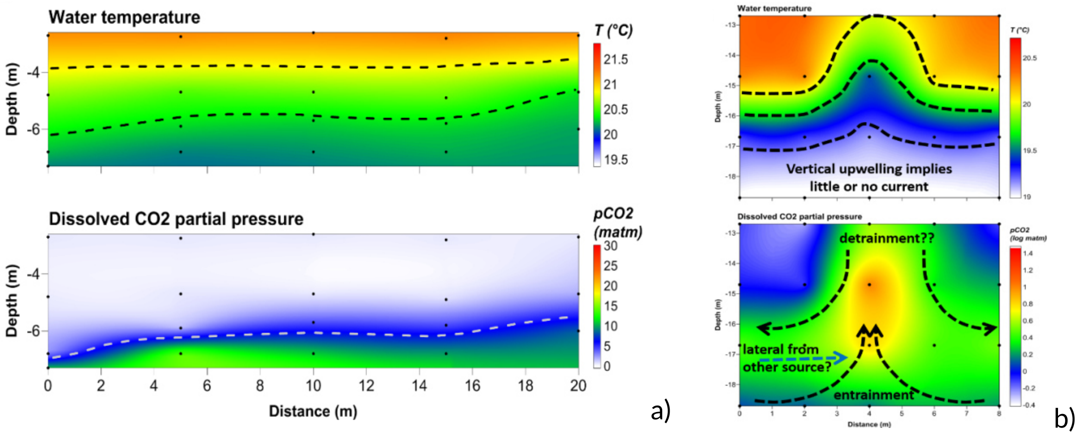

Figure 1 Results from the first (a) and second (b) GasPro grid deployments, with water temperature on the top and CO_2 partial pressure on the bottom. Note the log scale used for the pCO_2 values in (b).

During the observation period there were occasions where a circular or oval anomaly was observed to move into, across, and out of the monitored plane, however the lack of current data makes it difficult to determine the actual origin of these anomalies. Perhaps more interesting, instead, was the strong influence that temperature stratification and storm mixing had on the observed behaviour of dissolved CO_2. The initial period was characterised by calm conditions and strong stratification, with significant basal CO_2 anomalies often entering the plane from the right-hand side (Figure 1a) where waters are deeper. This behaviour implies upwelling of colder, CO_2 charged waters onto the shallower platform, with vertical mixing limited due to the stable stratification. This behaviour changed suddenly when a storm passed through the area, resulting in efficient water column mixing. During this event, and for the 2-day duration of the monitoring period, CO_2 anomalies were smaller in magnitude and moved more irregularly throughout the entire water column, sometimes even arriving from the top and moving downwards.

The second site was focused on a single bubble flare, with the central line and its four GasPro sensors located directly within the rising bubbles themselves. During this deployment, the weather conditions were much calmer and it is assumed that the main currents at this depth (20 m) were relatively gentle and primarily controlled by tidal processes. One of the most common behaviors observed was the occurrence of a relatively discrete vertical oblong halo around the central bubble flare combined with its impact on the horizontal temperature stratification. An example is shown in Figure 1b, where temperature doming in the center of the transect implies entrainment of deeper colder waters into the bubble stream, potentially also transporting basal waters with higher CO_2 concentrations into the flare core. This observation has implications for CO_2 behavior and efforts to model it, as this will impact on gradients and thus dissolution rates. It is also possible that the higher basal values in this figure may be, in part, a function of the process of detrainment of lateral waters from the rising flare, although this would be difficult to demonstrate. In contrast to that seen in this figure in other cases only the central flare is observed, with surrounding waters, and even the lowest point on the central column, having much lower dissolved values than what occur in the body of the flare. This shows how a single flare may be totally isolated or may, instead, interact with other, near-by flares. Other observed behaviors include the clear deflection of the flare to one side or another of the section, as horizontal currents shift the dissolved phase away from the source bubble flare, and the complete disappearance of the flare as currents force the flare completely out of the measurement plane.

Large-Scale Discrete Monitoring

Discrete Monitoring Methods

Sampling from an 8 m long Zodiac boat was performed during four seasonal campaigns along a 700 m long transect (7 points, 3 depths each) which crossed both venting and non-venting areas. Sample point precision was likely on the order of 10-15 m. A SeaBird 19 CTD equipped with sensors for temperature, conductivity, pressure, fluorescence, pH, and dissolved oxygen was lowered by hand at each transect point. A 5L Niskin water sampling bottle was hand-lowered at each point and triggered with a lead messenger. Once on board the Niskin was immediately sub-sampled for various analyses in the following order: dissolved O2, dissolved gases, pH, alkalinity, DIC, DOC, inorganic nutrients, major elements, viral and prokaryotic abundance, and bacterial community structure. All samples were placed in coolers with ice packs on the boat, then transferred to refrigerators or freezers on shore at the end of the day. Analytical procedures are reported elsewhere [Karuza et al. 2012; Ingrosso et al. 2016]. Two Acoustic Doppler Current Profilers (ADCP) were also deployed during the sampling periods.

Discrete Monitoring Results

The repeat measurements performed along the 700 m long transect showed the challenges of working from a small boat. First, sample location uncertainty was high due to limited GPS accuracy and boat movement caused by variable wind and currents. Second, sampling and associated sample preparation is time consuming and affected by meteorological conditions (e.g. rough seas) and daylight hours available. As such, the entire transect was sampled in one day only during one campaign, on two consecutive days during two campaigns and on two days separated by a day of rough weather during one campaign. Sampling on different days was often accompanied by a change in stratification and current conditions, which had a significant impact on the observed results. For this reason the integration of continuous ADCP current monitoring and the transect profiling was critical for a proper interpretation of chemical and biological data.

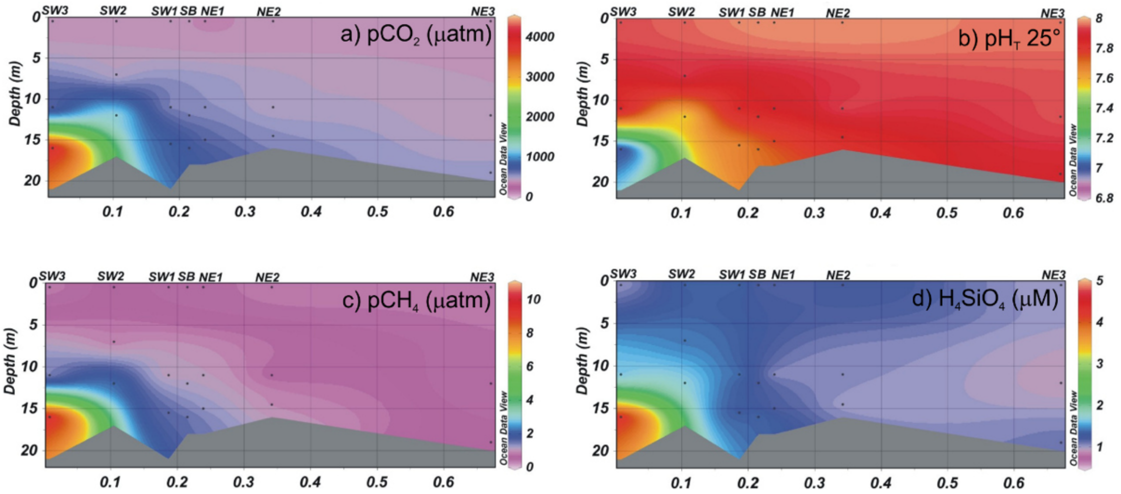

Figure 2 Select chemical data from the March 2012 sampling campaign along the long profile, with different parameters showing similar behaviour. Data plotted using ODV [Schlitzer, 2018].

Of the many results obtained during the transect work, perhaps the most important were related to the limited nature of observed anomalies and impacts despite the large volume of CO_2 being released at the site. The strongest chemical anomalies associated with leakage were observed during the one campaign conducted in a single day when the water column was stable and density stratified, with carbonate parameter anomalies (pCO_2, pH, DIC) located in the deepest part of the transect (Figure 2a, b). This transect also showed the clearest anomalies with associated parameters, such as CH_4 and H_4SiO_4 (Figure 2c, d). These results indicate how other, co-leaking species, if bio-chemically stable, can be used as tracers of the CO_2 leakage and water column migration processes. Whereas other campaigns did show some water column anomalies, these tended to be smaller in magnitude and spatial extent, again demonstrating the effectiveness of current mixing in diluting the leaked CO_2. In general, very little biological impact was observed, even in the well-stratified transect with the most significant anomalies.

Summary and Conclusions

Two different approaches were used to study CO_2 behavior in the Panarea water column. In the first, 20 GasPro pCO_2 sensors were deployed along 2D vertical transects around or near CO_2 leakage sites to monitor small scale, near field dissolved CO_2 behavior and migration. These probes, deployed for a few days each time and programmed to make measurements every 10 minutes, show the effects of temperature stratification, tidal currents, storm mixing, and bubble column entrainment on the behavior, distribution and concentration of dissolved CO_2 in the water column at the small scale over short time periods. In contrast, the second approach involved manual sampling during four seasonal campaigns of a 700 m long transect that crossed multiple leakage areas, together with current monitoring during the sampling periods. A total of three depths at seven points along the transect were sampled for dissolved gases, pH, and nutrients to assess large-scale process and seasonal effects. These results highlight the difficulty of discrete sampling of the water column, considering the dynamic nature of the currents that control CO_2 movement. That said, this work highlighted similar behavior of other parameters associated with the CO_2 leakage, such as silica, pH and CH4, as the spring field campaign provided the most consistent results and strongest anomalies due to gentler currents and strong temperature stratification.

The spatial-temporal monitoring at the Panarea site has highlighted the extreme temporal and spatial variability in pCO_2 values and distributions in the natural environment, an observation that is important for understanding the fate of leaked CO_2, its potential impact on the local ecosystem, and in the design of sampling and monitoring programs.

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