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Preliminary experiments and modelling of the fate of CO_2 bubbles in the water column near Panarea Island (Italy)

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Abstract

Although CO_2 capture and storage in deep, offshore reservoirs is a proven technology, as illustrated by over 15 years of operation of the Sleipner site in the Norwegian North Sea, potential leakage from such sites into the overlying water column remains a concern for some stakeholders. Therefore, we are obliged to carefully assess our ability to predict and monitor the migration, fate, and potential ecosystem impact of any leaked CO_2. The release of bubbles from the sea floor, their upward movement, and their dissolution into the surrounding water controls the initial boundary conditions, and thus an understanding of the behavior of CO_2 bubbles is critical to address such issues related to monitoring and risk assessment. The present study describes results from an in situ experiment conducted in 12 m deep marine water near the extinct volcanic island of Panarea (Italy). Bubbles of a controlled size were created using natural CO_2 released from the sea floor, and their evolution during ascent in the water column was monitored via both video and chemical measurements. The obtained results were modelled and a good fit was obtained, showing the potential of the model as a predictive tool. These preliminary results and an assessment of the difficulties encountered are examined and will be used to improve experimental design for the subsequent phase of this research.

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Keywords: CCS, CO_2, in situ bubble experiment, modelling

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1. Introduction

Carbon capture and storage is expected to provide an important, short-term contribution to mitigate global climate change due to anthropogenic emissions of CO_2 [1]. Offshore reservoirs are particularly favorable [2], however concerns exist regarding the potential for CO_2 leakage into the water column (with possible ecosystem impacts) and the atmosphere. To understand the fate and transport of CO_2 in the water column and to predict the potential impact that it may have on a marine ecosystem, it is critical to understand the initial input function into the system, in other words the transfer of CO_2 from the rising bubbles into the surrounding water [3].

As a CO_2 bubble rises, CO_2 will rapidly dissolve into the surrounding water while at the same time N_2 and O_2 will be stripped out of the water into the bubble. The balance between these two 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 be released to the atmosphere, however it is this transfer from the gaseous to the dissolved phase which will have a major influence on the initial spatial distribution of any leaked CO_2.

Although laboratory experiments can be used to examine transfer rates and bubble behavior, the study of natural systems can provide a more complete and realistic understanding. In particular scale is important, while physical – chemical dynamics related to currents can also move a system away from that predicted based solely on theoretical equilibrium considerations. For this reason the natural CO_2 emission site off the coast of Panarea Island (Italy) was chosen for in situ bubble experiments within the EC-funded ECO_2 project. Bubbles of a known size were generated using gas that is leaking naturally from the sea floor. Gas and water chemistry, as well as bubble parameters, were measured as the bubbles rose through the water column. This paper discusses the results of these field experiments and uses these real-world data as input to test the predictive capabilities of a bubble model.

2. Site description

Panarea is the smallest island within the 200 km long Aeolian Arc, located off the north coast of Sicily. A series of small islets located 3 km to the east of Panarea are situated on a shallow plateau whose water depth ranges from 0 to 30 m. In this area natural, deep-origin CO_2 is leaking from the sea floor into the overlying water column [4]. The composition of the leaking gas is relatively stable, with about 98% CO_2, 1.7% H_2S plus other trace gases [5]. The present study was conducted near the islet of Bottaro, in the bottom of a NW-SE trending, 10 m wide by 30 m long pockmark. Gas leaks from a series of strong individual points along its western border as well as a small area (c. 50 m^2) with more diffuse leakage. The present experiments were conducted about 3 m away from the diffuse leaking area, with gas for producing the bubbles collected from the strongest point leak along the pockmark border.

3. Methods

A series of experiments were conducted using a 1m wide x 1m deep x 3m tall, hollow-tube frame equipped with a vertical guide on the front face and a dark blue, graduated cloth for contrast and depth reference on the back; although the frame itself is 3 m tall, the guide and the cloth can be extended to a height of up to 10 m (Fig. 1a). Experiments involved measuring bubble parameters and the chemistry of the surrounding water column to produce input data for modelling efforts. Although numerous tests were performed, only the results of one experiment are presented here; in this experiment all parameters were measured over a 2.5 hour period and initial bubble diameter was estimated to be about 7 mm.

3.1. Bubble production

A Plexiglas box, with four different-sized tubes and associated flow-control valves mounted on the top, was used to capture gas leaking from the sea floor and produce different sized bubbles at the base of the experimental frame (Fig. 1b, c). The box was filled with gas from a strong leakage point to obtain an un-altered gas sample at the beginning of each experiment. A floating barrier was placed within the box to minimize gas-water exchange and maintain a constant gas chemistry. Once placed at the base of the experimental frame and weighed down to prevent

movement, a ruler was positioned in front of the tubes to measure bubble diameter at the moment of release. During the various experiments only one tube was open at a time, with flow adjusted to obtain a distance between rising bubbles of about 20 cm.

3.2. Bubble rise velocity measurements

Bubble rise velocity was measured by filming the ascent of individual bubbles using a high definition video camera (GoPro Hero2) mounted on a carriage that slides in a guide on the experimental frame (Fig. 1a, c). The wheeled carriage allowed for the smooth tracking of individual bubbles as they rose through the water column. By using the video time stamp and progressing frame-by-frame between the 20 cm spaced horizontal lines marked on the cloth backdrop it was possible to measure the rise velocity over each interval for each monitored bubble. The measurements were repeated various times to obtain a statistical distribution of rise velocities along the ascent path.

3.3. Bubble size measurements

Given that a horizontally facing video is unable to accurately measure bubble diameter due to the potentially variable distance between the bubble and the camera, the video camera was mounted facing downwards in the center of the experimental frame and a clear, graduated Plexiglas sheet was suspended 40 cm below it to create a stable reference system (Fig. 1b). Examining the video data frame by frame, it was possible to observe a bubble immediately before it touches the Plexiglas and measure its diameter. Measurements were made with the Plexiglas at 40, 80, 120, 160, and 200 cm above the bubble release point.

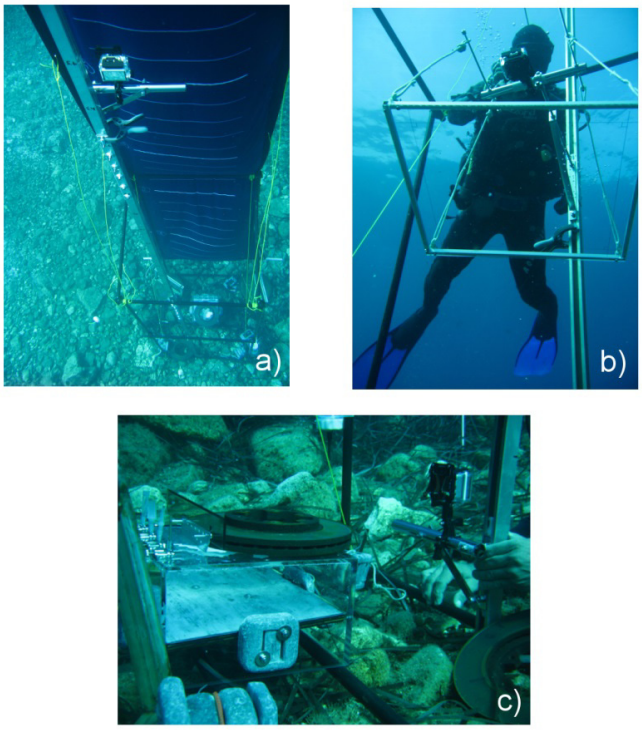

Fig. 1. (a) experimental frame seen from above, showing the video camera mounted on its carriage in the track and the dark blue background marked at 20 cm intervals; (b) diver making bubble size measurements by videoing bubbles as they hit a Plexiglas sheet suspended at a fixed height above the sea floor; (c) bubble making device with the four tubes, measurement ruler, and barrier between gas and water visible to the left and the video camera mounted on its carriage in the guide to the right.

3.4. Aqueous and gas chemistry

Water column physical-chemical parameters were measured besides the experimental frame using an SBE 19 *plus* SeaCAT profiler CTD equipped with sensors for temperature, conductivity, pressure, fluorescence, pH, and dissolved oxygen. Water samples were collected at four different depths (0.5, 1.0, 1.5, and 2.0 m above the sea floor) by divers using hand-held 5 L Niskin bottles; these samples were analyzed in the laboratory for pCO_2 using the headspace method, dissolved oxygen using the Winkler method, total alkalinity using open cell titration, and pH using the potentiometric method [6]. In addition, pCO_2 was also monitored continuously (once every 10 minutes) using two GasPro sensors [7] mounted on the frame at 0.5 and 1.5 m above the sea floor.

The changes in bubble chemistry along the flow path were measured by collecting samples at different heights using an inverted funnel with an attached glass VOA bottle, transferring the gas to pre-evacuated, 25 mL stainless steel canisters on the boat for transportation, and analyzing the samples for CO_2, N_2, O_2 + Ar, and CH_4 on two Carlo Erba 8000 gas chromatographs in the laboratory. Gas bubble samples were collected at the same heights where bubble diameters were measured.

4. Results and Discussion

Data from the two deployed GasPro pCO_2 sensors show how conditions changed during the 2.5 hours of the various experimental measurements (Fig. 2). Whereas values were low and in the range of background levels in equilibrium with the atmosphere (c. 0.3 – 0.4 matm) during the gas bubble sampling, all other measurements were performed during a 2 hour period in which elevated values of 0.7 – 0.8 matm were observed. Similar and larger pCO_2 peaks, such as this one immediately after a rapid drop in temperature, have been observed during other deployments of these instruments. These events have been attributed to either upwelling of deeper, colder, CO_2-rich waters or to local detrainment or lateral currents [7]. For the scope of the present study, and based on the extremely high CO_2 solubility, the maximum difference of about 500 μatm experienced during the study is not expected to have any significant effect on gas exchange rates or, as a consequence, the various measured parameters.

The CTD cast performed towards the end of this pCO_2 peak indicates that the water column over which the measurements were made (i.e., the bottom 3 m) was well mixed, as shown by the constant salinity and temperature values (Table 1). Similarly, laboratory measured total alkalinity (TA) and pH also defined a narrow range of values over this depth interval, with a maximum difference of 0.1 pH units between the bottom two water samples (Table 1). In sharp contrast, the gas bubble chemistry changes markedly, with samples collected over the bottom 1.2 m showing CO_2 decreasing from 84% to 58% while the other gases increase in concentration.

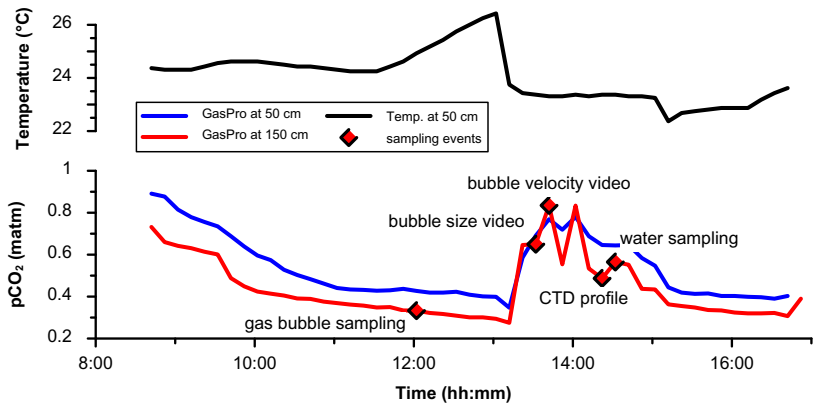

Fig. 2. The change of water temperature and pCO_2 during the experiment as monitored by two GasPro sensors fixed on the experimental frame at 50 and 150 cm above the sea floor. Individual points mark the times of the various other measurement and sampling events.

Table 1. Physical – chemical data from the CTD and from various laboratory analyses of samples collected during the experiment.

Depth (m)	Salinity	Temp. (°C)	TA (µmol/kg$_{SW}$)	pH$_T$ at 25°C	gas phase O_2 %	gas phase N_2 %	gas phase CO_2 %
8.8	38.34	23.22	2563.7	7.989			
9.8	38.34	23.21	2563.9	7.963			
10.5	38.34	23.21			11.5	32.9	57.9
10.9	38.34	23.21	2557.0	8.014	11.9	36.3	55.7
11.3	38.34	23.21			7.4	26.2	77.1
11.7	38.34	23.21	2564.0	7.903	5.4	15.3	83.7

These gas concentration trends are explained by the high solubility of CO_2 driving its rapid dissolution into the surrounding water, and the stripping of dissolved O_2 and N_2 from the water into the bubble. Together with the changing confining pressure of the overlying water column, it is this exchange into and out of the bubble (at different rates for different gases and concentrations) which controls the size evolution of a bubble as it ascends through the water column. Note that unfortunately it was not feasible to collect gas bubbles above 10.5 m due to their very small size and the time required to collect the necessary 40 mL of sample.

The size of the bubbles along the measured ascent path follows an almost linear trend, with diameters decreasing from the initial 7 mm at 11.8 m depth to less than 1 mm at about 10.1 m (Fig. 3a). It must be noted, however, that the bubbles at the initial release point, and for a certain portion of the initial measurement interval, are not spherical and thus an accurate measurement of their true diameter is difficult. Although the final diameter measurement was performed at about 10 m depth (Fig. 3a), videos of ascending individual bubbles followed them, on average, to a depth of about 9.5 m (Fig. 3b) over a total distance of about 2.3 m. For the most part the bubbles became too small to see beyond this point (possibly dissolving completely?), although one anomalous bubble was followed over 7 m before it rose beyond the mounted height of the experimental frame.

Rise velocity measurements are presented as the statistical distribution of 17 individual measurements for each distance interval (Fig. 3b). The range of estimated values is initially quite large for the first two intervals, possibly due to the difficulty for the divers to start their ascent and maintain the rising bubble in the center of the video screen. Higher up along the ascent path this error was greatly reduced, with videos being chosen to minimize this potential error.

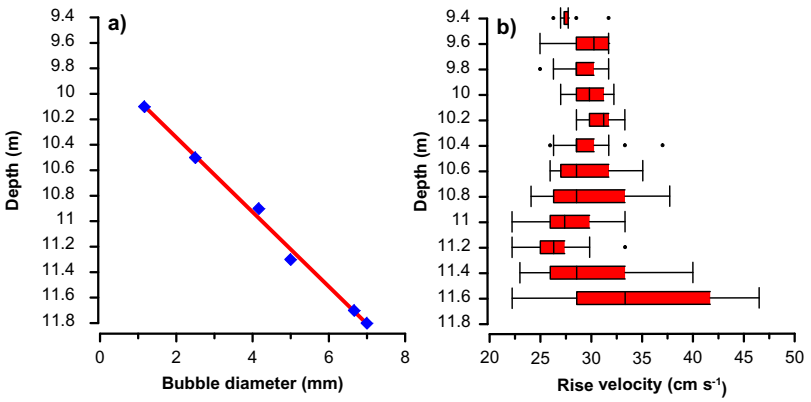

Fig. 3. (a) change in bubble diameter with height above the initial release point; (b) box and whisker plot summarizing the range of bubble rise velocities measured over each 20 cm interval, with the dots representing outliers, the whiskers marking the interquartile range * 1.5, the box outlining the upper and lower quartiles, and the central line the median value.

Above 11 m the average measured velocity is relatively stable between 28 and 30 cm s^{-1}, perhaps reflecting the balance between buoyancy and drag. However it is worth noting that in previous tests, where only rising bubble

videos were performed, a different behavior was observed. In these videos the bubbles rise quickly with a strong oscillation in the initial interval, followed by a sudden slowing and more vertical rise as the bubbles cross a threshold (perhaps when they become rigid spheres). The different observed behaviors illustrate the complexities inherent in working in real systems, where small-scale eddies, vertical current components, or even the presence of surface-active agents like natural surfactants or microparticles can influence bubble behavior and change it from what is predicted by theory or observed in controlled laboratory experiments.

The experimental data described above was modelled to test the predictive capabilities of the model itself and to examine data quality to improve future experiments. For this work the discrete bubble model (DBM) was used. The DBM was originally developed to predict oxygen transfer in artificial aeration systems in lakes and reservoirs [8], was later expanded to track the fate of methane bubbles in the Black Sea [9], and more recently was used to explore the potential fate of water column CO_2 in the context of sub-seabed floor CO_2 sequestration [3]. This model uses a simple mass balance to predict the gas flux across the bubble surface, with gas flux direction being dependent on internal bubble gas and ambient concentrations, as a function of the Henry's coefficient. In addition it uses bubble-size dependent relationships for the mass transfer rate and the bubble rise velocity. The most important parameters for this model include the initial bubble size and composition, water depth, and ambient dissolved gas concentrations, temperature and salinity.

A comparison of the measured and modelled data are given in Fig. 4 for both concentration (a) and bubble diameter (b) as a function of height above the release point (i.e., travel distance). A good match was obtained with the concentration data using the composition of the initial sample (84% CO_2) as the initial input function (Fig. 4a). In contrast, this initial concentration yielded bubble diameters that significantly overestimated the measured values (grey line, Fig. 4b), and only the use of a much higher concentration of 99%, i.e. closer to the known concentration of the gas being released from the sea floor, was able to give an estimate closer to that observed (green line, Fig. 4b). The good agreement with the gas compositional data indicates that the model is functioning correctly and is able to accurately simulate the gas exchange rates of the bubble during its ascent. In contrast the discrepancies observed between the measured and modelled bubble diameters may highlight difficulties in making accurate measurements of bubble diameters. The fact that the bubbles are not spherical upon their release, but rather oscillating ellipsoids, induces an initial uncertainty that may influence the subsequent simulations. Sensitivity analyses using the same composition but different starting bubble diameters may help determine if this could be an important factor. In addition, the complexities of working in the natural environment, both from a logistical point of view as well as in terms of the dynamic nature of the physical (e.g., eddies) and chemical (e.g., natural surfactants) characteristics of the water column, makes data-model matching challenging.

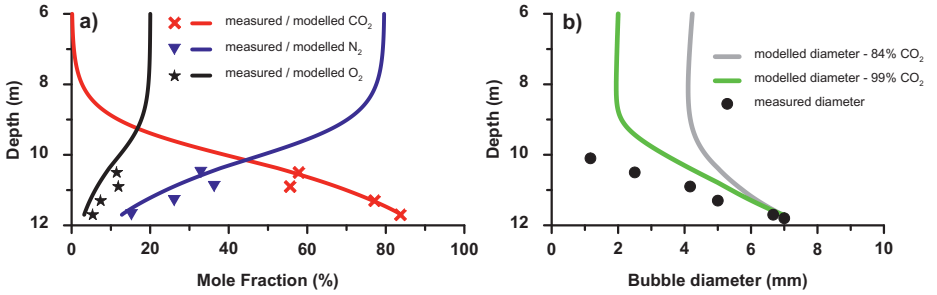

Fig. 4. (a) measured bubble gas chemistry compared with model results obtained assuming an initial composition equal to that of the first sample; (b) measured bubble diameters compared with model results assuming an initial CO_2 concentration equal to that of the first sample (84%) and the known composition of the leaking gas (99%).

5. Conclusions

Preliminary experiments examining in situ bubble behavior in marine waters have been performed off the coast of Panarea Italy at a depth of about 12 m. Chemical analyses of the gas bubbles and surrounding water, together with video measurements of bubble rise velocity and diameter, were conducted to characterize the system and to

provide input data for modelling purposes. The good agreement observed for the bubble gas composition indicates that the model is able to accurately account for mass transfer processes across the gas-water interface. A poorer agreement with the bubble size estimates may be a function of the uncertainty of this measurement in the field or experimental site complexities, although further controlled experiments will be needed to better understand the actual cause. Results from this experiment will be used to improve the setup and data collection methods for the next phase of the study.

This preliminary study has shown the need for detailed CO_2 bubble behavior experiments as applied to the field of CCS. For example the high solubility of CO_2 and the fact that this gas is transferred rapidly to the water column in the initial few meters has potential impacts for both monitoring strategies and potential biological impacts. In regards to monitoring, these results illustrate how the release of smaller bubbles may create short bubble flares that do not rise very high in the water column, an important issue when using hydro-acoustic methods to investigate leakage points. Instead if bubbles are above a certain threshold they may travel much higher because, even though all the original CO_2 may be dissolved, this loss of gas has been balanced by stripping of N_2 and O_2 from the water column. This loss of CO_2 close to the sediments also means that chemical monitoring, especially of pCO_2 and pH, will have a much higher possibility of success when measurements (continuous or intermittent) are made closer to the sea floor. Regarding potential impact, enhanced transfer of CO_2 near the sea floor may expose benthic organisms to more impacted waters, although this could be a transitory effect as waters are mixed via currents.

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References

[1] IPCC. Metz B, Davidson O, de Coninck HC, Loos M, Meyer LA eds. IPCC Special Report on Carbon Dioxide Capture and Storage. Prepared by Working Group III of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA; 2005: 442 pp.

[2] Schrag DP. Storage of Carbon Dioxide in Offshore Sediments. Science 2009;325:1658-1659.

[3] McGinnis DF, Schmidt M, DelSontro T, Themann S, Rovelli L, Reitz A, Linke P. Discovery of a natural CO_2 seep in the German North Sea: Implications for shallow dissolved gas and seep detection. J Geophys Res: Oceans 2011;116(C03013).

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

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

[6] Dickson AG, Sabine CL, Christian JR (Eds.) Guide to best practices for ocean CO_2 measurements. PICES Special Publ 2007;3:191 pp.

[7] Graziani S, Beaubien SE, Bigi S, Lombardi S. Spatial and temporal pCO_2 marine monitoring near Panarea Island (Italy) using multiple low-cost GasPro sensors. Env Sci Tech (in submission).

[8] McGinnis DF, Little JC. Predicting diffused bubble oxygen transfer rate using the discrete bubble model, Water Res 2002;36:4627–4635.

[9] McGinnis DF, Greinert J, Artemov Y, Beaubien SE, Wüest A. Fate of rising methane bubbles in stratified waters: How much methane reaches the atmosphere?, J Geophys Res 2006; 111:C09007.