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D 11.2. Report from Workshop 2: NOVEL TECHNOLOGIES

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- 1. Introduction

This document constitutes Deliverable 11.2 in the ECO_2 project. It summarizes the results from a workshop (workshop # 2 in WP11), held in, May 2013.

The scope of this deliverable is to document innovative storage monitoring technologies for <u>the</u> <u>marine environment</u>, based on research within the ECO_2 project and in light of the present state of the art. Should CO_2 migrate into shallow sediments and then subsequently into the overlying water column there is the potential that it will affect the chemical and ecological status of those environments. Significant efforts are being made to learn what features and changes to look for, or monitor, in order to rapidly detect such leaks.

The necessary public support for geological, including sub-seabed, Carbon Dioxide Capture and Storage (CCS) will not be given unless there is confidence that it can be conducted safely and meet climate change mitigation goals. The successful implementation of CO₂ storage as a large scale international option for reducing emissions will depend on several issues being resolved, such as the ability to demonstrate that CO₂ storage is safe, over timeframes of several thousand years, and the creation of an economic and regulatory environment that provides financial markets with the necessary incentives. Risk assessments usually deal with the likelihood of leaks and their magnitude whereas the marine ecological consequences of such leaks have only recently undergone detailed study (e.g. EU funded research projects RISCS and ECO₂).

Demonstrating that the long term behaviour of CO_2 can be predicted with some confidence requires knowledge of processes at depth as well as near-surface processes, including ecosystem responses to leaks. Furthermore, significant leaks will need to be accounted for national contingency plans and possibly within the emission trading schemes, requiring verifiable monitoring technologies.

The above is linked to "leakage" from geological reservoirs. This may seem a contradiction, as one is looking for sites for storage that will not leak. But 100% permanency can probably not be guaranteed even for a "100% safe" site, and for more logistically attractive sites, leakage may be more likely to happen, in the long term at least.

Europe's CO_2 emissions are expected to rise from a 2000 level of 3.1Gt to 3.5Gt by 2020 if left unabated. The EU has agreed to limit global warming to within 2°C, which means progressively reducing overall greenhouse gas emissions by up to 80% by 2050. This is why, in addition to existing technologies and options already accepted by policymakers, CO_2 capture and storage is also needed in Europe where about 33% of CO_2 emissions arise from stationary power



generation. As such, a significant proportion of the required emission cuts could be achieved using CCS at power stations.

For North-European countries sub-seabed storage is a most realistic storage scenario, and the world's only long-term, industrial-scale off-shore CCS project already has been running for over 17 years in this region (i.e. Sleipner). For these countries the North Sea, Norwegian Sea and the Barents Sea are all possible scenarios. Likely storage formations may be at the Utsira and Johansen fields in the North Sea, and the Froan Basin off Mid-Norway (Figure 1). For southern Europe, on the other hand, restricted basins in the Mediterranean, such as the Adriatic Sea, hold the greatest potential. Most of the issues related to monitoring would be similar for both northern and southern environments, although difference in ecosystems, average water temperatures and current / mixing regimes could influence potential impacts and monitoring strategies.

The 1st Meeting of Contracting Parties to the London Protocol, 2006, adopted new international rules to allow storage of CO_2 in sub-seabed geological formations. Such storage was made legal from 10 February 2007, under amendments to Annex 1 to the 1996 Protocol to the Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter, 1972 (London Convention). A guidance outline on how safe sub-seabed geological storage can be conducted was adopted by the Parties in 2007.

The report from the North Sea Task Force for CCS (2007) stated that long-term liability and responsibility is a crucial area that will require better definition and acceptance by all parties, and furthermore, that more work is needed on monitoring and verification. Lack of data and criteria were defined as present barriers for improving risk and environmental impact assessments. It was stated that many ecosystems in the North Sea are sensitive and that CO₂ storage operations should not compromise their long-term viability. It is for these reasons, regarding the North Sea and all other European marine settings that may be considered for off-shore CCS, that the ECO₂ project is focussing a significant portion of its research on the development and testing of innovative monitoring technologies. The preliminary results of this work are the focus of this report.

1.1. The leak issue and challenges

Although a well-chosen and well-engineered CO_2 injection reservoir should not leak, monitoring of both the deep system (e.g. 4D seismics, borehole pressure and chemistry, etc.) and the marine environment (e.g. hydroacoustics, water and sediment chemistry and biochemistry, etc.) is needed to guarantee storage integrity and ecosystem well-being.

Potential leakage pathways that must be considered when addressing CCS storage integrity and safety are faults and boreholes. Faults are natural features that can often be defined using seismic surveys, and thus highly faulted areas would be avoided in the CCS site selection process. In addition, not all faults would be potential leakage pathways, as the fault would have to be continuous from the storage reservoir to the surface and would have to be gas permeable along its length. Many studies have shown that various faults are actually barriers to flow, as



fault gouge or plastic sediment smears formed during the faulting process can effectively seal a fault surface. Some faults can leak, however, and there are numerous examples throughout the world where naturally produced, deep origin CO_2 is leaking from the sea floor into the marine environment. For example many ECO_2 partners are studying the Panarea natural laboratory, a site where large volumes of CO_2 are released along fractures and faults in a submerged, inactive volcanic plateau. This work has documented the size of the area of impact relative to the actual CO_2 source, and the chemical and ecological impacts in the water column and on the seabed for that particular release, and site.

Leakage can be defined as "movement away from the primary target formation", and seepage as "migration of CO_2 out of the ground (or seabed)" (Oldenburg and Unger 2003). In the further text, *leakage* is the common term used. In the CCS term "Carbon Storage" is now most commonly used, overtaking "Carbon Sequestration" which still is used, especially in the US.

Once the CO_2 is in the reservoir it will be important to keep it under surveillance and demonstrate that CO_2 stored sub-seabed does not reach the sediment/water interface. This can in principle be done in various ways by monitoring gases in the substrata, sediments or in the sea above. The overall large-scale behaviour of the stored CO_2 can be followed by seismic methods. However, the challenge remains as to how small a leak or release of gas could be detected through monitoring given the natural fluctuations. Technical progress is needed to speed up surveying methods and to refine low cost automatic monitoring equipment.



Figure 1. The Foran Basin off Mid-Norway is one possible site for sub-seabed CO₂ storage (NGU, 2004).

Regulators will need confidence that, if a leak should occur, the potential impacts on ecosystems are known, could be identified and monitored and that they can be included with confidence in predictive assessments of long-term site performance. Similarly, the confidence of the public will need to be built so that acceptance for the technology can be achieved at the broadest level. Some studies have begun to provide that knowledge and some testing and development of appropriate monitoring technologies has begun.



The injected CO_2 gas may not be only pure CO_2 but also mixed with e.g. H_2S . This changes the fate of the gas, and also the risk profile. Regulators must thus pay attention also to the altered environmental impacts of mixed stream injection as far as this is allowed by the international regulations (OSPAR etc.). The CO_2 may also displace and mobilize NH_4 and other light alkanes residing in the reservoir or aquifer, so that they may leak as well.

<u>Mobilisation of metals</u> by the stored CO₂ is another issue of possible concern. Investigations at the Frio saline formation in Texas included measuring the change in dissolved metal composition, following the injection of some 1,000 tons of CO₂. A substantial increase in metals was measured, and while this was first thought to come from the CO₂ reacting with the well casing, it was concluded that a substantial fraction of the metals came from mineral decomposition and dissolution in the reservoir itself (Kharaka et al. 2006). Preliminary experiments performed by NIVA also give support to the notion that low high CO₂ concentrations (low pH) may change metal fluxes in the sediment water interface.

As sub-seabed CO_2 storage is yet limited to a couple of sites, including the Sleipner field, there seems yet to be no direct experience or reports of leakages from such sites. The same seems to apply to long-lived EOR sites. From CO_2 storages (natural) under land, however, there is some experience from well operations.

In Utah, a 1936 oil exploration well penetrated a saline formation charged with dissolved CO_2 (Gouveia et al. 2005). The well (Crystal Geyser) since then has emitted CO_2 and brines in intermittent eruptions as a point source. The annual CO_2 amount is estimated to 11 000 tonnes, and concentrations levels in ground air near the site remain below the acute human health risk level of around 15 000 ppm. This example could provide an analogue to a non-repairable well failure at or along the border of a CO_2 storage site where pore water still affects the system (a long-term, single point maximum leakage flux analogue).

Another analogue to a well failure (injection or abandoned well) may be from the Sheep Mountain natural CO_2 reservoir in Colorado where a well failed in 1982, seven years after initial production. The flow rate was between 7 000 – 11 000 tonnes of CO_2 per day, over a 17 day period until the well was controlled. CO_2 also vented though soil and rock fractures nearby, and the total amount leaked was ca. 200 000 tonnes, indicating the potential magnitude (rate) of leaks in the future, also through the seabed.

1.2. The CO₂ wants to go up

The target sub-seabed reservoirs will be porous media such as sandstone incl. depleted oil/gas reservoirs and saline aquifers, overlain by non-permeable layers (overburden, cap-rock) to prevent leakage. At least for shallow aquifers, the overburden will commonly be either of carbonate minerals (limestones etc.) or siliclastic minerals like quartz, feldspar etc. forming sand/siltstones and shales.

Silicate minerals react slowly with dissolved CO_2 (carbonic acid) while carbonate rocks react faster. In the first case, the dissolved CO_2 will remain acidic and reactive for a long time. In the



latter case, the CO_2 may cause rapid change of permeability, but simultaneously the brine will be buffered and have its pH increased (get less reactive). It seems these two competing effects makes an assessment of which cap-rock is most prone to leakage a difficult task, and little work has focussed on such comparison (Wilson et al. 2007).

It is assumed that the CO_2 will be introduced deep under the seabed, enough (800+m) that it exists in liquid/supercritical form. The supercritical CO_2 will initially be buoyant in the subsurface, i.e. less dense than the surrounding brine or fluids. This means the gas may tend to rise through the porous media until it reaches the cap-rock above, where it can remain reactive to the minerals above for a long time.

Also, induced pressure differences in the formation may cause the CO_2 to move vertically or horizontally away from the injection region. Thus, in principle, over long time scales the gas may itself dissolve minerals and force its way upwards, or it may rise through any existing or new vertical fractures in the cap-rock (**Figure 2**). Reports from the Frio experiment document the substantial acidification of the brine, which could potentially eat through the surrounding rock and escape into higher aquifers there (Schiermeier 2006).

In a saline aquifer, the CO_2 that dissolves in the brine will add gravity, making the CO_2 -rich brine sink slowly, thus reducing the potential stress on the cap-rock or shales above. It has been calculated that up to 18% of the injected CO_2 could dissolve during the lifetime of the project (order 100 years), inducing convective currents in brine columns (Lindeberg and Bergmo 2003). On the longer term, most of the CO_2 will dissolve. Processes such as mineral trapping (reaction formation of solid carbonate precipitate) seem to be of less importance for such type of reservoirs (Torp and Gale 2003).







1.3. Horizontal extent of a storage reservoir

The areal extent of the pool of stored CO_2 will depend on the amount stored, the reservoir characteristics and the vertical scale of the active strata. Preuss et al. (2001) simulated the injection of 9 million tonnes of CO_2 annually over a 30 years. This corresponds approximately to the amount to be stored from a 1 GW plant over its lifetime. Assuming a 100 m thick strata, the pool would be 120 km² (**Figure 3**) increasing further with time by a factor of 1.4 due to buoyancy flow.

This figure is also in harmony with figures by Wilson et al. (2007) and indicates the size scale of the area on top of a specific reservoir that will be subject to long-term monitoring.



Areal extent of a CO₂ pool from a 1 GW power plant

Figure 3. The size of the areal extent of a geologically stored CO₂ pool from a 1 GW power plant after 30 years of injection. (From Golmen et al. 2008, after Pruess et al. 2001, Wilson et al. 2007).

OSPAR has accepted sub-seabed CO_2 storage within their geographic domain (the NE Atlantic). So several legal obstacles against sub-seabed storage, seem to have been cleared away, with the requirements of more studies on the leak risk and the environmental impacts, thereof.

1.4. Ecological indicators of leaks

Acidification of seawater will occur as a consequence of CO_2 leaking from sub-seabed reservoirs. It may then directly affect water and sediment chemistry and marine life in the surroundings. Such effects will probably be related to the large changes in seawater chemistry near the CO_2 leak point and may cause mortality for nearby infaunal deep-sea communities



(Barry et al., 2004) or affect marine sediment in-fauna or plankton in various ways if the CO_2 escapes upward towards the sea surface (Riebesell, 2004, Kurihara et al. 2004, Ishida et al., 2013).

Seeps of CO_2 gas through the shallow sediments can dissolve both in pore water and in the overlying seawater. Dissolving CO_2 in seawater means it becomes heavier, so it will tend to accumulate in layers or pools at the seabed. In this case, it is likely to cause environmental impact, possibly damage both in the sediments and in the water above, as exposure times will be significantly longer than the timescales of minutes related to the rising of gas bubbles to the surface. Simultaneously, such collection of escaped CO_2 may imply a method to detect leaks, either visually, by sensors, or indirectly by a modified ecosystem.

Sub-seabed CO_2 storage is actually a technology to also mitigate impacts on marine biota from increasing influx of CO_2 from the atmosphere to the sea, with a resulting reduction in pH. Nevertheless, this benefit for marine life may be locally or even regionally reduced or out weighted by negative impacts from leaks from sub-seabed reservoirs. Therefore the need for further understanding of how such leaks may occur, and how they may interact with and impact marine chemistry and biota are central issues for further studies.

Another issue is the <u>ecological effect of impurities</u> in the leaking CO_2 stream, either impurities following the injected gas, or impurities released or created from the interaction of CO_2 with substrata. The London convention recently amended the list of acceptable substances for subseabed storage to include CO_2 . However, the need to learn more both about the impacts of impurities and of the CO_2 itself was underscored (Greenhouse Issues No 84, December 2006).



Proper monitoring is to be addressed in the present Deliverable. The sketch above may illustrate how/when monitoring fits within other sequences of a CCS project, with an imaginary time axis, and the chain of developments, left-to right.

1.5. Leak occurrence and frequency

For the case of sub-seabed storage, there are many potential leak/accident spots, from the capture site via compression, pipeline transportation, injection platform and finally the storage reservoir. For the sites upstream of the reservoir, the period to consider is during the operation



only, on the time-scale of decades. This period may have relatively high annual leakage frequency figures – but remediation can usually prevent large leaks or serious damage.

The reservoir time scale is much longer; on the order of millennia. It is usually anticipated that the risk (annual leak frequency) associated with storage will be lowest immediately after sealing the reservoir, and then increase with time, perhaps approaching leak frequency close to figures for the injection period.

For offshore operations risk analyses (oil/gas) the initial leak rate is often taken as 5 times the production rate, and such a factor may be used as a baseline for estimating leaks during CO₂ injection. Korre et al., (2012) described the present status on leak quantification techniques, that still lack precision or documentation of this. After sealing of the reservoir, leaks in practice can take on any order of magnitude, depending on the cap rock geology, and flow path. Small seeps, which are most likely to take place, are difficult to model/quantify and take into account in risk assessments.



Figure 4. Schematic of how CO₂ from small leaks can accumulate as pools of CO₂-enriched seawater on the seabed (dissolved CO₂ increases the density of seawater). A monitoring network of sensors may possibly detect such accumulation. The ocean will also receive gradually more CO₂ from the atmosphere via natural influx (downward pointing arrows).

Leak estimates for land-based storage sites have estimated a cumulative probability of a leak over 1000 years of 0.34 (34% probability of a leak within this period). Leak amounts have been similarly estimated to 0.2 % of total amount of gas stored. When applying this to the total storage capacity in the North Sea (perhaps 100 GtC or more), the equivalent average leak rate will amount to several hundred thousand tonnes of CO_2 per year, most going into the sea above. This figure is not trivial, although it must be anticipated that such leaks will be dispersed regionally.



2.1. Novel modular subsea observatory for process studies at leacky abandoned wells Peter Linke, Mark Schmidt (GEOMAR)

Background information

Continuous measurements of dissolved gases such as methane, higher hydrocarbons or carbon dioxide become increasingly important for research, environmental assessment issues or the safe operation of underwater installations for oil and gas exploration as well as sequestration of carbon dioxide during CCS (Carbon Capture and Sequestration). Here we describe a novel modular subsea observatory which has been used to study dissolved gas concentrations at a leaky abandoned well.

Brief method description



The observatory system consists of a trawl-resistant lander (Floatation) and a sensor package. The lander was equipped with a 300 kHz ADCP (Teledyne), a storage CTD (SBE 37SM, SeaBird), and a hydrophone (icListen LF, Ocean Sonics) with internal data logger. For recovery the lander is equipped with an acoustic release which enables the floatation unit to detach from the lander base and ascend to the sea surface. It is connected to the base of the lander with a 300 m long line, which enables a recovery of the whole equipment as this contains the acoustic releaser (K/MT562, KUM), CTD, hydrophone and the weights. Furthermore, the base was equipped with two baskets which contained a 100 m long rope and a snap hook to connect the lander with the sensor package. The sensor package was equipped with the prototype of a novel IR methane sensor (Schmidt et al 2013) and a large battery container. Both instruments were deployed video-guided on the sea floor next to the crater rim by the modified launcher and were equipped with a beacon for acoustic relocation by ROV. During the first dive the pilots of the ROV were able to relocate and connect both instruments by the rope which enabled a combined recovery of the whole mooring after acoustic release.

Example of field application

The system has been used on a recent cruise to site 22/4b (blowout crater) in the North Sea. Here, a multi-disciplinary monitoring campaign was conducted for about 10 days, which addressed the applicability of different subsea modules for both, scientific background studies and industrial leak detection for hydrocarbons.





Measurement evaluation

The results demonstrate the short-term tidal impact on the spreading of a methane plume in the water column, which is reflected in the full dynamic range of the methane sensor (0 - 16,000 ppm). Membrane-inlet IR absorption sensors can be used for long-term measurements at the seafloor (e.g., lander-based deployment). The determination of, for example, varying methane concentrations in the vicinity of a methane seep have to be combined with determination of temperature, salinity, and pressure variations, as well with current measurements (i.e. using ADCPs). This combination is the basic information used to determine (dissolved) gas fluxes from natural seeps or leaking constructions at the seafloor. Such multi-disciplinary measurements are needed for present and future off-shore applications (e.g. abandoned wells, production and storage sites) and will lead into a commercially available Integrated Environmental Monitoring System being launched in 2014.

Advantages

The observatory is trawl-resistant and modular and can be equipped with a variety of sensors (e.g. CO_2 sensors).

Limitations

A miniaturization of the recently developed high sensitive methane sensor (HISEM) is prerequisite to use this technology onboard inspection class ROVs.

2.2. Survey and monitoring tool for leak detection

Stefan Sommer, Mark Schmidt, Peter Linke (GEOMAR)

Background information

Continuous measurements of dissolved gases such as methane, higher hydrocarbons or carbon dioxide become increasingly important for research, environmental assessment issues or the safe operation of underwater installations for oil and gas exploration as well as sequestration of carbon dioxide during CCS (Carbon Capture and Sequestration). Here we describe a newly designed Water Sampler Rosette system which is used to study dissolved gas concentrations.

Brief method descriptionThe system is towed and water depths are controlled by pressure readings of the attached Seabird CTD (SBE9plus). A digital video telemetry system (Sea & Sun, Trappenkamp - SST) providing bidirectional transmission of serial data (e.g. CTD or compass data) and real-time monitoring of the seafloor is used to control the distance to the seafloor in "bottom view" mode via a standard coaxial cable. The SBE 9plus underwater unit is equipped with 2 parallel pressure, temperature, oxygen sensors and conductivity sensors. 4 analogue channels are used for external sensor reading (SBE27 pH-, CO₂-, CH₄-, PAH-sensors, Contros). For the ex situ gas measurements bottom water is continuously pumped to the laboratory





through a tube (i.d.: 2.5 cm) and analyzed using a membrane inlet mass spectrometer (GAM 200, InProcess Instruments). The inlet of the tube is mounted on the CTD frame at the height of the in situ sensors. The tube on deck and throughout its way to the laboratory is insulated to prevent warming of the water. In the laboratory continuous sub-sampling takes place from the tube using a steel capillary that is connected to the membrane inlet.



Example of field application

The system has been used on several cruises to Sleipner and the site 22/4b (blowout crater) in the North Sea.

	HydroC [™] /CH ₄	HydroC [™] /PAH	HydroC [™] /CO ₂
Measuring range	200 nM – 50μM	0-500 ppm	200-1000 ppm
Resolution	15-19 nM	0.1 ppm	1 ppm
Response time (t63)	2 min	0.5 s	1 min
Warm-up time	~ 30 min	Less than 10 s	~30 min
Operational depth	4000 m	500 m	4000 m

Measurement evaluation

2.3. CO₂ leak investigations with the next generation imaging sonar technology Jens Schneider von Deimling, GEOMAR, Kiel, Germany

Background information

To evaluate environmental impacts of carbon sequestration requires setting baselines before human activities on the seafloor begin. This includes detection and quantification of natural gas ebullition on the seafloor especially on continental margins and river deltas, where natural seepage frequently occurs. During a CO_2 injection scenario accompanied measurements about gas leakage and/or injection-mediated fluid flow are required to identify local weakness of the storage strata. After injection long term observatory is needed to monitor the storage site in terms of gas leakage and other potential environmental changes.

In situ and remote/vessel operated hydroacoustic systems have demonstrated to be very effective tools for detection of gas bubbles in the Ocean. In the past years a next generation of hydroacoustic devices entered the market offering unraveled possibilities for imaging the water



column and thus hold great potential for more sophisticated hydroacoustic CO_2 leakage investigations.

Brief method description

Gas bubbles in the Ocean behave as extreme prominent acoustic scatterers. Even individual millimeter sized gas bubbles can be unambiguously be sensed with the proper frequency in the near range (<50m; Schneider von Deimling 2010, 2012), and larger gas flares in the far range (>1000m, Greinert 2006). Potential misinterpretations through backscatter from single fish or fish shoals can be mitigated by evaluating special data pattern, that are only caused by leakage (Schneider von Deimling et al. 2010, 2012).

Example of field application

During an ECO2 cruise with R/V URANIA the natural CO_2 gas bubble leakage site Panarea (Italy) was investigated with geochemical and hydroacoustic methods. We installed a broadband R2SONIC 2024 with 200-400 kHz together with prototype water column functionality, because this system has a superior range resolution compared to the shipborn KONGSBERG EM710 on R/V URANIA.

Measurement evaluation (including sensitivity)



Fig. 1 presents data (R2SONIC, 400kHz) revealing the bubble rise pattern of individual CO₂ bubble streams rising from 25 m water depth. Clear current deflection of the rising gas bubbles is visible. The very high range resolution allows separation between and tracking of individual gas bubbles and/or groups of gas bubbles as shown in Schneider von Deimling et al. (2012). Even very minor fluxes of <10ml/min can be detected with such a system and offers a non-invasive determination of terminal bubble rise velocities with an accuracy of +-1.5cm/s. This

estimates about the total flux can be afforded and compared to backscatter derived flux values. Moreover hydroacoustically derived parameters such as rise velocity, total rise height, and bubble sizes can serve as input parameters for further bubble dissolution modeling.

Advantages

- shipboard and in situ approach feasible
- Extremely sensitive to gas bubbles (CO₂, CH₄, or other gases)
- Several days to weeks operation by low power consumption
- Precise deployment through ROV or Lander technology
- Non-invasive determination of bubble terminal rise velocity, total rise height, and estimates about bubble size and dissolution behavior

Limitations

• Detection algorithm and flux quantification reliably work for minor flux scenarios only



• The system is sensitive to noise, that is expected to occur next to human activities and subsea operations at the storage location

<u>2.4. Autonomous probes for pCO₂ monitoring Stefano Graziani - Università di Roma "La Sapienza"</u>

Background information

Marine monitoring of dissolved gases is critical for a wide range of applications, from studies of the uptake of atmospheric CO₂ to safety and pollution monitoring of off-shore oil and gas infrastructure or Carbon Capture and Storage (CCS) sites. Although long-term, large-scale monitoring is important for such applications, such datasets have been extremely difficult to produce due to prohibitive costs and/or power supply limitations of existing technologies. To address these shortcomings the Università di Roma "La Sapienza" is developing small, lightweight, inexpensive, low-power consumption, autonomous, gas sensing probes ("GasPro") for deployment in surface water, groundwater, soil, and atmospheric environments. The GasPro-pCO₂ unit, developed within the EC-funded RISCS and ECO2 projects, is described here.

Brief method description

A gas permeable, but water impermeable, membrane separates the surrounding environment from a small-volume chamber containing an infra-red sensor. Physically isolated from this is a

larger chamber that contains control electronics, memory, and batteries. As a function of dissolved gas concentration, water temperature and salinity, and Henry's Law, an equilibrium quantity of CO₂ transfers into the sensor chamber (a type of "head-space") where its concentration is measured with the IR sensor. Measurements can be made at pre-determined time intervals, depending on the study needs and predicted gas exchange rate across the



membrane. At present the unit logs CO_2 concentration, temperature, and pressure. Battery life is on the order of 6 months for a sampling frequency of 1 / hour and memory is essentially nonlimiting with a 4Gb SD card.

Example of field application

Although the described technology is new and still under development, numerous field tests and experiments have yielded extremely interesting and useful results that would not have been possible with any other existing technique. For example, the units have most recently been deployed at the Panarea Island test site, where natural CO_2 is leaking from the sea floor. In the example on the lower left, 20 probes were suspended along a transect in the water column (see photo upper left) for 2.5 days and programmed to sample once every 10 minutes.





The resulting spatial and temporal distribution will be used for modelling CO_2 dispersion in the water column. In the example on the lower right a GasPro-pCO₂ was deployed in collaboration with partners OGS in a benthic chamber (see photo upper right) and temperature and CO_2 concentrations were logged for calculating flux rates from the sediments to the overlying water column.

Measurement evaluation (including sensitivity)

Manufacturer-quoted IR sensor Accuracy (%Full Scale) is 1-1.5% with Zero Resolution of 1ppm and Full Scale resolution of 15ppm(FS 5000), 100ppm(FS 5%), 500ppm(FS 20%), 0.5%(FS 100%), with minimal short-term drift. Extended usage will consume the lamp thus necessitating recalibration, however by minimizing lamp warm-up time and having a lower sampling rate for long-deployments, this problem can be reduced. For multiple unit deployments (like the transect above) all units can be deployed together as a block and left to monitor the same surrounding environment for a period of time prior to the actual experiment; this data can then be used to standardize results.

Advantages

- small, light-weight, inexpensive, low-power consumption, autonomous
- low cost means that large numbers of units can be deployed for high spatial resolution
- low battery consumption means units can be deployed for long time periods
- probes can also communicate with a control station for real-time data transfer to a webbased server
- biofouling is typically not a problem for long-term deployment, due to the membrane material used

Limitations

- Response time can be slow, due to gas diffusion across the membrane. Pumps can be added, but this increases power consumption and size of unit
- Data interpretation would be greatly improved by integrating a pH meter and conductivity sensor

2.5. Compact electrochemical in-situ pH/pCO₂/ORP multi-sensor Kiminori Shitashima by Kyushu University

Background information

Carbon dioxide capture and storage (CCS) in sub-seabed geological formations is currently being studied as a feasible option to mitigate the accumulation of anthropogenic CO_2 in the atmosphere. In implementing sub-seabed CCS, detection and monitoring of the CO_2 leakage from seafloor into the ocean is highly important. Therefore, observation of the diffusion behaviour of low pH/high CO_2 seawater due to leaked CO_2 with in-situ pH and/or pCO₂ sensors is effective. We have been developing a non-glass type of compact in-situ pH/pCO₂/ORP



(Oxidation-Reduction Potential) multi-sensor, and applying it to researches for hydrothermal systems, oceanic carbon cycle, ocean acidification and CCS.

Brief method description

Solid-state electrode which is an ion-sensitive field-effect transistor (ISFET) as the pH electrode and a chloride ion selective electrode (CI-ISE) as the reference electrode (RE) was used for the pH sensor. For pCO₂ sensor, the pH sensor was sealed with a gas permeable membrane which inside was filled with inner electrolyte solution. A Pt wire as a working electrode and a CI-ISE as RE were employed for ORP sensor. The electro-circuit unit of the in-situ pH/pCO₂/ORP sensor was three-channel type and consists of one main-board (controller) and three sub-boards (pH, pCO₂ and ORP). The main-board can control the plural sub-boards simultaneously.

Example of field application

The sensor has been applied to many research cruises and field observations in the world. The sensor was attached to CTD, mooring, ROV, AUV, glider and other observation instrument in offline (stand-alone) or online (RS232C, RS422 and RS485). The ISFET and CI-ISE electrodes were embedded in spear-shaped sensor tip, and the sensor was applied to measure pH in pore water of

sediment by sticking it into sediment. Vertical profiles of pH/pCO_2 in water column and timeseries variation of pH in sediment were obtained at hydrothermal area. The $pH/pCO_2/ORP$ sensor was installed to AUTSUB 6000 with NOC in RRS James Cook cruise 77 at the Sleipner site on September 2012. The sensors also were applied in QICS experiment conducted in Oban for May-September 2012.

Measurement evaluation (including sensitivity)

Several sea tests of the sensor carried out at various locations in the ocean showed high accuracy, quick response, and long-term stability. In the field, the in-situ response time of the devised pH sensor is as quick as 1 second or less, and the estimated measurement accuracy is ± 0.005 pH units and a depth rating of 6000 m. The in-situ (3000 m depth, 1.8°C) response time of the pCO₂ sensor was less than 60 seconds.

Advantages

- The sensor is compact, and can install to several observation instruments.
- The sensor can respond to pH change very quickly and can observe continuously with AUV/ROV/glider.

Limitations

• For long-term observation, in-situ calibration and biofouling are the problem that we should overcome. We will try to develop an in-situ auto-calibration system using MEMS technology.









• Electrical drift of the electrode also is fundamental and another issue. We plan to fabricate new ISFET-pH electrode that has characteristic of extremely small electrical drift.

2.6. The P-Cable high-resolution 3D seismic system – intelligent & versatile 3D seismic acquisition –

Stefan Bünz, Unversity of Tromsø, Norway

The P-Cable 3D high-resolution seismic system consists of a seismic cable towed perpendicular (cross cable) to the vessel's steaming direction (Figure right). An array of multi-channel streamers is used to acquire many seismic lines simultaneously, thus covering a large area with close in-line spacing in a cost efficient way. The cross-cable is spread by two paravanes that due to their deflectors attempt to move away from the ship. The P-Cable system has been developed over a period of more than 10 years in cooperation with P-Cable AS, Oslo, Geomar, Kiel and NOC, Southampton. The University of Tromsø owns a complete P-Cable system, the "Geosystems 3D Seismic Imaging (G3)" national infrastructure, funded by the Research Council of Norway.

The P-Cable system is designed and developed as a tool for marine geological research and the petroleum industry. It may be used in both frontier and mature regions in an intelligent, versatile way to acquire successive small-size surveys (25 to 250 km2) in areas of special interest. This is due to the fast deployment and recovery of the P-Cable and the short turns needed between adjacent sailing line



Why P-Cable?

- Conventional 3D seismic data acquired by the petroleum industry have yielded a wealth of new insight and greater understanding of geological structures and processes.
- The P-Cable 3D Seismic system is a newly developed system for acquisition of highresolution 3D data.
- This technology has proven data quality, surpassing conventional 3D and equal or better than HiRes 2D.
- Increase in lateral resolution is approximately one order of magnitude.

Research and industrial applications

- Drill site investigations (scientific and industrial)
- Sea bed properties for offshore installations
- Shallow gas accumulations and gas hydrates

- Fluid migration (3D, 4D)
- Geohazard assessments (mass movements)
- 4D seismic monitoring
- Deformation and faulting

P-Cable highlights

- Unparalleled data quality and resolution
- Fast deployment and recovery
- Relatively low cost
- Multiple surveys in one cruise
- High production rates
- Deployable from almost any vessel



Typical survey design parameters

Number of streamers:	12-24
Streamer separation:	6.25 – 12.5 m
Streamer depth:	1-3 m
Source:	High-frequency (mini-GI, sparker)
Source depth:	1-3 m
Frequency bandwidth:	30-400 Hz
Production rate:	up to 20 km²/day
Spatial resolution:	3-5 m
Temporal resolution:	down to 1 m





2.7. High-resolution interferometric synthetic aperture sonar (HISAS 1030) Tamara Baumberger, Alden R. Denny, Rolf Birger Pedersen CGB/UiB

Background information

Marine basic science investigations as well as marine applied studies strongly depend on the knowledge of the topographic characteristics of the seafloor. Until recently, multibeam echosounder systems and sidescan sonars were the most advanced technique to map the seafloor. The newly developed AUV mounted high-resolution synthetic aperture sonar (HISAS) opened a new era in seafloor mapping and imaging.



Brief method description

The HISAS 1030 sonar system is an advanced interferometric sidescan sonar developed by Kongsberg Maritime. It consists of a transmitter and two vertically displaced receiver arrays configured as an interferometer. The HISAS is capable of synthetic aperture sonar (SAS) imaging, resulting in a range independent obtainable image resolution better than 5x5 cm (depending on the conditions). High-resolution bathymetric maps are obtained by compositing the interferometric product between the two vertically offset receive arraysc. While technically range invariant the system normally provides a 400m swath. The HISAS frequency range is approximately 60 to 120 kHz, with a bandwidth of 30-50 kHz (Fossum et al., 2008).

Example of field application

The HISAS, in combination with the AUV Hugin, was several times successfully used by the ECO₂member UiB for detailed imaging of the seafloor. Deployed in June 2011, a fracture in the seafloor was discovered in the North Sea by using the HISAS mounted on Hugin. It was not possible to identify this fracture by conventional seafloor mapping using the multibeam echo-sounder system. The fracture was subsequently named after the vehicle – "Hugin Fracture." The central



and eastern part of the Hugin Fracture, imaged by using the HISAS, is shown here.

The HISAS was additionally applied for mapping and imaging lava fields and hydrothermal active areas at the Arctic Mid-Ocean Ridge. The high resolution of the obtained data allowed the identification of different volcanic events in the investigated area.

Measurement evaluation (including sensitivity)

The system has a theoretical image resolution better than 2x2 cm. To guarantee robustness of the conservative parameters, the practical resolution is better than 5x5 cm.

Advantages

- detailed imaging with a high resolution (better than 5x5 cm) out to 200 m from both sides of the vehicle
- high area coverage rates (typically 2 km²/h) given the resolution achieved.
- commercially available AUV system

Limitations

- Requires high navigational accuracy both in mmresolution vehicle position and in absolute position relative to the support ship GPS receiver.
- Surface properties, steep topography, flocculent layers or bacterial mats can adversely influence the systems range and reception.





Flowchart of implementation of this method (from Shihavuddin et al., 2013a).

2.8. Digital underwater imagery and photo mosaic - Automated segmentation, classification and thematic mapping

Tamara Baumberger, Nuno Gracias, Rolf Birger Pedersen CGB/UiB

Background information

Seabed image acquisition systems improved considerably over the last decade, and presently allow the collection of large sets of submarine images in a very short time. Nevertheless, the analysis techniques of collected underwater images did not develop as fast as the acquisition systems. Manual extraction of relevant data from every collected image is time consuming, and sometime prohibitive, for these large data sets. The recent development of an automated system for segmentation, classification and thematic mapping of digital underwater images allows the characterization of large benthic areas with less human resource and time investment.

Brief method description

This method describes an automated system for thematic mapping based on photo mosaics of images taken of sediments, shell hash areas and bacterial mats obtained during AUV operations. Thereby, the AUV has to be equipped with a high-resolution digital still camera to collect a large data set of seabed images. Subsequently, underwater mosaics are generated by registering and blending large sets of images acquired at a close range. To achieve a thematic map of the underwater mosaic images, eight processing steps are applied. The flowchart of implementation of this method is illustrated in Figure 1 (Shihavuddin et al., 2013a).

Example of field application

The development of this method was motivated by two cruises to the Sleipner area in the North Sea conducted within the framework of the ECO2 project. Specially tailored techniques were tested and applied for creating photo mosaic of bacterial mats on the seabed using high-



resolution imagery collected by the Hugin AUV. Subsequently, a recently developed method was applied to the obtained image data set. The automatic classification method allowed the identification of the approximate location of bacterial mats and shell hash areas within a large area surveyed by the Hugin AUV. Thus, the automatic generation of thematic maps is a vital instrument for seabed monitoring and marine exploration.

Method evaluation (including sensitivity)

Compared to other automated classification systems of seabed images, this method of automated classification and thematic mapping is very effective and has a high accuracy for the particular case of bacterial mats. The time consumption of this method is moderate in comparison with other classification systems (Shihavuddin et al., 2013b).

Advantages

- Has the highest overall classification accuracy and moderate execution time compared to other automated classification systems for seabed images.
- Can be easily extended to provide statistics of percentage cover of bacterial mats and to track changes over time over large areas.

Limitations

- Accurate image registration requires the presence of a minimum level of image texture, which may not always exist in featureless areas of pure sand. In such cases the performance of the image mosaicking becomes strongly dependent on the georeferencing provided by the AUV sensors
- This method is well tested for automated thematic mapping of bacterial mats. Mapping of other features needs still to be further developed and tested.

3. Conclusions

This report has provided a thorough evaluation of the challenges facing the development of an integrated monitoring capacity for the evaluation of an effective carbon sequestration site. The document details eight new technologies that have hugely advanced the state-of-the-art regarding monitoring for effective identification of potentially secure sites as well as the follow-up observations of CO₂ leakage. This report is a stepping stone towards the final ECO₂ report on guidelines for long-term monitoring which is currently in development for delivery in M42.

4. References

Barry, J.P., K.R. Buck, C.F. Lovera, L. Kuhnz, P.J. Whaling, E.T. Peltzer, P Walz, and P.G. Brewer 2004. Effects of direct ocean CO₂ injection on deep-sea meiofauna. J. Oceanogr. 60, 759-766.

DNV 2003: DTI CO₂ sequestration Risk Assessement. Appendix V: Risk analysis. Report Det Norske Veritas, Oslo, April 2003, 39p.

Fietzek P., Fiedler B., Steinhoff T., Körtzinger A. 2013. In situ accuracy assessment of a novel underwater pCO2 sensor based on membrane equilibration and NDIR spectrometry. *Journal of Atmospheric and Oceanic Technology*. (submitted)



Fossum, T. G., T. O. Sæbø, B. Langli, H. Callow, R. E. Hansen (2008), HISAS 1030 – High resolution interferometric synthetic aperture sonar, *Proceedings of CHC-NSC conference 2008*, Victoria, Canada.

Golmen, L., A. Sundfjord, J. A. Berge and G. Caramanna 2008. Geological storage of CO₂: The marine component. Impact on sediments, seawater and marine biota from leaks. A literature review. Report, NIVA, Bergen/Oslo No 5478, 50 pp

Greinert, J., et al. (2006), 1300-m-high rising bubbles from mud volcanoes at 2080m in the Black Sea: Hydroacoustic characteristics and temporal variability. *Earth and Planetary Science Letters* 244.1 : 1-15.

Guoveira, F.J., M. Johnson, R.N. Leif and S.J. Friedmann 2005: Aerometric measurements and modeling of the mass of CO₂ emissions from Crystal Geyser, Utah. NETL 4th Annual Carbon Capture and Sequestration conference, May 2-5, 2005.

IPCC 2005 (ed. Metz et al.): IPCC Special Report on Carbon Dioxide Capture and Storage. Cambridge Press, 443 s.

Ishida, H. ,L. Golmen, J. West, M. Krüger, P. Coombs, J. Berge, M. Magi and J. Kita 2012: The Benthic Chamber experiment in Storfjorden (Norway) 2005 – effects of CO2 on microbes, nanobenthos and meiofauna. . Mar Poll Bull. 2013.

Kharaka, Y.K., D.R. Cole, S.D. Hovorka, W.D. Gunther, K.G. Knauss and B.M. Freifeld 2006: Gas-water rock interaction in Frio Formation following CO_2 injection: Implications for the storage of greenhouse gases in sedimentary basins. Geology, Vol 34(7), 577 – 580.

Korre, A. S. Durucan, C. E. Imrie, F. May, M. Krueger, S. Schlömer, K. Spickenbom, H. Fabriol, V. P. Vandeweijer, L. Golmen, S. Persoglia, S. Piccoti, D. Praeg, S. Beaubien 2012: IEAGHG, Quantification Techniques For CO2 Leakage. Report 2012/02, IEAGHG, Cheltenham, UK, January, 2012, 160p.

Kurihara, H., S. Shimode, and Y. Shirayama, 2004: Sub-lethal effects of elevated concentration of CO2 on planktonic copepods and sea urchins. J. Oceanogr. 60, 743-750.

Lindeberg, E. and P. Bergmo 2003: The long-term fate of CO_2 injected into an aquifer. Proceedings, GHGT-6, Eds. Kaya and Gale, 489 -494.

NGU 2004 (Bøe et al.): CO_2 point sources and subsurface storage capacities for CO_2 in aquifers in Norway. Report NGU, Trondheim, 2004. 010, 132p.

North Sea Task Force 2007: Storing CO_2 under the North Sea Basin. A key solution for combating climate change. Report by the task force, Norwegian Ministry of Petroleum & Energy, and UK Dept. of Trade and Industry, 15 pp.

Oldenburg, C. and A. J. Unger 2003. On leakage and seepage from geologic carbon sequestration sites: Unsaturated zone attenuation. *Vadose Zone J.* **2003**, *2*, 287-296.

Preuss, K., T. Xu, J. Apps and J. Garcia 2001. Numerical modeling of aquifer dispoal of CO₂. Soc. Petr. Eng. Paper 6657.

Riebesell, U. 2004. Effects of CO_2 enrichment on marine phytoplankton. Journal of Oceanography 60, 719-729.

Schiermeier, Q. 2006: Putting the Caron Back. The hundred billion tonne challenge. Nature, Vol. 442, Aug. 2006, 620-623.

Schneider von Deimling et al., (2010), Acoustic imaging of natural gas seepage in the North Sea: Sensing bubbles under control of variable currents. *Limnology and Oceanography: Methods*, *8*, 155-171.

Schneider von Deimling, J. et al. (2012), Detection of gas bubble leakage via correlation of water column multibeam images. *Ocean Science*, 8(2), 175-181.



Schmidt M., Linke P., Esser D. 2013. Recent development in IR-sensor technology for monitoring subsea methane discharge. *Mar. Technol. Soc. J.* 47(3)

Shihavuddin, A.S.M., N. Gracias, R. Garcia, J. Escartin, R. B. Pedersen (2013a), Automated classification and thematic mapping of bacterial mats in the North Sea, *Oceans'13 MTS/IEEE*, Bergen, Norway, **130118-117**.

Shihavuddin, A.S.M., N. Gracias, R. Garcia, J. Escartin, R. B. Pedersen (2013a), Automated classification and thematic mapping of bacterial mats in the North Sea, Oceans'13 MTS/IEEE, Bergen, Norway, 130118-117.

Shihavuddin, A.S.M., N. Gracias, R. Garcia, A. Gleason, B. Gintert (2013b), Image-Based Coral Reef Classification and Thematic Mapping, *Remote Sensing*, vol. 5, 1809-1841; doi:10.3390/rs5041809

Shitashima K., Y. Maeda, and T. Ohsumi, 2013. Development of detection and monitoring techniques of CO₂ leakage from seafloor in sub-seabed CO₂ storage. Applied Geochemistry, 30, 114-124.

Shitashima, K.2010. Evolution of Compact Electrochemical In-situ pH-pCO2 Sensor using ISFET-pH Electrode. MTS/IEEE Seattle, OCEANS 2010, 5663782.

Shitashima K., Y. Maeda, Y. Koike and T. Ohsumi, 2008. Natural analogue of the rise and dissolution of liquid CO₂ in the ocean. International Journal of Greenhouse Gas Control, 2, 95-104.

Shitashima K., M. Kyo, Y. Koike, H. Henmi, 2002. Development of in situ pH sensor using ISFET. Proceeding of the 2002 International Symposium on Underwater Technology, IEEE/02EX556, 106-108.

Sommer S., Schmidt M., Linke P. 2011. EGU Poster

Torp, T. and J. Gale 2003: Demonstrating storage of CO2 in geological reservoirs: The Sleipner and SACS projects. Proceedings, GHGT-6, Eds. Kaya and Gale, 311-316.

Wilson, E.J., S.J. Friedmann and M. F. Pollak 2007: Research and development: Incorporating Risk, Regulation and Liability of Carbon Capture ansd Sequestration. Environ. Sci. Technol. Vol 41, 5945 – 5952.