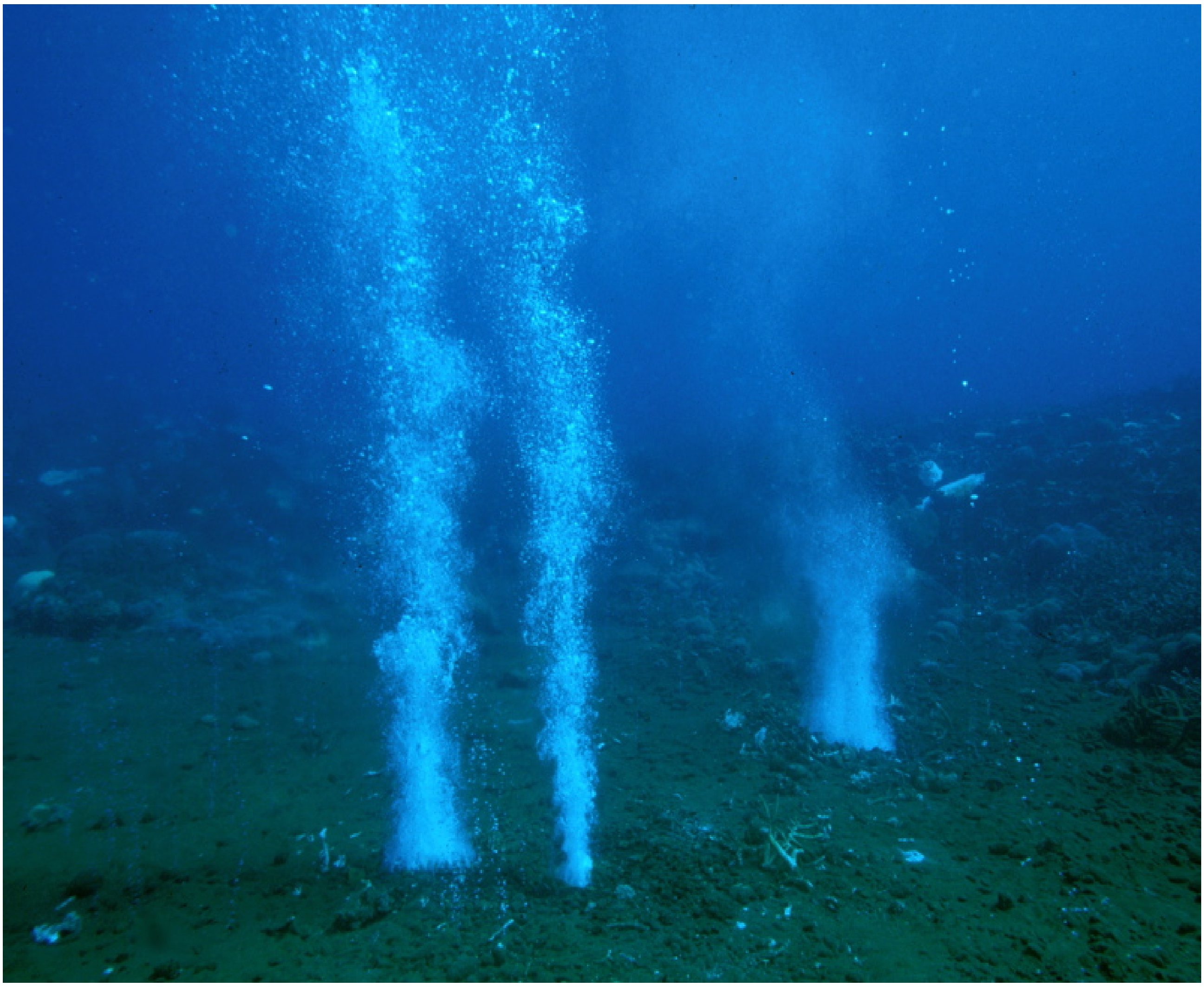
REPORT SNO 5478-2007

Geological storage of CO_2: The marine component

Impact on sediments, seawater and marine biota from leaks



Norwegian Institute for Water Research
– an institute in the Environmental Research Alliance of Norway

REPORT

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Title Geological storage of CO_2: The marine component. Impact on sediments, seawater and marine biota from leaks. A literature review.	Project No. 27237	Date November 2007
	Report No. Sub-No. 5478-2007	Pages Price 43
Author(s) Lars G. Golmen, Arild Sundfjord, John A. Berge, Giorgio Caramanna (University of Rome).	Topic group Oceanography	Distribution Open
	Geographical area NE Atlantic	Printed CopyCat

Client(s) Norwegian Research Council – CLIMIT programme	Client ref. Trygve Riis

Abstract

The report gives an overview of the current knowledge about what impacts CO_2 leaking from future sub-seabed storage sites may cause to the marine environment. Only a couple of such sites exist today, and no apparent leaks have been detected there. So experience must be gained from other sites where CO_2 is emitted naturally from the seabed into the sea, from natural analogues on land, or from experimental work. After learning more about the behaviour and reaction of certain organisms to high-CO_2 exposures, monitoring tools and procedures can be established in order to get an early warning of leaks. This may be combined with monitoring techniques for the physical and chemical characteristics of sediments and the seawater above.

4 keywords, Norwegian	4 keywords, English
1. CCS	1. CCS
2. Karbonlagring	2. Carbon Storage
3. Lekkasje	3. Leaks
4. Nordsjøen	4. North Sea

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ISBN 978-82-577-5213-2

Geological storage of CO_2

The marine component

Impact on
sediments, seawater and marine biota
from leaks

A literature review

Preface

The Norwegian Research Council, the CLIMIT programme, awarded in April 2007 a contract to the University of Bergen for a review study on possible marine impacts from storing CO_2 under the seabed.

As part of the study, NIVA, The Norwegian Institute for Water Research, was subcontracted by the university to deliver the present report on the marine biological aspects related to CO_2 impacts and leaks.

The following persons contributed to the report:

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NIVA, Bergen, November 2007

Lars G. Golmen

Cover photo: CO_2 leaking from sub-seabed strata at Tutum Bay, Papa New Guinea.
From Pichler et al., EOS No 23, June 2006. Permission for use given by author.

Contents

Summary

The present project was conducted by the Norwegian Institute for Water Research, NIVA, under a subcontract from University of Bergen as part of a larger project funded by the Norwegian Research Council, the CLIMIT programme.

The scope of this project was to review recent literature on the ecological effects of CO_2 leaks from sub-seabed storage sites and then suggest methods that may be applied for future monitoring of storage sites. An overview of risk of leaks is also given. For biological assessments, emphasis was put on deep, benthic communities that are most likely to be impacted from a leak, while pelagic communities further away and near the sea surface are less vulnerable.

Geological storage of captured CO_2, if planned for appropriately, is considered to be a safe and viable method to combat climate change while allowing societies to still use fossil fuels during a transitional period leading into a fossil-fuel free era.

For CO_2 storage it is important to select sites that will not leak, both for environmental and safety reasons, and for the legal accounting of stored CO_2. Still, there will always be some small risk that leaks may occur, and 100% permanency can probably not be guaranteed even for a “100% safe” site. It will thus be necessary to learn what features and changes to look for, or monitor, in order to be able to rapidly detect leaks coming to the sediment/water interface.

Regulators need to be confident that the pre-assessments of potential impacts on ecosystems if a leak does occur are trustworthy and that leaks can be identified and monitored if they actually happen. The acceptance of CCS and confidence on storage safety among the general public will build on similar confidence.

If CO_2 starts to leak from sub-seabed reservoirs it may 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 faunal deep-sea communities.

CO_2 gas emerging through 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, and affecting especially benthic communities. In this case, it is likely to cause environmental impact.

The report describes what animal groups or species that may be used as indicators for leaks, without coming to a final conclusion due to lack of data and specific knowledge. It is concluded that more research into both the physical behaviour of any leaking CO_2 and the ecological consequences of this must be further conducted. This is an urgent issue should Norway comply with its commitments to implement CCS with sub-seabed storage on a full, industrial scale by five years or less from now.

1. Background of the study

1.1 The CO_2 emission problem

Anthropogenic emissions lead to increasing CO_2 concentration in the atmosphere (**Figure 1**). This is expected to lead to climatic changes with subsequent severe impacts on nature and human infrastructure. Much progress has been made in understanding the climate system and climate change especially during the last two decades. Although projections of change and its impacts still contain many uncertainties, even the conservative or optimistic projections imply significant impacts. In order to improve this sinister situation, a portfolio of remediation actions and technologies may be invoked either globally, by nations, by companies, by local communities and by individuals.

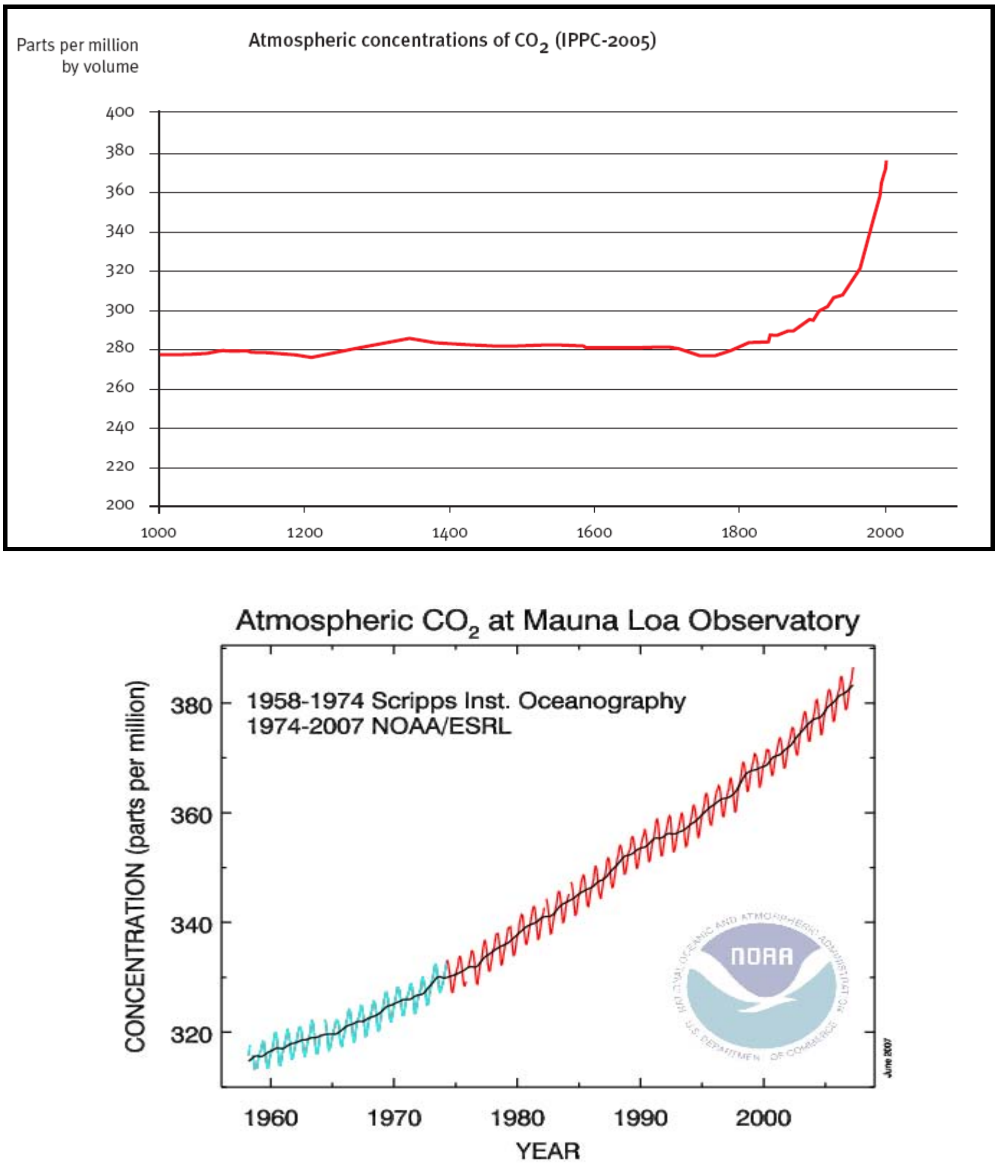


Figure 1. Top: Atmospheric CO_2 concentration the last millennium. Bottom: Atmospheric CO_2 concentration measured at the high-altitude (3,400 m) Mauna Loa Observatory in Hawaii, 1957-2007. Courtesy National Oceanic and Atmospheric Administration (NOAA), Climate Monitoring and Diagnostics Laboratory (CMDL).

One such technology is storage of CO_2 captured from the burning of fossil fuels. This is a direct way of preventing such emissions to atmosphere at large (global) scale. World projections of energy use show that fossil fuel dependency will continue to 2030 and beyond, while sustainability will need CO_2 global emission reductions by more than 50% by 2050.

The necessary public support for geological, including sub-seabed, Carbon 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 CO_2 storage as a large scale international option for reducing emissions will depend on several issues being resolved, such as the ability to demonstrate that CO_2 storage is safe, over timeframes of several thousand years; and creating 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 while e.g. marine ecological consequences of such leaks have not been treated in much detail (IEA 2006).

Demonstrating that the long term CO_2 behaviour 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 in national contingency plans and possibly within the emission trading schemes, requiring verifiable monitoring technologies.

Geological storage of CO_2 is presently the dominating and most realistic technology discussed. Other alternatives do exist, such as ocean storage by injecting the CO_2 into the deep ocean, or onto the deep seafloor as gas, dry ice or hydrate. Ocean storage will probably be less expensive, less risky by operation and more feasible than geological storage, but concerns about the environmental impacts from the CO_2 on the ocean and permanence has led to a halt in further development of ocean storage. Still it exists as an option, and the EU seems to keep the door open by recently stating that “whether this [method] is acceptable depends on what other mitigation measures are being taken” (Euroabstracts, April 2007, p 11).

Much of 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 (or “migration”) may be more likely to happen, in the long term at least.

The scope of this project is the study of effects of CO_2 leaks from sub-seabed CCS sites. This is in line with several pending international study efforts related to geological storage of CO_2 where also leaks to the terrestrial environment is being studied as well. CO_2 migrating into shallow sediments will affect the chemical and ecological status. It will be necessary to learn what features and changes to look for, or monitor, in order to be able to rapidly detect leaks coming to the sediment/water interface.

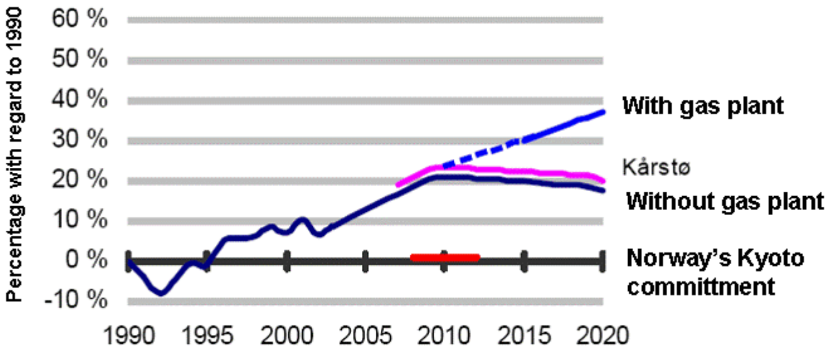
1.1.1 The European and Norwegian situation

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. A major proportion of the emission cut needed by then could be achieved using CCS at power stations, and the North Sea is a likely candidate for storage.

The Utsira saline aquifer in the North Sea has a theoretical capacity to store hundreds of gigatonnes of CO_2. The true capacity is probably smaller than this, as the central and northern parts of the formation may be too shallow for the gas to stay liquid, and also where there are shallower outcrops where leaks may occur.

Norway has no large fossil-fuel power plants on the mainland at present, but plans exist to install several such plants in the near future, at Kårstø, Mongstad, Tjeldbergodden and elsewhere. Norway already emits ca 10 mill tonnes of CO_2 from the offshore industry. So, even though Norway is self-supplied with hydro-power for the national electricity grid, it produces more than 50 mill tonnes of CO_2 totally, from various sources, and this figure may increase significantly and far beyond the Kyoto target in the near future (**Figure 2**). Due to the large export of oil and gas Norway contributes to approximately 3 % of the world total CO_2 emissions. Therefore the issue of CCS should be quite urgent and important for Norway. Likely storage formations may be at the Utsira and Johansen fields in the North Sea, and the Froan Basin off Mid-Norway (**Figure 3**).

The UK-Norway North Sea Task Force for CCS is set up to develop common principles for managing and regulating the transport, injection and permanent storage of CO_2 in the North Sea sub-seabed. At their meeting on 15 June 2007, it was stated that it is necessary to address potential environmental impacts of CCS activities throughout the lifetime of the [storage] project, such as: “site selection, characterisation, development, operation and decommissioning”.



Source: Statens forurensningstilsyn (SFT) 2005

Figure 2. Scenarios for Norwegian CO_2 emissions.

Their report (North Sea Task Force 2007) states 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 CO_2 storage operations should not compromise their long-term viability.

For Norway, sub-seabed storage is probably the most realistic scenario. The present study will therefore concentrate on this scenario, including aquifer storage. Possible leakage through the overburden into the overlying seawater is then a central study topic, with the North Sea, Norwegian Sea and the Barents Sea as relevant scenario locations.

1.2 The leak issue and challenges

Leaks or seepage from geological storage has gained increasing attention during the last years, as it remains an issue still to be dealt with and resolved.

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 given the natural fluctuations. Technical progress is needed to speed up surveying methods and to refine low cost automatic monitoring equipment.

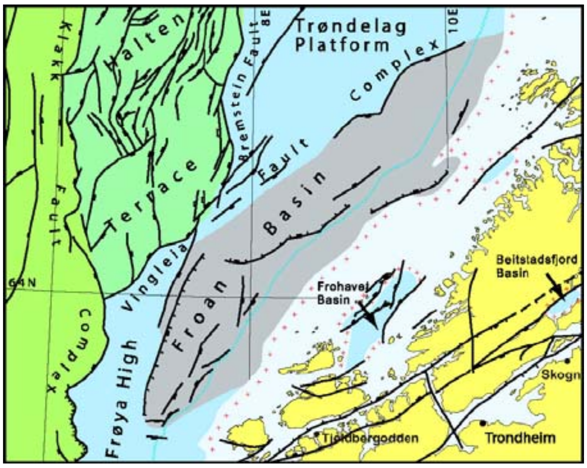


Figure 3. The Foran Basin off Mid-Norway is one possible site for sub-seabed CO_2 storage (NGU, 2004).

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.

Mobilisation of metals by the stored CO_2 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 tonnes of CO_2. A substantial increase in metals was measured, and while this was first thought to come from the CO_2 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 high CO_2 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 in the North Sea, 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.

1.3 The CO_2 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 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. 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).

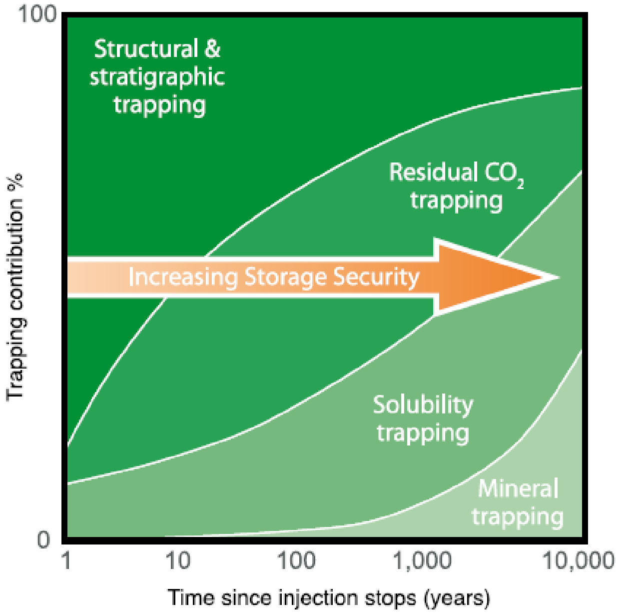


Figure 4. Stored CO_2 may gradually go from physically trapped to residual/solubility trapping and finally to mineral trapping. From IPCC (2005).

1.4 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. Pruess 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 km^2 (**Figure 5**) 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.

1.5 Legal issues

This study will not deal with legal issues concerning CO_2 storage. But it may be mentioned that Such storage under the seabed is now accepted under amendments to the international London Protocol. The parties agreed in November 2006 that: “guidance informing them on the means by which sub-seabed geological sequestration of carbon dioxide can be conducted, in accordance with Annex 2 to the Protocol, and in a manner that is safe for the marine environment, over the long and short term, should be developed as soon as possible. This will, when finalized, form an important part of the regulation of this activity. Arrangements have been made to ensure that this guidance will be reviewed for adoption at the 2nd Meeting of Contracting Parties in November 2007.”

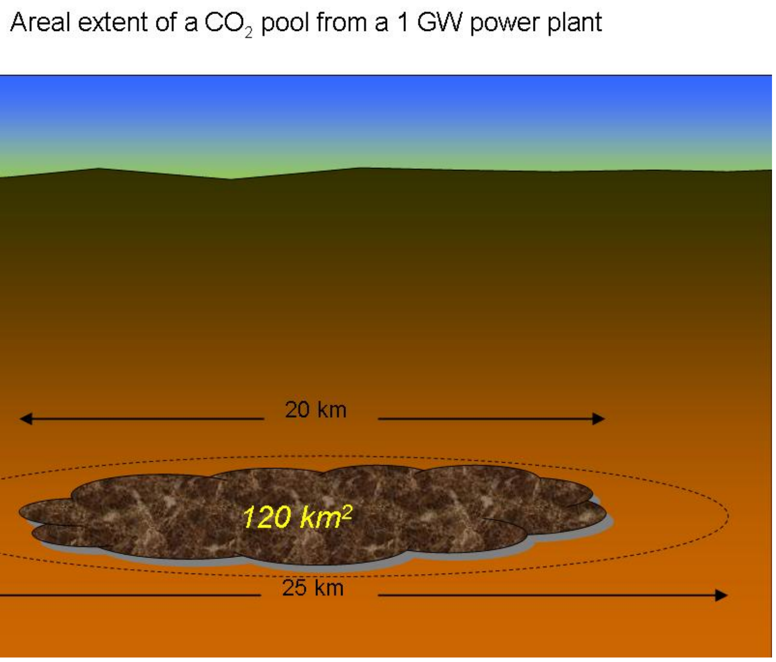


Figure 5. The size of the areal extent of a geologically stored CO$_2$ pool from a 1 GW power plant after 30 years of injection. (After Pruess et al. 2001, Wilson et al. 2007).

OSPAR recently 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. Before this, even experiments with CO$_2$ in the sea was prohibited or opposed to (Giles 2002, Golmen 2002).

1.6 Scope of the present study

On background of the above "leak" issues, a literature review study on sub-seabed storage has been performed in 2007 by a group in Bergen consisting of University of Bergen (project leader), CMR and NIVA. The main project was on contract from the Norwegian Research Council, their CLIMIT programme.

The main goal of the project was described as follows:
Perform a review of present knowledge on environmental impacts from geological storage of CO$_2$*,, identify important knowledge gaps, and define research activities and projects with the aim to reduce the most crucial ones.*
Specific project objectives:

- Review the knowledge on acute and long term impact on the marine biota and ecosystem, and identify knowledge gaps.
- Review the present understanding of physical processes at and within the sea bottom, with relevance to how CO$_2$ will enter the water column. And, identify knowledge gaps.
- Review the present understanding of how CO$_2$ will be transported and diluted within the ocean water column.
- Review present status of marine monitoring and detection of CO$_2$ within the benthic and in the water column.
- Write a review report that defines several activities and research projects that should be performed in order to reduce the knowledge gaps.
- Arrange a national workshop on the theme.

The project was divided in three thematic work packages:

1. **Impact on sediments, seawater and marine biota (WP2 - NIVA)**
2. **The benthic boundary layer dynamics (WP3 - UoB)**
3. **Monitoring and detection of seeps and CO2 in seawater (WP4- CMR)**

The present document reports on WP2, which had the following work description:

Acidification of seawater may 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 plankton in various ways if the CO_2 escapes upward towards the sea surface (Riebsell, 2004, Kurihara et al. 2004).

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 ecological effect of impurities 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 sub-seabed 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).

Risk assessment
CO_2 capture
Transport
Storage
Monitoring
Prediction
Remediation
Mitigation

Proper monitoring is a keyword to be addressed in the present project. 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.

2. 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 CO_2 injection. 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.

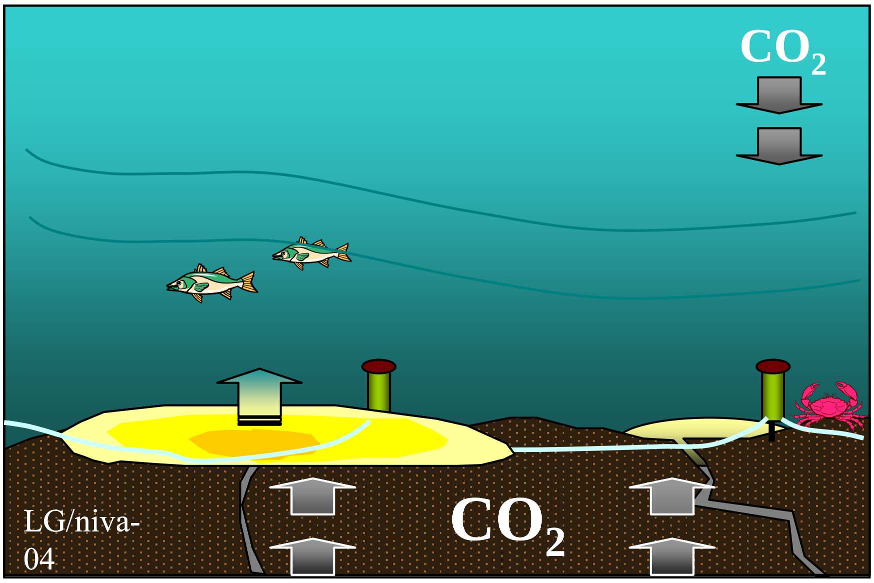


Figure 6. Schematic of how CO_2 from small leaks can accumulate as pools of CO_2-enriched seawater on the seabed (dissolved CO_2 increases the density of seawater). A monitoring network of sensors may possibly detect such accumulation. The ocean will also receive gradually more CO_2 from the atmosphere 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 Consequence assessments

These are usually based on max tolerance values of CO_2 in air, for humans and for the remaining environment. Most humans can tolerate short exposures (10-15 minutes) to CO_2 on the order of 10% air concentration. For a minor part of the population (10%) such exposure may still be fatal.

Modelling studies have quoted 15 000 ppm, (1.5 %) CO_2 as a limiting value in assessments for human risk, and 2 000 ppm for environmental impact (DNV 2003). These concentrations correspond to levels at which adverse effects on humans and the environment, respectively, apply.

For leaks from operations, the likely leak rate and duration must be calculated based on a specific knowledge about the installations, detection and warning systems and the security/HSE procedures. This constitutes by itself a large matrix of data. Leaks to air can be modelled by atmospheric boundary layer dispersion models, according to input of wind data, air temperature etc.

The consequence assessments must be based on either actual data/maps on population near the facility, or on more generic data on population density. Environmental damage assessments can be based on actual inventories of natural resources, possibly extra vulnerable resources, or on approximate or generic data.

2.1.1 Seabed leaks

Existing assessments of leaks from sub-sea operations or sub-seabed storage have mostly been for shallow waters, < 150 m depth. This usually implies that CO_2 will exist in gaseous form, rising rapidly to the surface and outgas to the atmosphere above, so that any impacts in the water or on the seabed have been assumed to be small, and thus ignored.

This may be an oversimplification as 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 gets heavier, so it will tend to accumulate in layers or pools at the seabed (**Figure 6**). In this case, it is likely to cause environmental 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.

2.2 Risk analyses

Any ecological consequence evaluation from leaks should be based on risk scenarios related to both CO_2 capture, handling and storage also will have to take into account the various operational sites, with different scenarios for each one (IEA 2006). For direct impact on humans (not scope of present study), critical sites may be the CO_2 recovery at the source (e.g. power plant), and the injection plant. **Figure 7** shows different elements contained in a total risk assessment process.

For an offshore storage project based on CO_2 collected from sources on-shore, the following items/modules may have to be considered separately for risk assessment (for a pipeline transport scenario):

- CO_2 recovery at source
- Converging pipelines
- Booster stations
- The main pipeline
- The injection plant
- The CO_2 riser to the offshore platform
- The pipeline to the storage reservoir

Risks of fatalities will be based on dangerous or lethal dose figures such as the 10% concentration and 15 minute exposure for humans. Other organisms will have lower limiting values. The 2 000 ppm is often quoted as the limit above which no environmental benefit can be determined, and above which actual damage is likely to be much higher. For humans, fatality for exposures such as 15 000 ppm can be estimated by assuming this is lethal to 10% of the population.

About half a gigatonne of CO_2 is naturally supplied annually to the atmosphere from the earth interior through volcanos and fracture zones. Some of these may be "natural analogues" to CO_2 leaks form CO_2 storage that can provide data for risk assessment. The most recent "high-end" case is the Lake Nyos (Cameroon) incident in 1986, where 1 700 people died after being exposed to geochemically bound CO_2 that dissolved in the water above and subsequently caused a large CO_2 gas eruption from the crater lake.

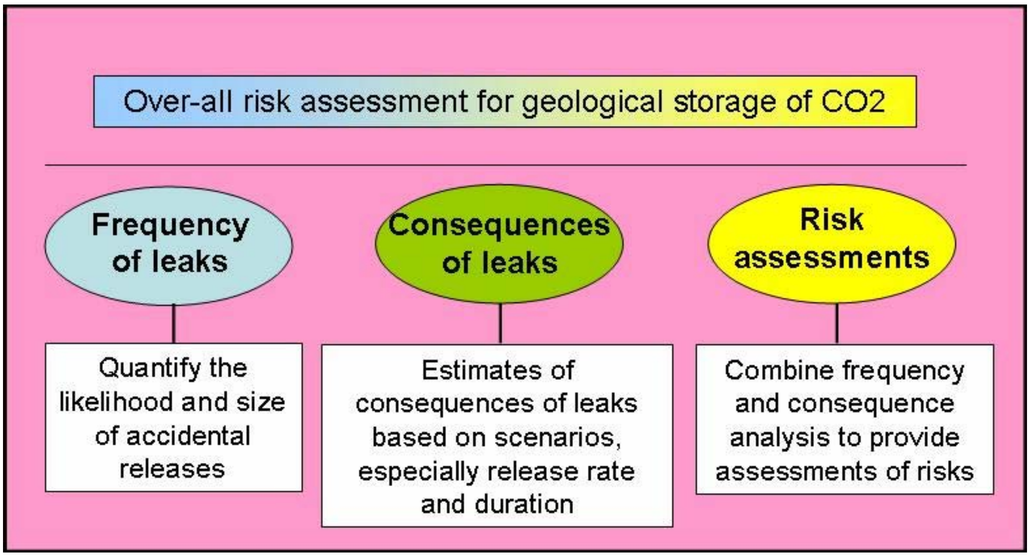


Figure 7. Elements of a total risk assessment for geological storage of CO_2. from Golmen (2005).

3. Seawater CO_2 chemistry

When CO_2, either in gas or liquid phase, is introduced into sea water it will gradually dissolve. The CO_2 reacts with the water until an equilibrium of ionic and non-ionic species is reached. The different species are dissolved free carbon dioxide ($CO_2(aq)$), carbonic acid (H_2CO_3), bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}). Together, these are labelled dissolved inorganic carbon (DIC).

When a given amount of CO_2 is added to the sea water, a new balance between the carbon species is established. CO_2 and water forms carbonic acid:

$CO_2(aq) + H_2O \rightleftharpoons H_2CO_3$

Carbonic acid, in turn, rapidly dissociates into bicarbonate:

$H_2CO_3 \rightleftharpoons HCO_3^- + H^+$

which balances with the amount of carbonate:

$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+$

This latter equilibrium is driven towards the left as CO_2 (and H^+) increases – carbonate ions already in the water will react with H+ to form more bicarbonate.

The full set of interactions between the carbon species can thus be decribed as follows:

$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons HCO_3^- + H^+ \rightleftharpoons CO_3^{2-} + 2H^+$

Free hydrogen ions (H^+) are released as the larger DIC pool adjusts to find a new equilibrium. Positive ions are acidic, meaning that the pH of the sea water is reduced as CO_2 is added: $pH = -\log_{10}[H^+]$.

The above can be summarized as follows: when more CO_2 is introduced, the pH will be lower, the amounts of dissolved (aqueous) CO_2 and bicarbonate will increase, and the number of carbonate ions will decrease. The total content of dissolved inorganic carbon, C_T, e.g. in units of µmol/l, is given as:

$C_T = [CO_2] + [HCO_3^-] + [CO_3^{2-}]$.

3.1 Buffering capacity and pH

The normal, preindustrial pH of the ocean water was probably around 8.1 – 8.2. Standard seawater (SWS) as delivered for calibration of salinity samples etc holds a pH of about 8.1 based on the pH scale for seawater: $[H^+]_{SWS} = ([H^+] + [H_2SO_4^-] + [HF])$ (Millero et al. 2008). Still the various strata and parts of the ocean experience natural variation of pH that can amount to 0.5 units or even more in some locations.

The fact that carbonate reacts with H+ ions to form bicarbonate implies that not all the H+ ions released from increasing total DIC act to acidify the sea water. This "buffering capacity" depends on the availability of carbonate ions. The more CO_2 that is added, the less carbonate will be available to offset the pH decrease. The relative amount of each of the three carbon species in the equilibrium also depends to some extent on temperature, pressure and salinity/alkalinity.

The relative proportions of the three DIC species in relation to different pH levels that may be caused by CO_2 leaks are shown in **Figure 8**. That figure also shows the charge distribution of the major anions and kations in normal seawater. Note that the DIC species constitute only a minor part of the ions.

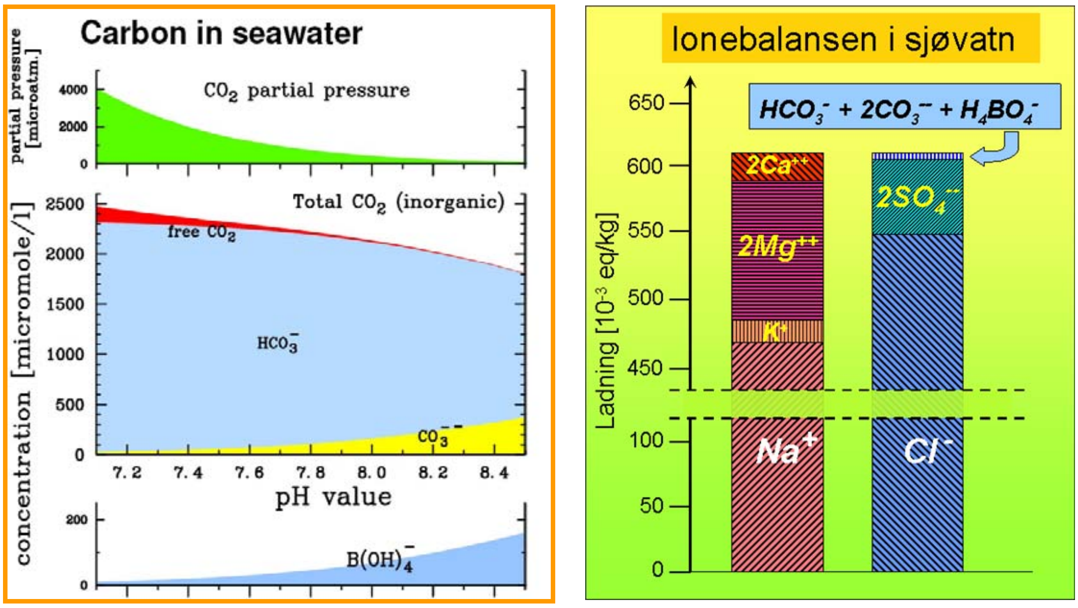


Figure 8. Left: Relative proportions of the DIC species at different ocean pH levels. From C. Heinze/Carboocean. Right: The ionic composition of normal seawater, for the major elements (modified after Brooker and Peng, 1998).

An important consequence of the decrease in carbonate is that the biological formation of carbonate minerals (e.g. shells and skeletons of marine organisms) is impeded. The balance between calcium carbonate ($CaCO_3$) and carbonate, $CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-}$, is shifted to the right with increasing CO_2/decreasing carbonate and pH. This means that at low pH values calcium carbonate will dissolve. The resulting release of carbonate will allow for more bicarbonate to form, thus offsetting the acidification somewhat, but at the expense of the ability of calcifying organisms to grow.

4. CO_2 and marine ecology

In the context of sub-seabed CO_2 storage, offshore waters may be of most relevance to consider, at least for the Norwegian situation, although in some countries nearshore locations as well may be under consideration. For the offshore setting, the strata near the seabed and the uppermost part of the sediments will probably be most important, both for ecological risk assessments and for ecological monitoring.

The marine ecosystems may be divided roughly into pelagic and benthic ecosystems, which again may be divided into several vertical strata corresponding to the main water characteristics, and into water masses like brackish water, coastal water and oceanic water. Hence the pelagic systems may be split into epipelagic (shallow) and mesopelagic (deeper) strata.

The deep water usually represents a quite homogenous environment with respect to temperature and salinity. The pelagic ecosystems in deeper parts are usually fairly rich in species and biomass, and typical numerical dominants among the larger zooplankton forms may be pelagic shrimps, euphausids, mysids and chaetognaths. Other important zooplankton organisms in the deepwater at certain seasons are copepods. Several of the pelagic species perform substantial diurnal or seasonal vertical migration, even into the upper advective layers.

4.1 The benthic boundary layer

The benthic boundary layer is the layer nearest to the seabed, including the upper parts of the sediments (**Figure 9**). This is a layer with significant vertical exchange of water and other matter, in both directions. The zone has high importance for the biology and chemistry of the local environment, and physical and chemical/biological processes in this layer will determine much of the behaviour and fate of CO_2 escaping from below.

Physically, this layer is the primary location for dissipation of hydrodynamic energy and exchange of heat, solutes and particulates between the water and the sediments. Remineralization of settled organic material, debris and shells is vigourous in this layer. A wide variety of benthic animals, plants and microorganisms live there, and intensive transport of solutes and (re)suspended particles takes place, causing high chemical and biological reactivity.

In the deep sea, the thickness of the layer is normally equivalent to the Ekman scale, which is the ratio (u_*/f) between the friction velocity, u_*, and the Coriolis parameter, f. It can reach several tens of metres or more. In shallow waters it may be better defined by the elevation at which the flow matches the potential flow, and may contain the whole water column is stratification is weak. For computational hydrodynamics the logarithmic layer is often referred to, where the flow velocity is assumed to follow a logarithmic decay towards the bottom, in similarity to what is often measured. This can be of a few metres thick or more. Down on the centimeter-scale, friction dominates over eddy mixing and may create a viscous sublayer over the sediment surface. Very close to the sediments a water ”film” on the sub-millimeter scale exists where molecular diffusion exceeds eddy diffusion (**Figure 9**). This is of most relevance where there are dense, nearly non-penetrable sediments. Assessments and models for benthic layer processes may include some or all of these layers.

In porous sands the hydrodynamic forces may reach down into the sediment and define the Brinkman layer which also is of (sub)-milimeter scale in thickness. In porous sediments water flow and surface topography induces lateral pressure gradients that drive appreciable advective flows through the upper centimeters to decimeters. This has large importance for solute and particle fluxes across the bulk sediment- water interface.

Biological and physical activities promotes mixing within the sediment and across the interface. Some bacteria, microalgae and invertebrates act contrary by producing exopolymeric substances which tend to clog up the pore spaces and seal the sediment surface, thereby slowing the exchange across it.

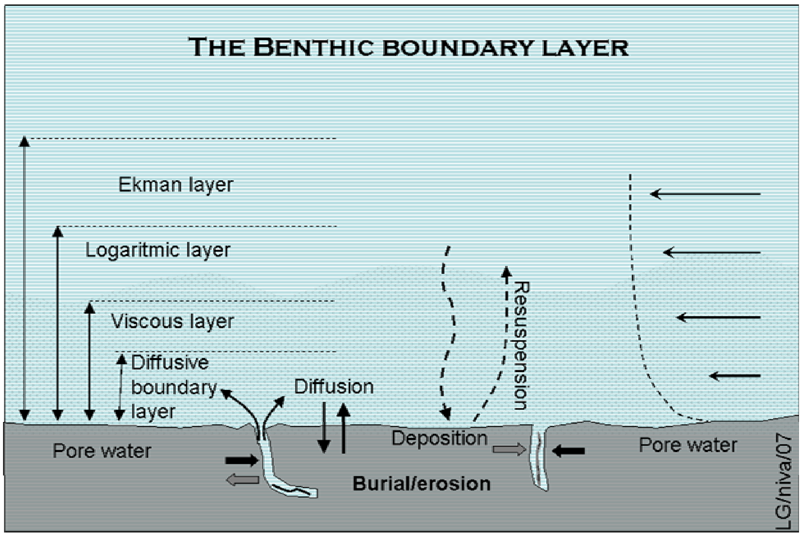


Figure 9. Physical sub-layers within the benthic boundary layer with some transfer paths of matter indicated. The Ekman layer is where the rotation of the earth and bottom friction affect the flow structure. The logarithmic layer represents a typical velocity profile, and the viscous sublayer is where effects of molecular viscosity are important. In the diffusive boundary layer transfer of matter is controlled by molecular diffusion.

4.2 Biological impacts from CO_2

It is expected that even a moderate rise in seawater CO_2 may be critical for the most sensitive species, making those act as early warning “canaries” of CO_2 leaks. Although the number of species with acute sensitivity may be small, even tolerant species may react. Long term, sub-lethal effects at the ecosystem, population and individual levels are likely in the case of a long-lasting leak.

The sediment macrofauna in a typical offshore location will contain all major benthic animal groups (e.g. polychaets, molluscs, crustaceans and echinoderms) with high number of species and diversity of the major groups, as the offshore regions represent a diverse habitat in food resources and grain size composition which may support many species. Typical predatory fish near the bottom can be ling (*Molva molva*) and tusk (*Brosme brosme*) which are harvested commercially.

Elevated CO_2 levels near the seabed and in ambient water will affect the physiology of fish and other animals. Present knowledge ranges from effects on acid-base regulation to influence on respiration, excretion, energy turn over, and mode of metabolism. The main properties and biological impacts of CO_2 in water may be summarized in the following points:

- Compared to all other gases, CO_2 is very soluble in water (at 0°C, CO_2 is 35 times more soluble than O_2, and is still 25 times more soluble at 30°C).
- CO_2 affects pH, so that release of CO_2 into seawater results in increased concentrations of H^+ (lowered pH).
- The fact that most natural water has little CO_2 content makes CO_2 levels in fish blood low compared to air-breathers.

- Fish cannot regulate its respiratory system by changes in CO_2 level (as air-breathers do), but must sense O_2 changes instead.
- CO_2 may be excreted as HCO_3^- (from the kidney) as well as molecular CO_2 (from the gills), depending on the environmental pH and carbonate levels. This is a way of regulating blood pH (physiochemical buffering).

The effect on the physiology of marine fish species of increased concentrations of CO_2 in sea water, and the associated effects of increased HCO_3^- and pH, is dependent not only on the magnitude of those increased concentrations, but also on the tolerance of the particular marine animal.

Information is limited on the tolerance and physiological responses of most species. However, fish can be grouped in two broad categories, having different taxonomies and ecologies (Pörtner and Reipschläger 1996):

- Pelagic fishes which inhabit the water column. These can be further divided into species inhabiting inshore waters and off-shore oceanic waters. This group is adapted to constant, low CO_2 concentrations, and is expected to have a low tolerance to fluctuations in CO_2 and pH.

- Demersal (benthic) fishes which as adults spend their lives on, or close to, the sea bed, and can tolerate variations in CO_2 resulting from varying oxygen consumption and anaerobic metabolism of bacteria and fauna.

The fauna of open offshore waters will be adapted to a hig-oxygen environment, except for in-fauna in the sediments. One may therefore expect a fauna of rather limited CO_2 tolerance in these waters, compared to organisms living in low-oxygen water and near interfaces to anoxic layers. They may also be exposed to low water temperatures and thus have a reduced metabolic rate. However, long term exposure of high CO_2 concentrations may lead to sub-lethal or even lethal effects even on tolerant species, making such organisms as well suitable to act as possible indicators of CO_2 leaks.

Where CO_2 and other gases escapes naturally through the seabed and into the seawater, the bottom fauna will over time adapt to the conditions of the source. This is observed at anomalous sites, such as black smokers and hot vents where extreme forms of fauna may have formed and exist. At other (shallower) locations, the fauna can remain more or less undisturbed outside a limited radius from the source. Closer to it, a change in characteristics occur, with possibly only bacteria existing near the centre of the emission. Such bacteria colonies are often clearly visible.

4.3 Tolarence treshold levels

Threshold values represent a useful tool for the evaluation of the biological impacts from a certain ambient parameter on a certain species or test organism. The threshold value may be defined as mortality rate (response) related to a certain dose (concentration and exposure time), or to the appearance of specific physiological, behavioral or physical disorders that can be related to the impact parameter. **Figure 10** shows an example of exposure data for marine organisms to reduced pH levels.

Similar experiments for the study and determination of tolerance levels of CO_2 exposure should be planned and designed to exclude disturbances from other ambient parameters like temperature, O_2 etc., which should be kept constant.

Some experience may be drawn from fresh water fish. Long term exposure of rainbow trout to elevated CO_2 (50-60 mgL^{-1}) leads to severe kidney damage, characterized by calcification and granuloma formation in kidney and stomach, followed by secondary lesions, a condition denoted as nephrocalcinosis. The condition has been observed in farmed rainbow trout *(Oncorhychus mykiss)* both in freshwater and in sea water (Bjerknes et al. 1994; Poppe et al. 1995). Increased blood bicarbonate, due to physiochemical buffering, could lead to increased urinary excretion of bicarbonate with a subsequent rise in urine pH, which may again lead to precipitation of calcium hydrogen phosphate. Similar conditions have been reported from other fish species (e.g. turbots), and is often referred to as "hepato-renal syndrome".

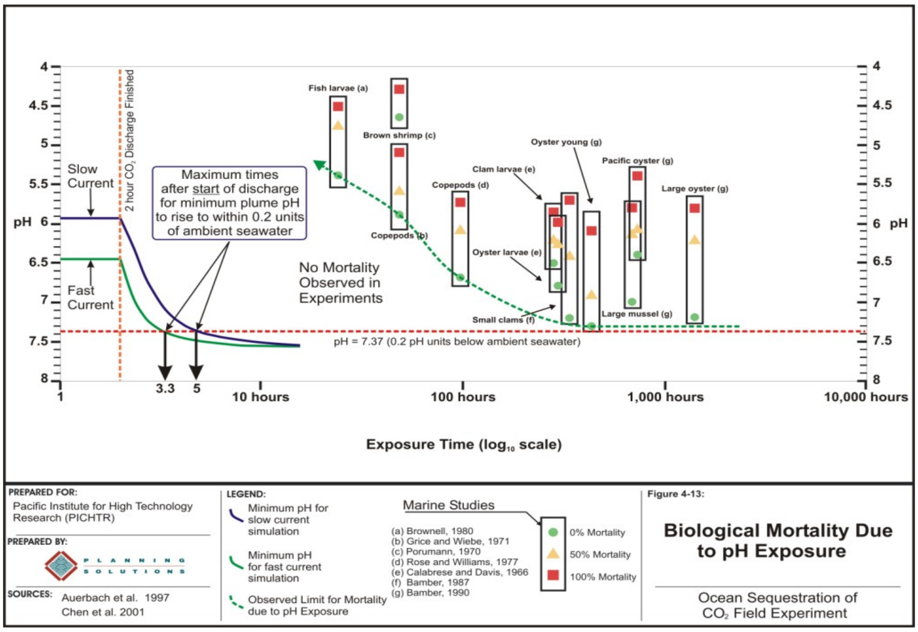


Figure 10. A compilation of results for exposure tests on marine organisms due to reduced pH (not necessarily due to added CO_2.) The figure was made in 2000 by PICHTR, Hawaii and MIT in connection with pre-studies for a CO_2 injection experiment.

Effects of CO_2 are mediated through lowering of pH (Magnesen and Wahl 1993), which may have a toxic effect on the fauna or a hampering effect on the production of calcareous structures. The tolerance will vary from one species to another. If CO_2 that leaks, causes effects on the benthic layer community level (e.g. changes in tropic dynamics, shift in relative abundance of feeding types, changes in diversity and dominance patterns) such results may be transferable to mesopelagic communities.

4.4 Feasibility of impact studies

In the present context of CO_2 leaks it is important to study the possible impacts on the natural communities, populations and individuals, under conditions as close to a real leakage situation as possible. This means that the effects of CO_2 enrichment preferably should be studied *in situ*. The feasibility of doing effects studies directly on populations at several hundred meters of depth is rather low.

Some *in situ* studies of metabolic activities of deep water species have been made (examples given by Shirayama 1995, and Berge et al. 2006). But in general the technology available for *in situ* studies will cover various types of remote qualitative and quantitative sampling procedures (by e.g. grabs, sleds, trawls, and plankton nets), which give species compositions, abundance and biomasses, possibly coupled to optic or acoustic instrumentations giving spatial information primarily of dense aggregations of plankton and fish. The sensitivity of these methods to detect any impact of CO_2 depends on the effects being manifested as changes in species composition, abundances and spatial distribution (behavior). In many cases one must anticipate lethal effects, i.e. individuals to disappear to give quantifiable effects on species compositions and abundances. If the idea of an exposure experiment is not to push the system to lethality, there is reason to doubt that effects can be detected *in situ* by such traditional methods. There are, however, a couple of possibilities that may be considered.

For sub-lethal biological effects of CO_2 to be ecologically significant they should directly or indirectly lead to changes in population growth and reproduction. Individual size and biochemical composition (e.g. lipid content and/or fatty acid composition) of important pelagic and benthic species represent in a sense the integrated effect of past growth conditions, and can be measured on samples taken by conventional means. Also population structure of certain forms (such as crustaceans): relative abundance of various stages and fecundity of adult females, may be studied on basis of conventional samples, and should reflect impact of ecological significance.

Although many experimental studies have been done on the effects of CO_2 (and of pH) on marine organisms in general there may still be aspects of the sub-lethal effects of CO_2 on deep organisms which ideally should be studied in laboratory experiments, possibly under high pressure. Examples are effects on behaviour and on metabolic functions. The relevance of such studies relies not only on the creation of a realistic exposure scenario, but also on the feasibility of obtaining live organisms from these deepwater communities and keep them in the laboratory in such a way that they function normally. For the latter it is essentially unknown to what extent the decompression from depth to the 1 atm laboratory situation will influence the functions and responses one will study.

Leaving this, it is clear from past experiments that several species may be used successfully in experiments. Examples from the past are the copepods (Hirche 1983, Alvarez and Matthews 1975, Båmstedt and Holt 1978) euphausids, benthic decapods and bivalves. All these species have been kept in aquaria for extended periods of time and have been used for e.g. feeding and growth experiments.

4.5 Benthos

Sub-seabed storage of CO_2 may affect marine life and especially benthic organisms if CO_2 accidentally leaks e.g. through the cap rock and into surface sediment and overlying water. Such effects are especially related to the large changes in seawater chemistry that is anticipated in the vicinity of a site were the CO_2 is accidentally released. Most important is probably the lowering of the pH (several pH units according to model studies).

It is therefore relevant to pay special attention to benthic animal communities. However, there is limited data about the environmental effects of low pH seawater on such communities. Some experiments have been performed in the deep sea and in mesocosms and laboratories, but very few in-situ, in shallower waters. Data are therefore urgently needed to quantify the potential impact of leakage on benthic marine organisms and processes.

There are already clear indications that CO_2 leakage will cause high mortality rates and stress for nearby infaunal deep communities (Barry et al., 2004, Thistle et al. 2007). Unpublished results from mesocosm experiments also indicate effects of low pH on benthic diversity in shallower waters in fjords (Steve Widdicomb unpublished results). Also experiments performed on sediments at 400 m depth in a Norwegian fjord (Ishida et al. 2006, Berge et al. 2007) showed effects of elevated CO_2 concentrations on biological processes e.g. reduced bacterial density and increased nanobenthos and Archaea (a prokaryote group different from Bacteria) densities. Methane formation and sulphate reduction was also affected.

Previous studies found little evidence of harmful effects in marine organisms of a decrease of 0.5-0.1 pH units in their habitats (Knutzen, 1981). More recent investigations have indicated a more complex response to lowering of seawater pH. Some types of sediment living animals (meiofauna) are relatively tolerant to a pH reduction of less than 0.5 units (Barry et al, 2004). Other species like echinoderms are more sensitive and it is reported that growth of four-armed pluteus larvae of sea urchins is effected by lowering of pH by approximately 0.1 pH units (Kurihara et al. 2004). There are, however, also indications that some individuals of adult stages of sea urchins my survive in acidified water for expended time periods and that mortality is reduced to almost zero if the acidification cesses, but a pH of 5.6 will cause 100% mortality within 2 weeks (**Figure 11**).

Lower susceptibility to pH reduction is expected for marine organisms in coastal surface water than in deeper parts of the ocean due to the higher natural variability in pH in the surface, especially in coastal areas. The blue mussel *Mytilus edulis* is a common intertidal organism. Experiments have demonstrated that growth of this organism is decreased at a pH of 7.1 and virtually no growth is observed at a pH of 6.7. The effect seems to set in between pH 7.4 and 7 (Berge et al. 2006).

The sediments that make up the majority of seabed habitats play a crucial role in many important marine processes including the cycling of key nutrients within coastal and shelf sea ecosystems. It has been demonstrated that CO_2 induced lowering of pH may effect nutrient fluxes through the sediment/water interface (Widdicombe and Needham, 2007). Their experiments show that nitrite flux changes when pH falls from 8.0 to 7.3. However, in the case of nitrate, ammonium and phosphate a much greater change in pH is required (pH between 7.3 and 6.5) before responses are observed.

The limited present knowledge on effects of CO_2 on benthos indicates that an accidental leak through the cap rock or a well and into surface sediments and overlying seawater will influence benthic species quite heavily, at least in the near field of the leak. We still need more detailed knowledge on possible effects in order to foresee the full consequences of a leak. Even though the likelihood of a leak is probably small and that the ecological consequences thereof may be limited, it is still of importance to be able to assess the environmental damage on biota at stake and to enable proper monitoring arrays and methodology to be applied at storage sites.

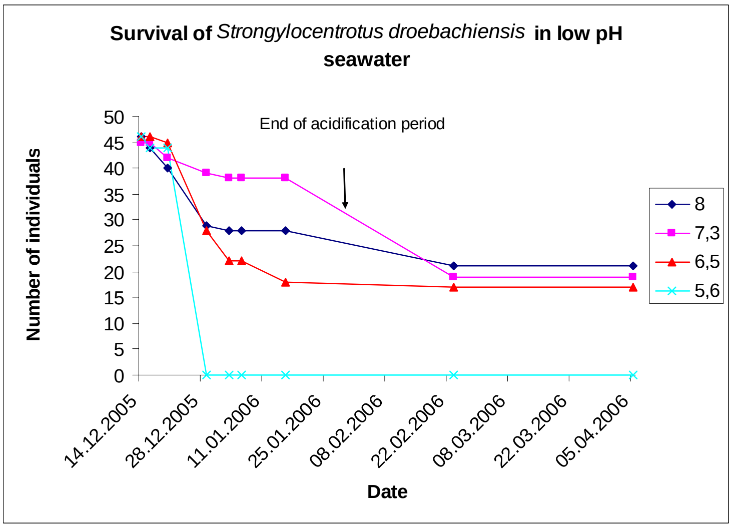


Figure 11. Survival of sea urchins exposed to CO_2 induced acidification seawater. The urchins were exposed to 4 levels of acidification were pH=8 is considered the control situation (NIVA, unpublished data).

4.6 Ocean acidification

The ocean is now under influence from the increasing atmospheric concentration of CO_2 that causes increase in pCO_2, and a decrease in pH and CO_2^{2-} concentration. This *ocean acidification* is expected to continue to a level of 0.3 – 0.4 below the present pH level at the end of the present century (IPCC

2007), and is projected to create significant effects on calcifying organisms in the upper, productive layers.

Such organisms rely on ample concentrations (supersaturation) of building material in the seawater such and calcite and aragonite. As the pH decrease, this supersaturation condition may not longer prevail, causing a gradual decline in the growth conditions for shells, corals etc. Due to the vast geographical, ecological and economical scale of this scenario it looks much more sinister that those that may be set up due to CO_2 storage leaks.

Scientific studies on ocean acidification is still in its infancy, even though quite clear warning signals were given already 40-50 years ago (Bolin and Eriksson 1959, Fairhall 1973), research on ocean acidification is still in its infancy. Much of the recent literature on ecological impacts stem from studies on ocean storage of CO_2, especially by Japanese and US groups. As the chemical and biological settings are much the same for the two CO_2 exposure situations, experience can be exchanged between scientific communities that work on either issue.

Although storage of captured industrial CO_2 in the ocean or sub-seabed may have local impacts from increased pCO_2/decreased pH, it must be remembered that the result of reducing the greenhouse effect and ocean acidification globally by applying such CCs technologies by far outweights the possible local impacts.

5. Monitoring of the seabed

5.1 General considerations

As the offshore oil and gas industry moves further offshore and deeper so also is the development of more and more advanced techologies escallating to comply with the new environmental challenges. Recent progress in oceanographic research in the deep water and benthic layer has been much accelerated by such new industrial technologies and novel approaches.

Seawater chemical and hydrodynamic properties can now be measured with instruments of high spatial and temporal resolution and with large data-sampling capacity. These include boundary layer current and turbulence measurements with miniaturized flow and skin-friction sensors, 2- and 3-D flow measurements via PIV (Particle Image Velocimetry) or LDA (Laser Doppler Anemometry), as well as the use of laboratory flumes for experimentation and instrumentation, such as benthic landers, for direct observations on the sea floor and collection of *in situ* data.

On the smallest scale, the increasing use of microsensors for a variety of chemical and physical parameters has been of prime importance to the understanding of transport processes and microbial activity at the sediment-water interface (McCave 1976, Boudreau and Jørgensen 2000). Simultaneously, advances in theoretical and numerical modelling have made it possible to test ourhypotheses with regard to BBL phenomena and to comprehend quantitatively BBL processes from extensive and complex field data.

Yet, our understanding of the complex physics of BBL and the interactions between fluid flow and sediment topography is still limited.

Successful studies on the deep layers of the ocean rely on the ability to extract useful information from a vast inventory of data, and the qualified interpretation of large spatial or temporal scales. Often intermittency dominates the picture with short and infrequent periods of extremely high shear stress, caused by high current velocity or wave action or flow instabilities. *In situ* experiments on CO_2 exposure must also catch such events in order to provide a more realistic picture of seabed dynamics.

The interactions between living organisms and their physico-chemical environment may be unexpected or unpredictable. Biology affects nearly all aspects of the benthic boundary layer: dampening of turbulence, aggregate dynamics, sediment deposition and resuspension, boundary roughness, interface topography, sediment porosity and diffusivity, nutrient exchange, porewater chemistry, etc.

Several free vehicles have been constructed over the past decades, initially, mostly for short-term and stationary deployment. Mobile "rovers" have been developed that can operate on the seafloor for weeks or months, while repeatedly doing measurements and manipulations. These move from place to place in order to cover a variety of sediment surfaces and to escape the disturbance caused by their own presents and experiments. Furthermore, long-term time-lapse video recordings of the deep-sea floor over the seasons have provided new and stunning pictures of the highly dynamic environment of the sediment-water interface (Bourdeau and Jørgensen 2000).

For sub-seabed CO_2 storage it will be important to apply tools that can prove that stored CO_2 does not reach the seabed (this is the ultimate demonstration of containment, underpins carbon credits, re-assures the public etc). This can be done for instance by monitoring gases in the sediments of the sea above it. However, the challenge remains as to how small a release of gas could be detected given the natural fluctuations in (dissolved) gases. Technical progress is also needed to speed up surveying and to refine low cost automatic monitors. This can be addressed through an integrated assessment of a range of gas monitoring approaches, further developing and assessing methods used for industrial demonstration projects at sites/natural analogues where leakage is known to occur.

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 "permanence", i.e. 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. Recent studies have begun to provide that knowledge as well as testing and developing appropriate monitoring technologies. This work is also clearly understandable to the general public.

Some near-seabed tools for monitoring leaks:

a. Gas monitoring tool development
b. Remote sensing
    - direct gas detection
    - pH measurements
    - sediment displacement
c. Impacts on microbiological communities
d. Impacts on invertebrates
e. Impacts on marine vertebrates

5.2 Prior experiments and experience

Several investigations and experiments have been performed in order to assess and quantify the ecological impact from increased CO_2 concentrations at or near the seafloor. Prior experience from related experiments, and from "natural analogues" sites, may be worth-while considering here.

5.2.1 Benthic chamber experiments

In-situ marine exposure tests by using benthic chamber systems (**Figure 12**) have been performed in Japan and also Norway in recent years (Ishida et al. 2006). They have shown that a seabed microbiological communities exposed to elevated CO_2 concentrations are affected. This also applies to meiofauna and nanobenthos.

The presently used Japanese free fall type benthic chamber has three equal chambers is a modification of the design of the German GEOMAR Institute (Witte and Pfannkuche 2000; Pfannkuche and Linke 2003). The system allows penetration of each chamber to a predetermined depth of sediment so that the same headspace volume of water and other physical parameters can be pre-set and kept as equal as possible. The concentration of CO_2 (pCO_2) or other gases in the chambers can be adjusted to a pre-determined level in each chamber. To increase the pCO_2 in the chambers, KANSO developed a device that can inject seawater with high pCO_2 into each chamber. The pCO_2 of the water in each chamber space can then be monitored by pH sensors and dissolved oxygen by DO sensors. To calibrate the data obtained by sensors and to obtain additional water quality data, seawater can be sampled autonomously up to 6 times using 0.5 or 1 litre aluminium bags.

The Benthic Chamber system is a powerful, reliable and cost effective tool for performing experiments on small sections of sediment in situ also at medium and large depth in the ocean. For such large depths, there are few real alternatives to making pre-programmed, in-situ exposures, due to the difficulties of bringing sediments up and to shore without to much disturbance of the sediments and the organisms adapted to the deep sea conditions.

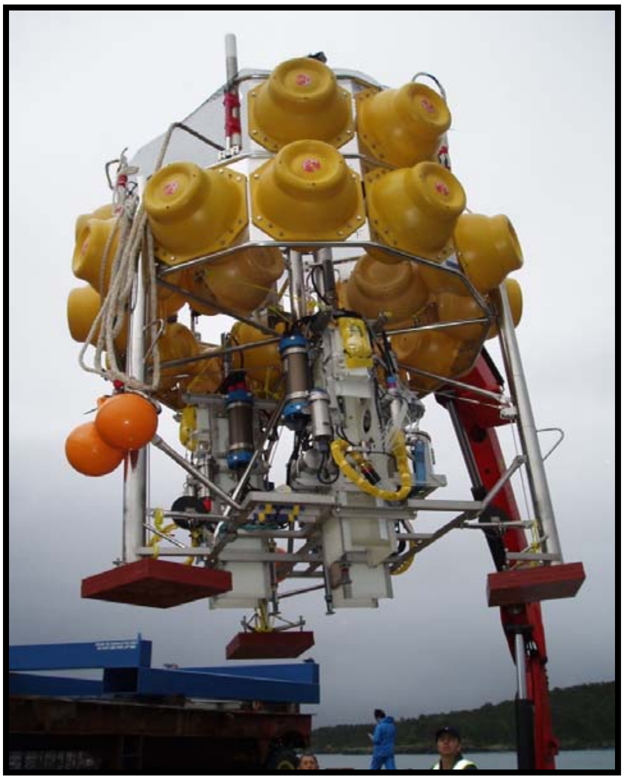
Experience shows that the sediment within the enclosed chambers remains quite undisturbed during exposures. The experimental conditions during experiments within the chambers can be well controlled both through recordings performed by electrodes and by the water samples withdrawn automatically throughout the experimental period.

The size of the chambers renders the system suitable for testing effects of CO_2 etc on sediment geochemistry and small organisms, especially bacteria and nanobenthos but also meiofauna. Present results indicate stimulation or inhibition of distinct groups of micro organisms as a consequence of the exposure of the sedimentary environment to elevated CO_2 concentrations.

Measurements of physical/chemical characteristics that require small sensors or samples of sediment can be performed both in-situ and in the lab after recovery.

Experimental data from using a BC helps to improve our understanding of the effects of rising CO_2 level and pH decline in the ocean. Experiments provide valuable as input to ecological models for CO_2 impact assessments. The BC can also be used for pre-surveys at proposed sub-seabed CO_2 storage sites, in order to assess the vulnerability of the bottom ecosystems to (accidental) leaks of CO_2.

From studies by devices such as a benthic chamber system it should be possible to identify candidates in the microbial flora/fauna, whose presence, absence or ratios of abundance could provide easily detectable and accurate indicators for the leakage of CO_2 from deep reservoirs into near-surface marine ecosystems. Results indicate that the bacteria/archaea ratio could be such an indicator, but this needs to be confirmed by additional, refined experiments.



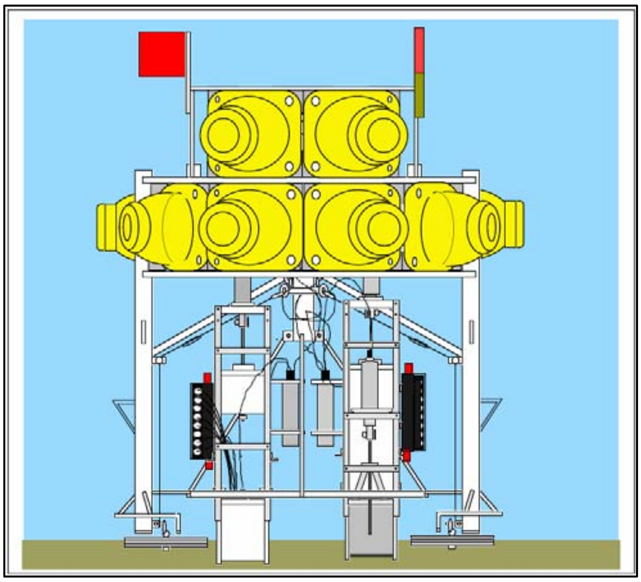


Figure 12. Left: the benthic chamber ready to be deployed in Storfjorden, Norway in August 2005 during CO_2 exposure tests there (Ishida et al. 2006, Berge et al. 2007). Right: Sketch of the chamber rig on the seabed, by Hirsoshi Ishida, Japan.

5.2.2 The MBARI experiments

The Monterey Bay Aquarium in California has hosted several deep-water experiments with CO_2, by studying the behaviour of the liquid CO_2 and it's dissolution, and the reaction to CO_2 by fish and other deep water organisms (Brewer at al. 2004, Barry et al. 2004). Also Norwegian researchers (from UoBergen) have taken part in these experiments that have been lead by prof. Peter Brewer.

The experiments have been performed at depths of more than 3000 m off California by using advanced ROVs (**Figure 13**), and have provided valuable insight both on physical and biologcial aspects of adding CO_2 to the deepwater.

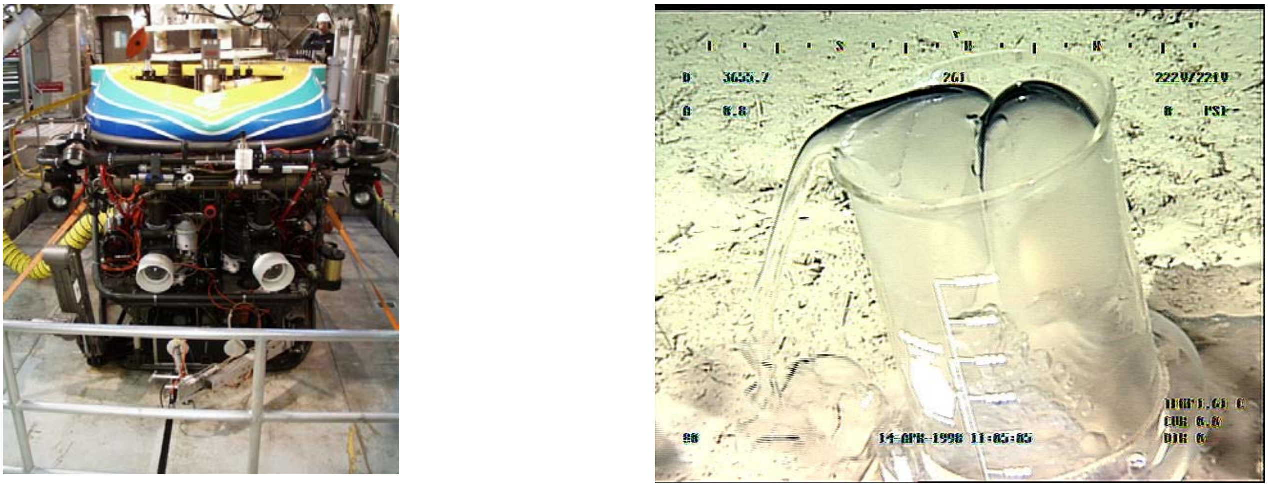


Figure 13. Left: The ROV at MBARI used for deep water CO_2 experiments. Right: A beaker at the seabed filled with liquid CO_2. Photos by P. Brewer and his group.

5.2.3 The Loihi underwater vulcano in Hawaii

As part of the international CTI-project on ocean CO_2 sequestration, surveys and biological exposure experiments were made at the Loihi Seamount near Hawaii (USA), in 2002. This was done to gain experience from a “natural CO_2 analogue”. Loihi is a tall underwater seamount, extending from >5000 to ~1000 m depth. The centre of the volcanic crater is at ~1300 m depth. In the crater and along the crater walls there are areas with vents and chimneys, with different emission rates and different chemical composition and signatures. The hydrothermal vents emit up to 100.000 tons of CO_2 per year. CO_2 concentrations exceeding 400 mmol kg-1 have been encountered in seawater near-by.

Compared with other known hydrothermal vent sites, the temperature of the emitted fluid is low relative to the CO_2 content. The content of other (toxic) chemicals is also comparatively low. This makes the Loihi site useful for biological observations and experiments, since any effects on biota will predominantly be due to elevated CO_2 and not temperature or other chemical constituents in the vent effluents.

In December 2002, members of the International project on CO_2 sequestration investigated the area by using the manned submersible PISCES V (**Figure 14**), launched from the R/V Ka’imikai-O-Kanaloa.

In addition to visual/video observations the submersible carried gas and water sampling equipment and a CTD with an *in situ* pH-sensor. An example of the difference in pH between areas away from and inside a vent plume is shown in **Figure 15**. Previous measurements at Loihi have shown pH as low as 4.2-4.4 (Karl et al., 1988; Sedwick et al., 1992).

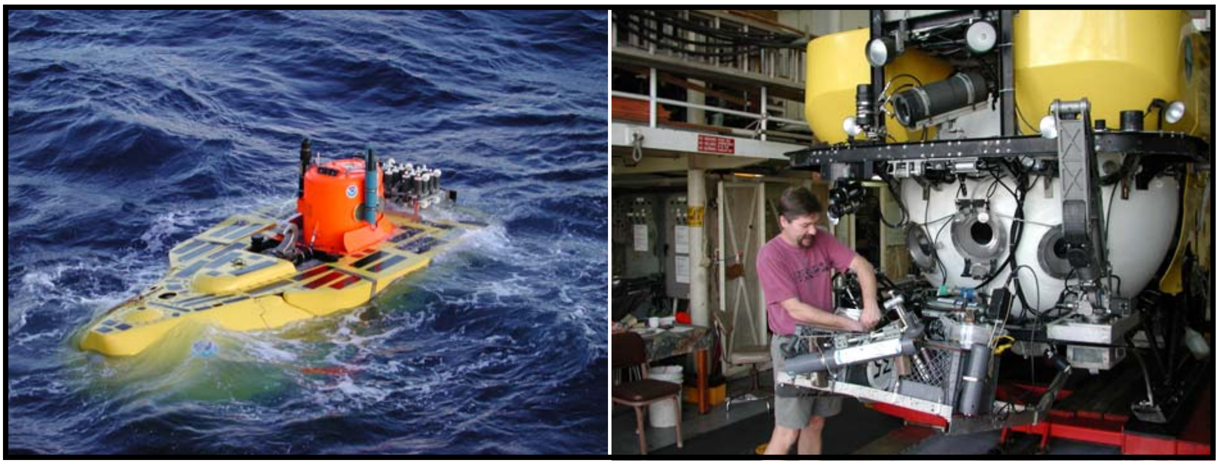


Figure 14. Submersible PISCES V used for the Loihi experiments in 2002.

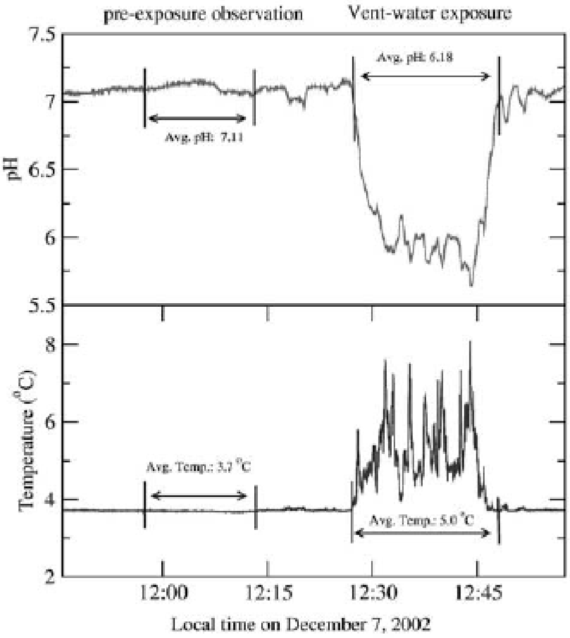


Figure 15. Upper frame: Measured pH outside (left) and inside (right) a vent plume in the Loihi crater. Bottom frame: Measured seawater temperature for the same transect. From Vetter and Smith (2005).

The biological studies at Loihi consisted of 1) trapping and exposing animals to vents, and 2) experiments where bait was used to attract scavengers and monitor their behaviour near the vents. A rather low number of species were found in the area. Amphipods were most abundant while eels were the most dominant scavengers. A much larger number (1-2 orders of magnitude) of animals were found at Loihi/near vents than at distant control sites.

The exposure experiments showed the following (Vetter and Smith 2005):

1) First, increasing amphipod activity in the trap (trying to escape)
2) Within 10 minutes of exposure start, 90-95% of animals were inactive (anesthetized)
3) When the traps were removed after one hour of exposure, all animals woke up and resumed active swimming
4) As submarine ascended after experiments, animal activity ceased when temperature exceeded 10-11 ºC and die at 13 ºC.

The experiments at Loihi indicate that the studied animals (amphipods) can survive short-term exposure to high CO_2 levels. The experiment was not designed for long-term exposure.

The scavenger experiments showed that bait parcels positioned away from the main venting areas were approached by scavengers within minutes of deployment, and consumed within 24 hours. Bait deployed within vent plumes were untouched – scavengers were seen to be first attracted but then avoiding the bait when getting very close to plume. These animals appear to be able to detect and avoid low-pH areas. The observation of large numbers of scavengers in the crater suggests that more carrion (biological waste material) is deposited near the vents. This could be due to higher mortality rates in pelagic species that are unable to escape actively. The above also implies that there could be accumulation of detritus within the "core" venting areas – there could be elevated morality rates and at the same time less scavenging.

The experiments at Loihi suggest that changes in species composition/abundance – and behaviour – can be used as indicators of CO_2 leaks. In natural-source experiments like this it is crucial to measure all other relevant parameters; e.g. temperature, other chemical constituents, bacterial activity, to make sure that observed biological responses are due to the effects of CO_2 and not to other factors.

5.2.4 Panarea natural analogue

Near the island of Panarea (Aeolians, Italy) CO_2 vents are found at 10-25 m bottom depth (**Figure 16**). Previous surveys carried out by the University of Rome - La Sapienza - have shown that the topography is rather flat, prevalently consisting of gravel and sand. Gas leaking areas are varied, with both diffuse and strong localized vents, with a wide range of flow intensities. The gas vents are mainly aligned along the tectonic features of the area.

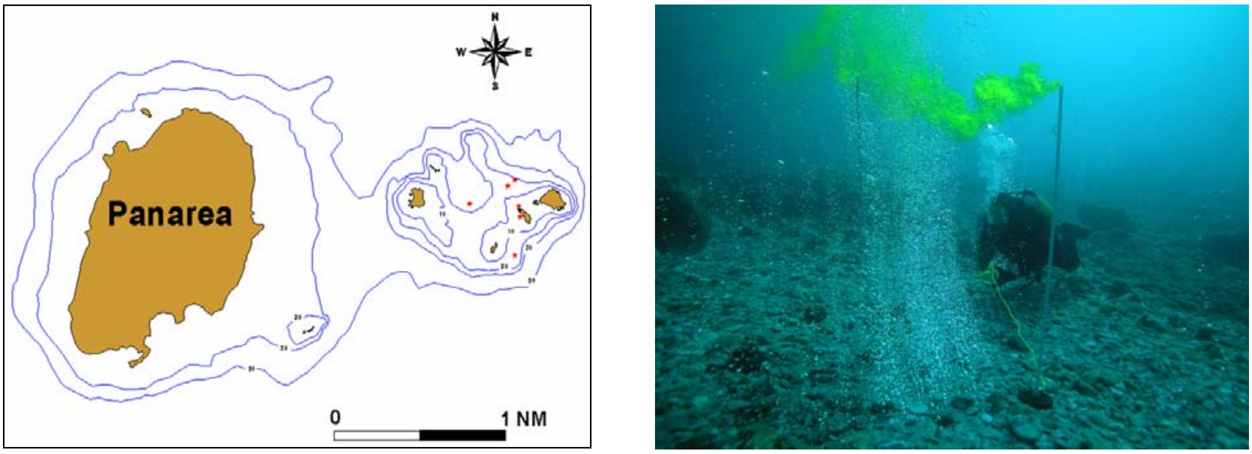


Figure 16. Left: The Panarea area. Gas vents are indicated by red dots. Right: Gas seeps near Panarea, Italy, during a tracer release survey. Photo by Giorgio Caramanna, Roma.

The measurements and analysis of the Panaera area so far comprised:

- Underwater sampling of fluids (water and gas), solid deposits and biological material
- Gaschromatographic analysis of the gases
- Development of fluid samplers and sampling techniques to be used underwater (i.e. gas and water sampling, gas flow measurement, biological monitoring)
- Measurements with ADCP current meter, CTD (hydrography), and *in situ* pH-sensor (Univ. of Rome in collaboration with NIVA)
- Video and photographic documentation (**Figure 16**)

The gas plumes contain a high proportion of CO_2. Sample analysis indicates the following minimum annual mean flow rates for the dominant gas constituents: CO_2 – 850 000 m^3/m^2, hydrogen sulphide (H_2S) – 20 000 m^3/m^2, methane (CH_4) - 105 m^3/m^2.

In situ pH measurements allow for the water volume influenced by strong CO_2 dissolution to be delimited under varying environmental conditions (**Figure 17**).

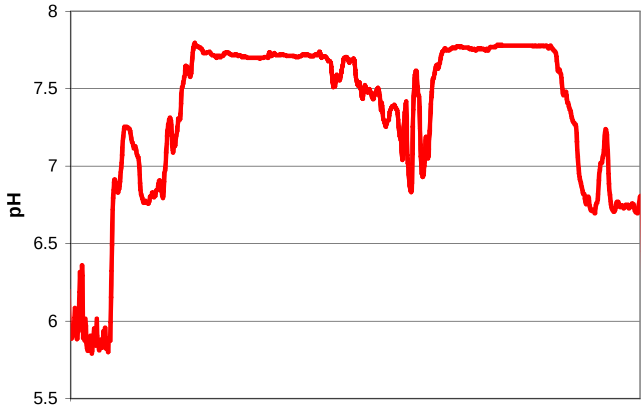


Figure 17. Plot of pH measured during a dive between strong vents. Background pH values in the vent area were ~7.75-7.8 (compared with ~8.0 on nearby reference station). Inside vent plumes pH could be lower than 6.0.

The wide range of leaks, the shallow depth and local infrastructure are favorable for the use of Panarea as natural analog for the study of CO_2 leaks on the marine ecosystem. It appears to be a good location for testing of “state of the art” technology for underwater monitoring of CO_2 (e.g. buoys ,gas and pH sensors and underwater stations). Further studies to verify the effects of CO_2 on marine biota can also be carried out at Panarea. The relative ease of measuring small-scale as well as background currents and hydrography in this shallow area allows for necessary data for numerical modelling of plume behaviour and CO_2 dissolution to be gathered.

6. Summary and suggestions

The report attempts to describe the present status regarding the leakage concerns related to sub-seabed storage and furthermore to describe likely ecological impacts of CO_2, with parameters or organisms that may be suitable as indicators. The latter will be of importance when establishing a monitoring and survey programme at specific storage sites, which we anticipate and highly recommend will become compulsory.

Scenarios of possible leaks will at any rate be hypothetical and with significant uncertainty both on size, duration and timing of an event. And the existing knowledge about ecological impacts is too limited to enable us to pinpoint actual indicator species. Still, this preliminary review allows for some thoughts into what should be target research and development tasks in the near future.

There is a documented knowledge gap in the understanding of marine ecological responses to CO_2. This also applies to what may be suitable indicator species, acting as “canary birds” to warn about a leak. Furthermore, there is need to develop new tools and methods both to study impacts, and for future monitoring of sites. Some such developments, e.g. of sensors, may go hand-in-hand with ecological studies and successful products will become components of future monitoring. New sensors may be applied both in the lab and in-situ, accompanying ecological experiments.

The nature of the problem and the hostility of the environment where to conduct research imply there will be a significant risk of failure associated with some projects. This has to be taken into account, both in funding and when appointing e.g. PhD students to specific tasks. Care must be taken to ascertain that the candidates get sufficient material for their dissertations. The more risky or long-lasting projects should be left for permanent staff at the institutions to handle.

The previous descriptions were tentatively based on a Norwegian setting, but the material presented will be relevant in a wider context as well. Most existing information and studies on CO_2 exposure to organisms have at any rate been gathered elsewhere, only a couple of studies have been performed in Norway. This fact in itself calls for enhanced efforts in Norway where CCS with sub-seabed storage is a key political issue that has been flagged vigorously the past couple of years.

A handful of Norwegian researchers are involved in relevant research already, and several are engaged in international networks and projects. If Norway should play up to it’s international expectations on CCS, a significant increase in the spending on R&D relevant to this is required, and this also counts for the storage aspects.

At the beginning of 2008 there is an existing baseline of activities, personnel and equipment in Norway that may be available for follow-up studies. Furthermore, there are some projects about to begin, or in the pipeline, that may provide financial opportunities for follow-up. Below we mention a couple of such examples, without attempting to be complete.

6.1 Some leak indicators

The previous presentation point to some physical characteristics and animal groups etc that may be more sensitive than others and act as indicators of leaks, although single species for this purpose have not been found yet. The following list shows some such indicators, or anomalies to look for.

- Unusual mortality of organisms (e.g., amphipods, decapod shrimp and teleost fishes).
- Unusual mortality of fish, squid, or other free-swimming organisms in the water column.
- Biologists observe unusual mortality of benthic organisms/changes in biodiversity
- Changes in the bacterial community. Experiments indicate that bacteria/archaea ratio can be a possible indicator

- Observation of a stream of CO_2 droplets reaching the surface.
- pH levels below 6.0 are observed.
- Large aggregations of organisms are observed, possibly indicating a CO_2 enriched plume.

6.2 Suggestions for follow-up projects

6.2.1 The Norwegian CO2Fieldlab project

This project will commence in early 2008 and may provide a possibility to study CO_2- sediment interaction and marine impacts, although the emphasis will be on geological and terrestrial aspects. One objective is to provide data needed to verify scientific principles and to test, validate, and eventually refine existing computer and laboratory models concerning the behaviour of CO_2 in the unlikely but yet possible scenario that it migrates through the cap rock and into the shallow sediments. The other objective is to find or develop robust methods for monitoring and detection of any leaks of CO_2 through the seabed by visual (photographic), acoustic, chemical or biological methods, or a combination of such methods.

Various scenarios for the behaviour and fate of CO_2 reaching the top of the sediments has been envisioned.

A: to study the behaviour of CO_2 in shallow sediments, including interaction with pore water. This CO_2 may either come from the deep injection of the geological part of the project. Or, alternatively, from gas deliberately injected into shallow layers of the sediments (a few meters deep, **Figure 18**). The latter will ensure that significant results can be achieved through the project period of three years. The first one would be the preferred route, but it cannot be guaranteed that gas actually will migrate from the deep injected pool laterally or upwards within the time dedicated to the study. A list of topics:

1. Measure actual fluxes of CO_2
2. Monitor the fate of CO_2 dissolving in the seawater, e.g. if it collects in enclosed "pools"
3. Monitor/measure the dissolution of CO_2 in pore water
4. Examine pH changes in the pore water and possible effects on metal fluxes through the sediment/water interface;
5. Sample and measure sediment chemistry due to redox processes (CO_2 reducing oxides to metals etc)
6. Determine changes in sediment microbiology and meiofauna
7. Determine effects on and changes in macrofauna abundance and biodiversity

B: Studies of gas entering the seawater. Such a setting will have many objectives, e.g.:

1. Investigate CO_2 (droplet) cloud dynamics, visual characteristics and fate of the CO_2
2. Examine pH in the cloud/plume and on its margins;
3. Clarify effects that hydrates might have on CO_2 dissolution;
4. Trace the evolution of CO_2-enriched seawater resulting from CO_2 dissolution;
5. Assess potential impacts on aquatic bacterial biomass, production, and growth efficiency associated with induced changes in seawater pH in the vicinity of the injection or leak point and
6. Examine the variable effects of a range of CO_2 leakage rates.
7.

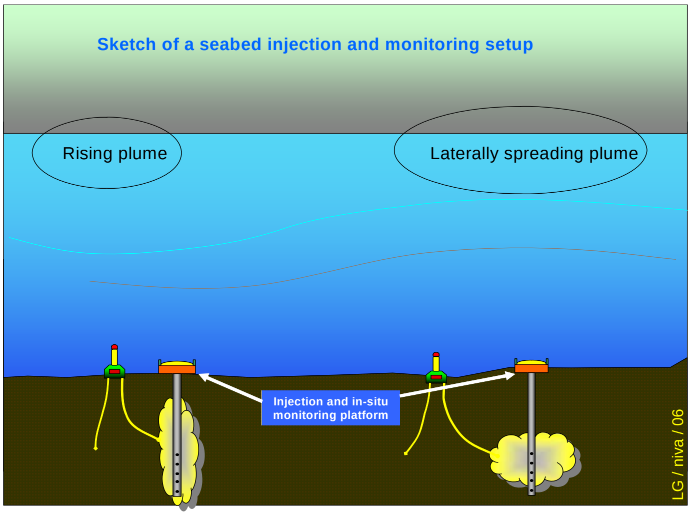


Figure 18. A suggested set-up with a shallow seabed CO_2 injection platform and monitoring devices, for two plume scenarios.

6.2.2 Benthic chamber alternative design

As a follow-up to the present study it is proposed to obtain a new chamber system in Norway. The rather limited size of the existing chambers [20 x 20 cm in width, 28 cm in total height] does not allow for studying macrofauna, and also poses some limitations for meiofauna analyses. The system has three chambers which to some extent limits the number of replicate treatments. In the Storfjorden experiments in 2005 this was partly compensated for by performing two similar deployments, one right after the other.

Ii is possible to make the chambers larger, and also to put one or more extra chambers to the assembly, by expanding the surrounding cage if necessary. In order to evaluate the impact to the ecosystem of possible leakages from sub-seabed storage it is probably more optimal to develop an experiment design that increases CO_2 also directly in the pore water. The existing benthic chamber system can be modified to accommodate such a design. Preliminary studies do, however, show that pore water pH (and pCO_2) will gradually change also when the CO_2 enriched water are added to the headspace, as before.

Macrofauna are important prey organisms for bottom living fish. New experiments should therefore also focus on CO_2 exposure of larger animals (macrofauna). This may require a modification of the setup, possibly by some sort of collection of larger animals and placing inside chambers or in cages exposed to CO_2.

The BC experiments have been rather short-lasting, on the order of 10-20 days. Longer exposures may result in anoxia in the chamber headspace water due to respiration and metabolism, thus changing the experimental conditions. Longer exposure time may be required for some types of impact studies. This might be accomplished by adding some oxygenated water to the headspace, while still keeping the pCO_2 level constant.

Experiments with the chamber should be performed both inshore (deep fjords) to gain experience and baseline data and offshore, also including possible storage sites.

6.2.3 Natural analogues to escaping CO_2

In Norwegian waters or near-by there are only a few known natural analogues. The Haakon Mosby mud volcano in the western Barents Sea is primarily a NH_4 emitter, but may still be a valuable site for developing/testing sampling and monitoring methods.

Cold NH_4-seeps have been reported from several locations in the North Sea. Such cold seeps of thermogenic methane usually emit gas continuously, but may become inactive if subsurface gas and fluids are depleted. Such methane reservoirs usually lacks proper seals and free gas can migrate in sediments above to the sea floor. Usually streams of methane bubbles are detected, with patches of filamentous, microbial mats on the sea floor. High fluxes of methane usually lead to the development of methanotrophic microbial communities. Anaerobic methanotrophic archaea dominate submarine seep communities as they profit from the abundance of sulphate utilised as an electron acceptor (Niermann et al. 2005).

Seeps found at the Troll, Tommeliten, Gullfaks and Kvitebjørn fields in the North Sea have been documented (Hovland et al. 2007). Some seeps create pockmarks several metres deep. The continuous seeps are mainly of methane gas, where large patches of *Beggiatoa* bacterial mats occur, and are subject to international studies on microbiology. Research at such seeps presently focus on methane, but may also provide valuable locations as CO_2-“analogues”.

6.2.4 Sensors and equipment

Many kinds of instruments and sensors may be applied to monitor a future storage site.

A remotely operated vehicle (ROV) can observe features of the seabed and the behavior of any gas droplets or bubbles. At times it will conduct surveys across the seabed and collect samples from the water column and the bottom.

- Small instrument packages can be deployed from the research vessels on fixed moorings and will collect data from those locations.
- A research vessel can lower instruments to take conductivity-temperature-depth (CTD) measurements + additional sensors (for example for pH measurements) at varying distances from the site.

Relevant parameters:

- pH (using probes mounted on the ROV and on fixed moorings or on CTD instruments cast from a vessel).
- Carbon chemistry (including pH; measured in samples collected by a ROV and CTD bottles brought onboard ship).
- Sediment chemistry (pH, metal, samples collected by ROV/grabs/corers/DGT-probes
- Aquatic microbiology (bacterial production, respiration and community structure; measured in samples collected in bottles brought onboard ship).
- Hydrography (temperature, salinity and density measured using CTDs and instruments mounted on a ROV or fixed moorings).
- Benthic biology (from samples collected by a ROV or grab samples).
- Video observations using cameras mounted on a ROV.

The table overleaf shows instruments and measurements that can be associated with monitoring.

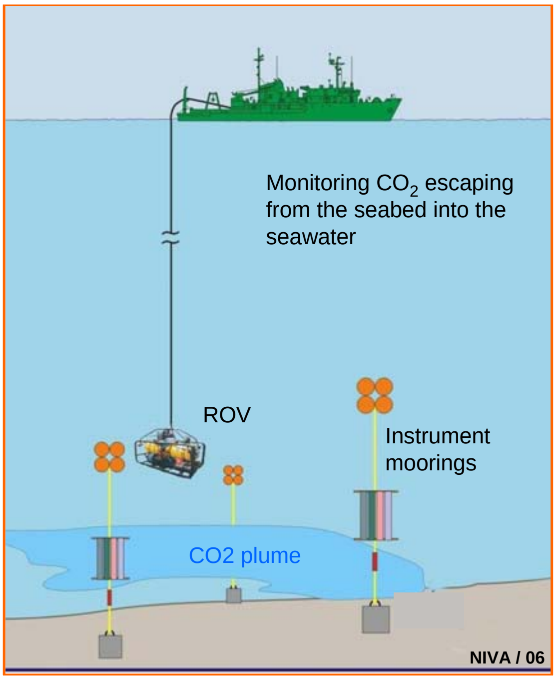


Figure 19. Sketch of a research vessel monitoring an escaping CO_2 plume from a leak. Figure adapted from the Ocean storage field experiment, PICHTR, Hawaii.

Table 1. Some parameters and methods that can be applied during a CO_2 survey.

Platform	***Instruments/*Measurements**
ROV	***pH Meters.*** pH meters preferably with real-time data transmission to the research vessel via the ROV umbilical. ***Video Camera/Recorder.*** Observations of biota in water column and on the seafloor to observe reaction. Because reactions are expected to be small and occur over a period of time, most analysis of these data would be done after the experiment is completed. ***PH Meters.*** pH meters with real-time data transmission to the research vessel. ***Geological Samplers***. Sampling devices to collect sediment and rock samples from the bottom for later laboratory analysis related to benthic biology and microbiology. Microbiological data will allow estimates of bacterial production, respiration, and community structure. ***Video Camera/Recorder.*** Observations of any CO_2 droplets. Real-time data transmitted from the ROV to the vessel via cable or observed and recorded internally. ***Video Camera/Recorder.*** Observations of benthos to observe reactions of fauna. ***Conductivity, Temperature, Depth Sensor.*** CTD sensors should also be included in the sensor package on the ROV to characterize the seawater bodies through which the mobile survey system travels. ***Water Column Samples.*** Samples collected using the CTD collection bottle for on board analysis of carbon chemistry and microbiological processes.
Fixed moorings	***pH Meters.*** pH levels – data are stored for analysis after the mooring is recovered.
Vessel	**Vessel requirements**

The instruments described may be used to monitor ambient conditions and perturbations resulting from a leak. Instruments on the ROV (e.g., a solid state pH sensor, a more traditional glass electrode pH probe, a fluorometer, an Acoustic Doppler Velocity meter (ADV), and a video camera) would measure continuously. These measurements can be available in real time and may be used to help guide the survey path followed. These surveys will focus on the near field.

6.2.5 Micobiological monitoring

To assess potential impacts of CO_2 sequestration on environmental health, variations in bacterial biomass, productivity, and growth efficiency can be determined and compared to conditions in the ambient water column. Measurement of nutrients (dissolved and particulate organic carbon and organic nitrogen) may be conducted for corollary analysis. These measurements would identify changes in substrate availability that can alter bacterial activity due to CO_2. The analysis of bacterial cycling rates may be combined with an analysis of the variation in bacterial genetic diversity to interpret stresses that might arise from pH changes.

6.3 How long to monitor a site

It has been argued against CCS that storage will require monitoring and control of leaks for millennia in order to be viable. This may not necessarily be the case. The first critical phase will be during start-up of injection. Any faults in the cap-rock or other pathways for escaping gas may reveal itself shortly after pressure increase.

Continuous monitoring throughout the injection period (30-40 years) will probably be necessary. If no leaks are detected by then, a permanent programme may be established that involve a low-effort, long-term control e.g. by annual inspections.

For the long-term monitoring the critical period may be up until the CO_2 concentration in the atmosphere has peaked and levelled off (**Figure 20**). If minor leaks occur after this, the global warming impact may be small. (But impacts of leaks e.g. on local aquatic life may still be serious.)

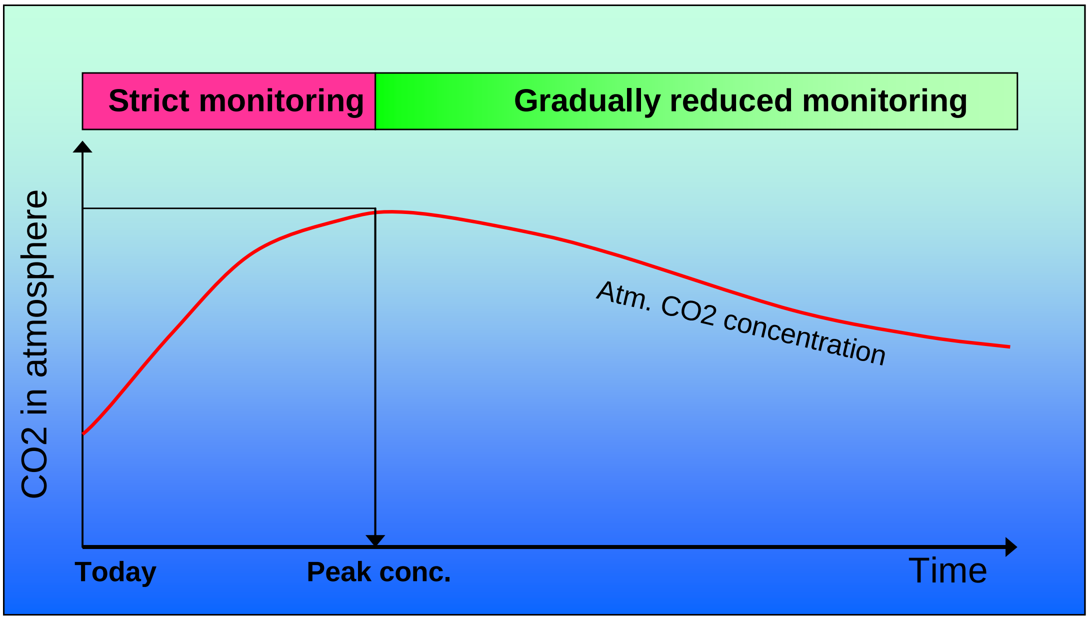


Figure 20. A scenario for long-term monitoring.

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