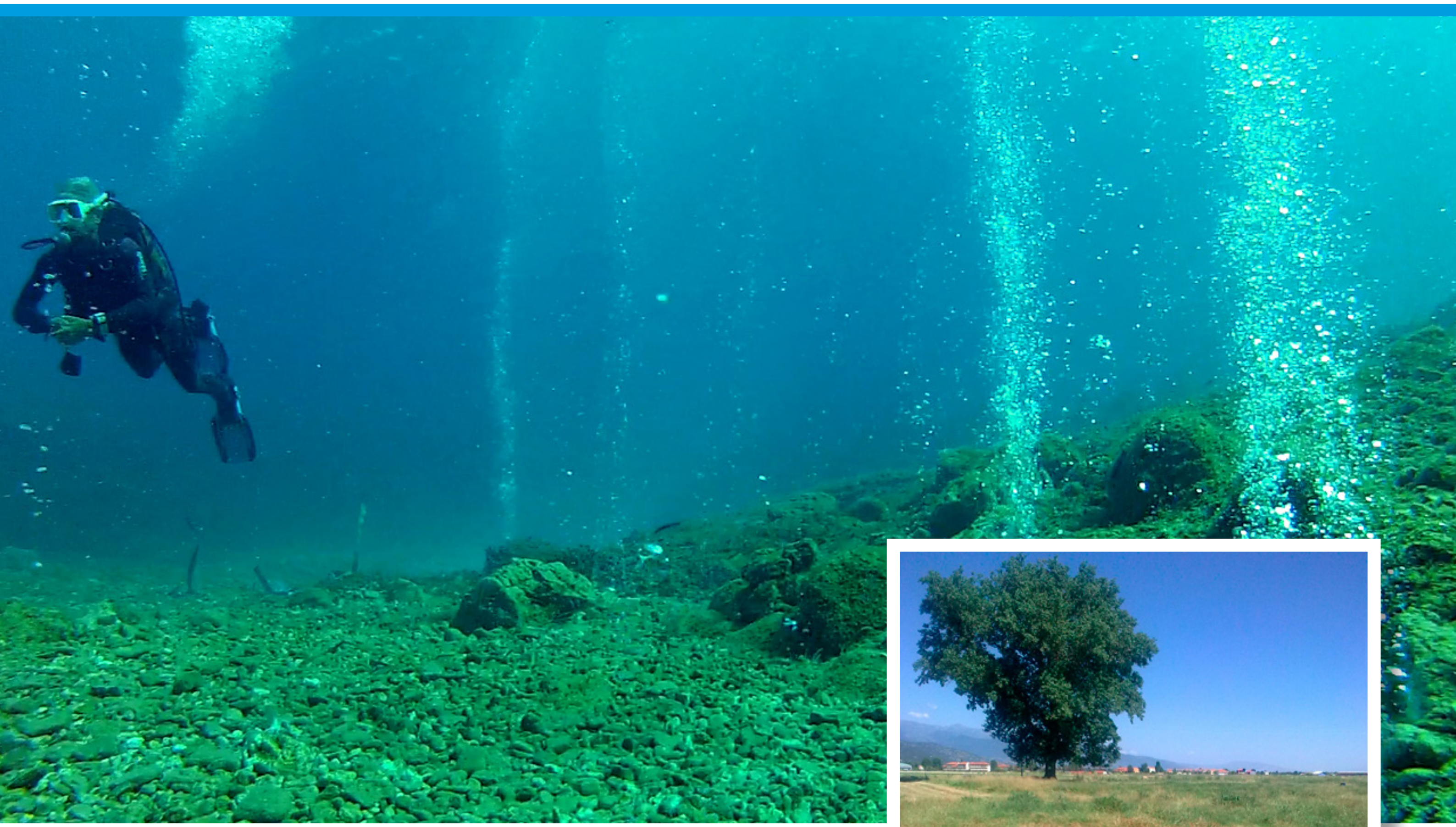

A guide to potential impacts of leakage from CO_2 storage

European Union
7th Framework Programme

Cover photos illustrate two examples of natural CO_2 seeps that have been studied in the RISCS project. Off the coast of the island of Panarea in the Mediterranean Sea, natural volcanic CO_2 seeps along fractures to produce bubble streams from the sea bed. Near the town of Florina, northern Greece, the impacts of naturally-produced CO_2 on vegetation can be easily seen, where very high CO_2 concentrations produce a central zone of bare soil which is surrounded by a narrow margin of more tolerant plants and stronger growth due to fertilisation effects at lower CO_2 concentrations. Although such places are not analogous to storage sites, these natural seeps allow us to investigate the potential impacts of CO_2 leakage on terrestrial and marine environments.

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A guide to potential impacts of leakage from CO_2 storage

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The report has also been reviewed by a range of external stakeholders including representatives from relevant industries, environmental non-governmental organisations (NGOs) and some regulatory bodies, who the authors gratefully acknowledge.

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EXECUTIVE SUMMARY

This report summarises the conclusions and recommendations developed by the RISCS Consortium, based on four years of research into the potential impacts of leakage from CO_2 storage sites. The report has been developed in parallel with the experimental research, field-based investigations, modelling studies and analysis undertaken during the RISCS project.

The research programme, from which these recommendations have been formed, was designed to assess the nature and scale of potential impacts on a range of reference environments, should leakage occur from storage sites located in both terrestrial and marine environments. Dispersion of CO_2 in the onshore near-surface environment and in seawater has been simulated. Potential impacts have been assessed on representative examples of plants, mainly agricultural crops, groundwaters and on individual marine species and communities.

Aspects of the research have been presented and published separately and can be accessed through the project website: www.riscs-CO2.eu.

Evidence to date indicates that leakage is of low probability if site selection, characterisation and storage project design are undertaken correctly. In Europe, the Storage Directive (EC, 2009) provides a legislative framework, implemented by Member States, which requires appropriate project design to ensure the storage of CO_2 is permanent and safe. The work undertaken in the RISCS project, including comparisons with other published results, allows us to draw the following high-level conclusions:

- Impacts from CO_2 leakage are expected to be small compared to impacts caused by other stressors. These additional stressors include, but are not limited to, changes in land use, extreme onshore weather events, periods of abnormal weather and activities such as bottom trawler fishing, as well as the impacts that CCS seeks to mitigate such as climate change and ocean acidification.
- It is recommended that storage operators and relevant Competent Authorities demonstrate that an appropriate level of understanding has been developed of the potential impacts that might arise if a leak did occur from the specific site being considered for CO_2 storage.
- Evaluation of risks of leakage and potential impacts should be undertaken at each site, since each will have specific characteristics which will influence the nature and scale of the environmental response. The context of what specific impacts mean for a particular storage site (e.g. selection of crops) is fundamental and should be explained where relevant.
- The research undertaken in RISCS, and reviewed research published elsewhere, indicates that there are no reasons why a storage project could not be sited within any of the large-scale environmental types that have been studied here.
- Potential impacts will be further reduced by careful site selection and appropriate monitoring and mitigation plans.
- All monitoring programmes should use ecosystem evaluation techniques. Monitoring technologies and assessment methodologies have been developed and tested that allow the impacts of CO_2 in terrestrial and marine environments to be assessed.
- Indicator species that occur within specific onshore sites have been identified that can be monitored in conjunction with other environmental factors to assess the scale of an impact and the efficacy of any remediation.

Furthermore, it is concluded that:

- Carefully selected reference sites, both onshore and offshore, could be a powerful tool for providing ongoing baseline data against which storage sites can be compared. They would allow changes related to factors other than CO_2 leakage to be assessed. Sites managed via joint industry initiatives may be a suitable approach to enable a smaller number of reference sites to be developed for use by several storage projects.
- Evidence indicates that areas that might be affected by leakage will be localised. Individual seeps can be up to a few tens of metres across, and groups of these seeps might occur along fault zones. However, the total area of these seeps would still be a very small proportion of the area that might be used for CO_2 storage. This applies to onshore and offshore sites and includes potential impacts on groundwaters. This implies that monitoring techniques able to detect leaks at these small scales over large areas should be deployed if leakage is suspected.
- Monitoring a number of parameters in addition to those directly indicative of CO_2 levels will help to separate natural variations in CO_2 content from leakage, such as measuring nitrogen, oxygen and isotopic contents of soil gas or recording temperature and dissolved oxygen in marine systems.
- Baseline surveys will be required and are a fundamental part of demonstrating site performance. Ecosystem baseline surveys should be carried out at proposed storage sites to ascertain changes resulting from any leakage. These will also assist in Environmental Impact Assessments. It would also be beneficial if reference sites were similarly assessed and monitored so that any ecosystem changes attributed to CO_2 leakage can be compared to results from the non-injection site.

Specific recommendations for operators and regulators to consider are:

- Site-specific monitoring will aid confidence building and demonstrate that the duty of care for safe, permanent storage has been met appropriately.
- Baseline surveys should be designed to account for a full range of natural variation, which may occur over more than one year. Changes at the storage site due to other external factors should also be taken into account, for example through the use of reference sites. Communication of these baseline results to the local stakeholders (such as residents and NGO's) is advisable to create dialogue and increase knowledge of the natural system and its variability.
- Investigations for storage sites should include an assessment to determine whether the Conservation Objectives of Natura 2000 sites and any other protected areas are significantly affected by the project
- Leaks may have a cumulative, additional impact on ecosystems already stressed by other factors, such as low salinity marine environments, existing contaminated areas or marginal systems that are already restricted in their development.
- The timing and duration of the exposure will influence the scale of the impact. Timing is important because the stage of development of plants and animals affects their response, whilst the ecosystem in its entirety may be able to cope with enhanced CO_2 for a short duration.

- The scale of the likely impacts examined in the RISCS project means that they are considered manageable both by the ecosystem and by relevant stakeholders (operators and regulators).
- Offshore sites where mixing in the seawater column would allow dilution of CO_2 would be preferred because if a leak were to occur the natural mixing processes in the seawater could enhance dispersion and thereby minimise impacts. Similarly, onshore sites that avoid potential build up of CO_2 in confined areas would also be preferred, as under normal conditions light winds can quickly disperse any leaking CO_2.
- Natural recovery in dynamic marine systems is expected to be relatively rapid i.e. mostly within one 'growing cycle' or season, due to the large pool of ecosystem resources and small scale of the impacted area, although this may not apply to all scales of leakage.
- In terrestrial systems, replanting of crops should be possible in affected areas once leakage has ceased, as no long term effects are expected based on experiments on crops. However the longer term recovery of pasture land has not been fully evaluated.

1 INTRODUCTION

This Guide to potential impacts of leakage from CO_2 storage (the 'Guide') is one of the key outputs from the RISCS (Research into Impacts and Safety in CO_2 Storage) project. The project was funded by the European 7th Framework Programme and industry partners and ran from January 2010 to December 2013. RISCS assessed the potential effects of CO_2 leakage from geological storage on both onshore and offshore near-surface ecosystems and on potable groundwater. This assessment was achieved through laboratory and field experiments, through observations at sites of natural CO_2 seepage and through numerical simulations. The Guide summarises some of the key findings of the project.

The purpose of the Guide is to provide information on the best approaches to evaluate potential impacts of hypothetical leakage from CO_2 storage sites and to provide guidance on appraising these impacts. It is hoped that this information will be relevant to regulators and operators in particular, but also to other stakeholders who are concerned with CO_2 storage, such as national and local governments, and members of the public.

1.1 Scope of the Guide

The Guide considers the potential impacts of leakage. This information could be used when assessing the potential risks during detailed project design, enabling specific aspects of the site characterisation to be planned. Once site selection and characterisation has been undertaken, the information provided by the Guide could be further used to develop environmental monitoring plans. Corrective measures plans (mitigation and remediation) and site closure plans might also benefit from consideration of the Guide. Regulators and other stakeholders might also use the Guide to assess the appropriateness of those plans. The Guide does not make specific recommendations for a formal Environmental Impact Assessment, although the information should be relevant for this type of assessment.

The assessment of environmental impacts will be a key feature of the design and permitting process for CO_2 storage projects, and will focus mainly on the potential impacts arising during the construction of infrastructure and during the routine operation of the storage site. Potential impacts arising from the leakage of CO_2 following injection may be considered as part of the assessments, as a regulatory requirement. The Guide specifically addresses potential impacts following leakage of CO_2 from geological storage; although similar impacts could also arise from leakage from pipelines, these have not, in general, been considered explicitly.

The RISCS project has specifically undertaken research into the potential impacts of leakage in a European regulatory context, in both terrestrial and marine environments of most relevance to Europe. However, some of the results obtained should be of wider relevance for similar environments elsewhere and under other regulations. The Guide and supporting research focussed on the impacts of leakage rather than the processes leading to leakage within the reservoir or caprock.

The RISCS project conducted a broad range of research to understand the possible impacts that might occur in the event of CO_2 leakage from geological storage systems. Issues relating to CO_2 injectivity, storage capacity and containment integrity were outside the project's scope. Similarly, the potential impacts of water or other formation fluids being displaced from the storage complex by injected CO_2, even though the CO_2 does not itself leak from the storage complex, were also not considered, although it is noted that these impacts could potentially be significant. A lot is already known about the potential impacts of brine displacement from studies of aquifer salination. Impacts of a financial nature or those that have implications for community acceptance and safety are not included in the Guide.

The Guide is not intended to be the final report for the RISCS project, nor is it intended to be a technical discussion of detailed results. Rather, the objective is to provide an accessible summary of these results and to provide suggestions on possible approaches to evaluating potential leakage impacts. More detail on the main findings of the project is available in reports, presentations and publications that are available from the project website.

1.2 Guide contents

The Guide is structured around eight reference environments which have been defined to represent, in a broad manner, the types of ecosystems that might be encountered above CO_2 storage sites in Europe. Four terrestrial environments and four marine environments have been defined. Credible, but nevertheless unlikely, scenarios for the leakage of CO_2 following injection into a storage formation are described for these environments.

The potential impacts, as identified by research performed in the RISCS project and elsewhere, which might occur on specific components of the reference environments following leakage, are then described. The implications of these impacts for future CO_2 storage projects and possible options for mitigating them are considered, though options for remediation have not been the prime focus of this work.

2 CO_2 STORAGE

The latest conclusions from the Intergovernmental Panel on Climate Change (IPCC, 2013) are that warming of the climate system is unequivocal and that increases in greenhouse gases, including CO_2, in the atmosphere have been accompanied by warming of the atmosphere and oceans, reducing snow and ice, ocean acidification and sea level rise. The IPCC earlier stated that there is an immediate need for implementation of various actions to reduce CO_2 emissions to mitigate these changes, including increased energy supply from renewable and nuclear sources, increased energy efficiency and moving to fossil-fuel based power with carbon capture and storage (IPCC, 2007).

CO_2 is a colourless gas intrinsic to animal and plant respiration and which occurs in the atmosphere, in the soil environment and in many naturally-occurring gas fields. CO_2 contributes to the climate change impacts described above via the greenhouse effect. CO_2 levels are substantially higher now than at any time in the last 750 000 years. Beginning with the industrial revolution in the 18th century, the combustion of fossil fuels has elevated levels from a concentration of approximately 280 parts per million (ppm) in the atmosphere in pre-industrial times to around 390 ppm today. Concentrations are increasing at a rate of about 2–3 ppm/year and are projected to reach a level between 535 and 983 ppm by the end of the 21st century. Together with rising emissions of methane and other greenhouse gases, and the associated feedback effects, it is suggested that, without mitigation, these changes may cause an increase of 1.1–6.4°C in 2090-2099 relative to 1980-1999. The average earth surface temperature correlates well with the amount of CO_2 in the atmosphere (i.e. as the CO_2 levels in the atmosphere have increased, the surface temperature has gone up at the same time). Consequently some scientists have suggested setting goals to try to limit concentrations to 450 or 500 ppm, in the hope of limiting global temperature increases to less than 2°C.

CCS aims to prevent anthropogenic CO_2 emissions being released into the atmosphere by capturing it at large point sources and injecting it into deep porous geological formations (Figure 1) so that it remains permanently trapped, effectively returning the carbon underground from where it was originally produced as coal, oil or natural gas. The CO_2 gas can be captured at a fossil-fuel fired power plant before or after the fuel is burnt (pre- or post-combustion capture), by burning the fuel with oxygen (oxyfuel combustion) or following its generation at other point sources (e.g. cement works, steel works, refineries and coal to liquid plants). After the CO_2 is captured it can be compressed and transported by pipelines or by ships to a suitable geological storage site, either on- or offshore where it can be pumped deep underground via one or more wells. Different types of storage formation have already been used including depleted oil and gas fields and saline aquifers[1]. These sites have been monitored before, during and after CO_2 injection and have been shown to be storing the CO_2 securely.

Storage will take place in specifically selected reservoir rocks, typically porous and permeable sandstones or limestones, which can be shown to be suitable for storing the CO_2. To ensure that storage is permanent and safe, the sandstones should be overlain by layers of low permeability 'caprock' to prevent the upward migration of the CO_2. At temperatures and pressures that are typical

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[1] For more information, the following websites provide useful overviews:

http://www.ieaghg.org/index.php?/20091218110/what-is-css.html

http://www.zeroemissionsplatform.eu/ccs-technology/storage.html

http://www.ipcc.ch/pdf/special-reports/srccs/srccs_summaryforpolicymakers.pdf of reservoir rocks at depths of more than about 800 m (i.e. at temperatures above 31.1 °C and pressures above 72.8 bar), CO_2 forms a relatively dense fluid phase (a supercritical fluid) although this is still less dense than the water already present. The consequent decrease in volume above those temperature and pressure values allows more CO_2 to be injected into the same pore space. Many reservoirs that are already being used for storage, or that have been identified for possible future use, are at depths significantly deeper than 800 m.

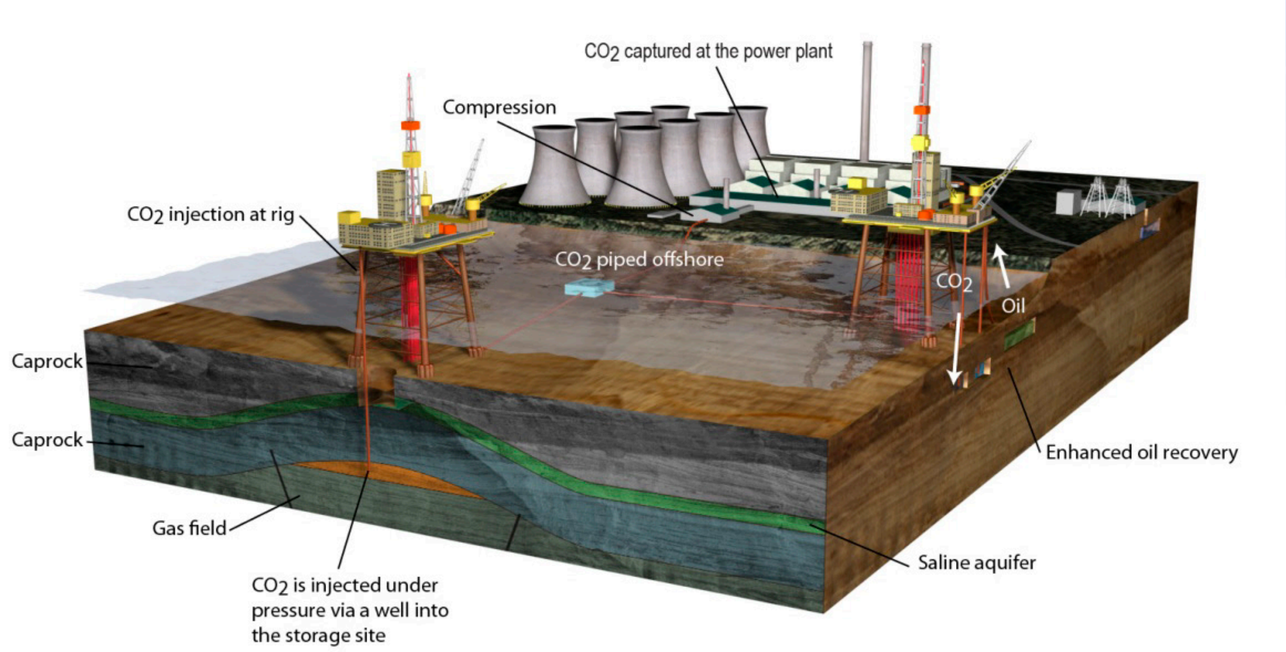

Figure 1 Storage concept – here for offshore storage. Note that in reality, the rocks that will be used for storage will be typically at depths greater than 800 m and the vertical scale of this diagram is not a true representation of actual depths, being shown for illustration purposes only.

In Europe, suitable storage formations occur both in offshore areas, such as the North Sea, and in onshore areas, such as northern Germany, France, Spain and the Netherlands, as well as regions in other countries. Many of the physical and chemical processes that occur naturally when CO_2 is injected occur very slowly, on geological timescales, but it is generally expected that the reactions will increase the proportion of CO_2 which is trapped in a dissolved or mineral form (i.e. making it less mobile).

Although the individual technologies to enable CO_2 storage are relatively mature, there are large uncertainties about the additional costs of implementing them and the technical challenges of integrating them. Consequently government-supported demonstration projects, such as the Dutch ROAD project and the UK CCS Commercialisation Programme, are currently being planned to evaluate these uncertainties, as well as technical and safety aspects, at a large scale. If current CO_2 emissions reduction targets are to be met, then large-scale deployment of CCS will be needed within the next two decades[2].

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[2] A number of assessments have concluded that achieving targets for the concentration of atmospheric CO_2 will require deployment of CCS at a global scale. A recent example is the International Energy Agency's CCS Roadmap available at: http://www.iea.org/publications/freepublications/publication/CCS_Roadmap.pdf and the IPCC's Special report on CCS http://www.ipcc.ch/pdf/special-reports/srccs/srccs_summaryforpolicymakers.pdf

3 TYPES OF LEAKAGE

Following the definition given in the EC Directive on geological storage of CO_2 (EC, 2009) 'leakage' refers to the release of CO_2 from a subsurface 'storage complex'. The storage complex is defined as a storage reservoir or reservoirs and the surrounding rocks that can affect the overall integrity and security of storage. A specific storage complex will be defined for each proposed storage project and will have characteristics specific to that site. Depending upon the site, a storage complex may include more than one CO_2 storage reservoir; there may be 'secondary containment formations'. Therefore, 'leakage' in this sense does not necessarily mean the emission of CO_2 from the earth's solid surface, but rather the escape of CO_2 from the body of rock within which it is intended to be contained (Figure 2).

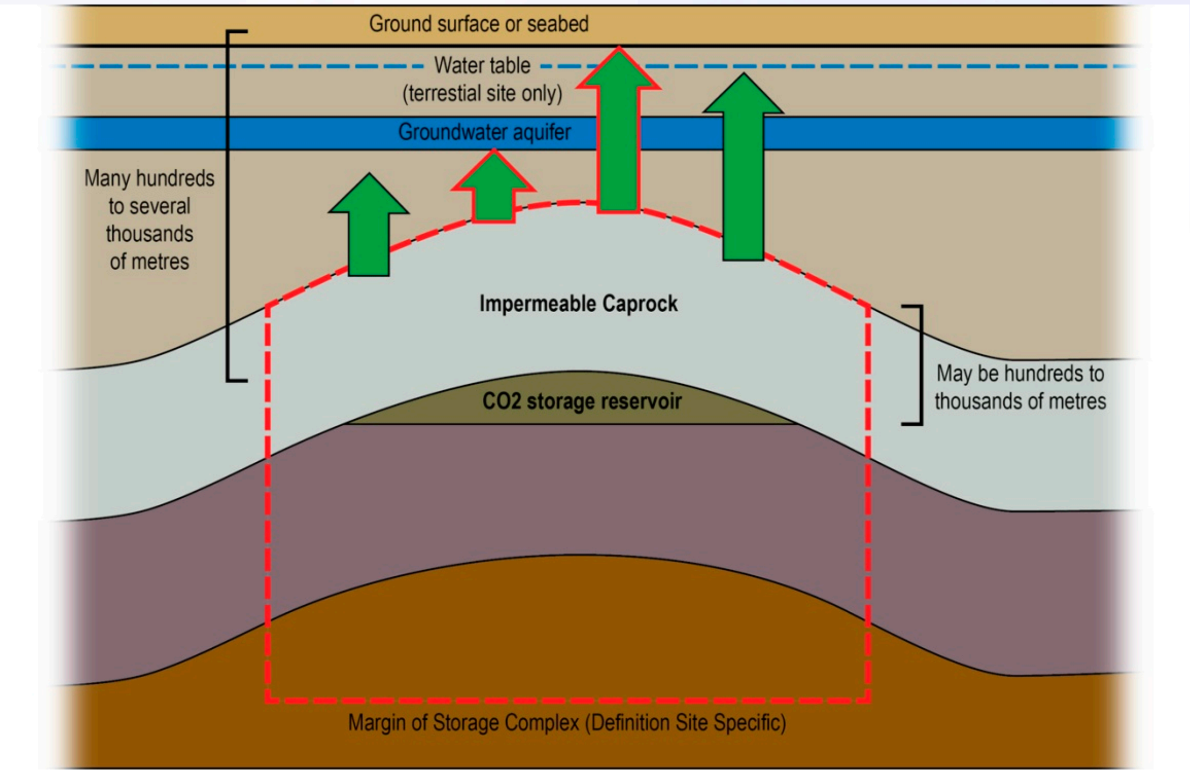

Figure 2 Schematic illustration of a CO_2 storage complex and the meaning of leakage in accordance with the EC Storage Directive (EC, 2009). RISCS is concerned primarily with the impacts of the leakage illustrated by the green arrows outlined in red and not with processes within the storage complex, outlined by the red dashed line, or with leakage which does not impact on groundwater resources or near surface environments. At a suitably sited and well-operated CO_2 storage site, there will be a very low probability that CO_2 will leave the storage complex (i.e. leak).

Depending upon the nature of the migration pathways for the CO_2 through the rock, leakage from a storage complex could give rise to different kinds of emission at the earth's solid surface. The RISCS project has considered three main kinds of emission pattern, in both terrestrial and marine environments (Figure 3):

- emissions at single point leaks (a few metres to tens of metres across), most likely due to old improperly sealed wells, although surface expressions of leakage may be considerably wider than the width of a well, owing to dispersion of CO_2 in the shallow subsurface (Figure 3a);

- emissions at multiple points (each one typically a few metres or tens of metres across) distributed along the intersection between a fault zone and the earth's solid surface, such that the leakage points lie within a zone that is much longer than it is wide (perhaps several kilometres to tens of kilometres long and a few metres to tens of metres wide; Figure 3b);
- diffuse emissions, over a wide area (perhaps up to tens to hundreds of metres across; Figure 3c).

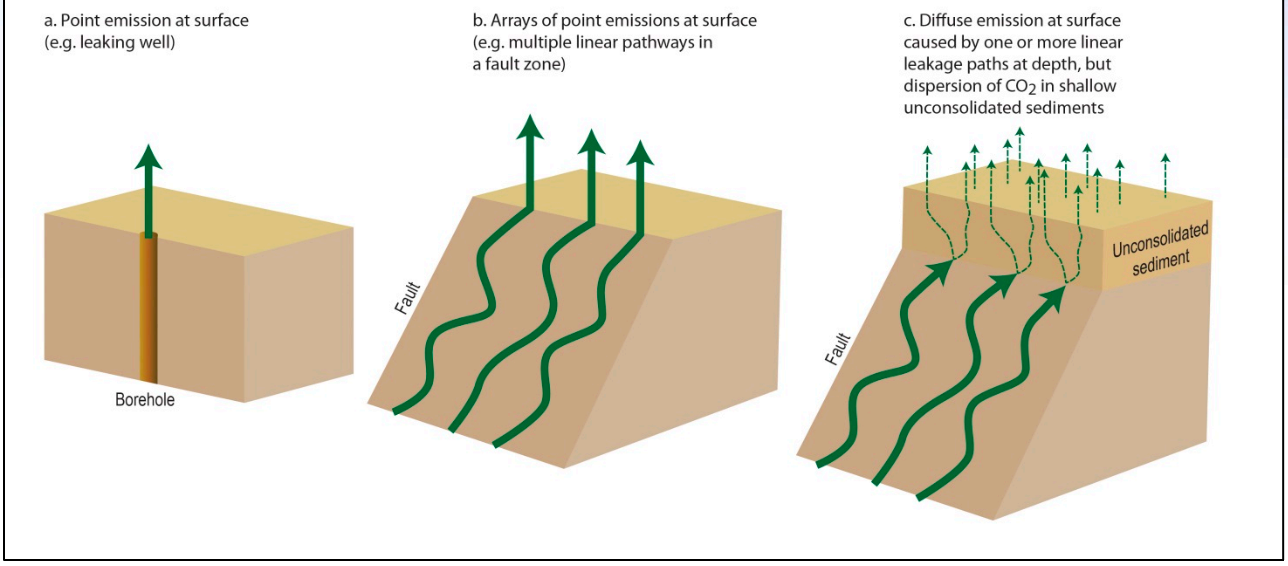

Figure 3 Schematic illustrations of leakage patterns considered by RISCS. CO_2 movement is indicated by green arrows. In b. only pathways in a fault plane are illustrated. Diffuse emissions at the surface could also be produced by a similar process involving single linear pathways such as poorly sealed boreholes.

Although all these patterns have been taken into account when describing the potential impacts of CO_2 leakage, based on the research undertaken in RISCS, only the first two patterns have been studied in detail. The reasons for this treatment are two-fold:

- It is not clear how any unexpected leakage of CO_2 out of a subsurface storage complex would occur over a wide area, as illustrated in Figure 3c.
- There is no clear upper size for an area of leakage before it is deemed to be 'diffuse' (e.g. Figure 3c) rather than 'localised'. The potential impacts of diffuse emissions can be considered by suitably upscaling models designed to investigate localised emissions.

The leakage of CO_2 over a spatially continuous wide area is considered unlikely, because inevitably CO_2 would tend to move through the most permeable pathways present in a rock mass and these pathways will tend to be predominantly localised although lateral migration in the unsaturated zone is possible due to density effects. Examples of localised pathways include improperly sealed boreholes or one dimensional permeable channels within fault planes (Figure 3a and b). There may be relatively permeable rocks occurring within the rock sequence above the caprock that immediately overlies a

CO_2 storage reservoir, which have the potential to conduct CO_2 over a relatively wide area. However, such permeable rocks are unlikely to form continuous pathways to aquifers outside the storage complex or to the surface of the solid earth. More localised pathways, such as faults or boreholes, would probably form much of a leakage path.

Published literature (e.g. Oldenburg and Lewicki, 2005; Lewicki et al., 2007) tends to describe natural CO_2 seeps as being 'diffuse' when:

- CO_2 is emitted at many points that are distributed across a wide area, and that show no obvious alignments or topographical expressions, such as hollows in the ground surface;
- CO_2 is emitted across an area where there is no obvious point source or topographical expression such as a hollow in the ground surface (although such an area may be quite spatially restricted, perhaps only a few metres across).

Many of these reported 'diffuse' emissions can be considered as point emissions in the context of the RISCS project. For example, Lewicki et al. (2007) referred to CO_2 emissions over an area of approximately 50 m^2 at Mammoth Mountain in California as being 'diffuse' because no distinct vent could be identified. However, this area is only approximately 8 m across and therefore can be treated as a localised release when assessing impacts. It is also important to recognise that certain natural seeps are diffuse (in the sense described by the first bullet above) because they are underlain by spatially extensive and temporally continuous sources of CO_2, such as a degassing magma body. Such CO_2 sources are dissimilar to the CO_2 accumulations that would occur in an underground storage reservoir because they may provide a more continuous and constant CO_2 supply.

Emissions of CO_2 that appear to be diffuse are most likely to reflect dispersion of leaking CO_2 in the unsaturated zone, most likely in poorly- or unconsolidated sedimentary deposits, including soils, that overlie the deeper pathways (Figure 3c).

Leakage can be expressed at the earth's solid surface, or in the subsurface above the containment complex (e.g. in an aquifer, as illustrated in Figure 2), by the presence of a free CO_2 phase or the presence of water in which leaking CO_2 has been dissolved. The RISCS project has considered all these circumstances.

It is also possible that water containing dissolved CO_2 may produce (exsolve) a free CO_2 phase if the water flows from greater depth (higher pressure) to shallower depth (lower pressure). This process is thought to explain the emission of free CO_2 from Crystal Geyser in Utah, an abandoned and partially open oil exploration well that was drilled in 1935 (Shipton et al., 2004; Lewicki et al., 2007). Dispersion of CO_2-bearing water in the subsurface is a potential mechanism by which diffuse surface CO_2 emissions might arise at the solid earth's surface.

The possible duration of any leakage will depend upon the characteristics of a particular site and the nature of the storage project. Time-limited factors will operate both within the storage complex and along any flow path between the boundary of the storage complex and any subsequently impacted subsurface domain, such as an aquifer or the earth's solid surface. The rate at which leakage can occur along any particular pathway will determine the duration of the leak for any given volume of stored CO_2; conversely for any given rate the duration of the leak will be longer for larger stored CO_2 volumes.

Important additional factors that will influence the duration and termination of leakage are:

- the ease with which the leak can be recognised and remedial action can be taken (e.g. a leak from a borehole during the operational phase of a project is likely to be recognised quickly and stopped soon afterwards, whereas a leak from a fault after the operational phase might take some time to recognise and be more difficult to stop);
- progressively permanent trapping of CO_2 within the storage reservoir and surrounding rocks within the storage complex:
    - some CO_2 will always be permanently trapped within the pores of these rocks by a process called 'residual trapping';
    - some CO_2 will dissolve into formation water, which consequently will become relatively dense and may sink (in any case, formation water may be relatively immobile compared to much lower-density free CO_2);
    - some CO_2 will take part in chemical reactions with the groundwater and rocks and will be immobilised as solid mineral phases);
- the physical nature of any leakage pathway, including its dimensions (length in the direction of CO_2/CO_2-charged water flow and area perpendicular to this direction), permeability, whether the pathways are straight or tortuous and the characteristics of pathway walls (whether smooth or rough);
- the permeabilities of the wall rocks along the leakage path and, if the leakage path is a borehole, the permeabilities of any engineered materials that are present;
- the pressure gradient along the leakage path (which will depend to a large extent upon the pressures of natural fluids in the surrounding rocks and the pressure of CO_2 within the storage reservoir), which affects both the flux of CO_2 and its partitioning between different phases;
- the temperature gradient along the leakage path, which affects how the CO_2 will partition between different phases;
- the thermal conductivities of the wall rocks of the leakage pathway and, if this pathway is a borehole, the thermal conductivity of engineered materials within the borehole;
- the nature of fluid phases along the pathway, such as the presence of naturally occurring liquid or gaseous hydrocarbons, in addition to groundwater;
- the chemistry of groundwater with which the CO_2 or CO_2-charged water comes into contact along the flow path, in particular the salinity of the water, which will influence the partitioning of the CO_2 among different phases;
- the chemistry of the wallrocks of the leakage pathway and, if the leakage pathway is a borehole, the chemistry of engineered materials within the borehole (since certain reactions between CO_2, water and solid materials have the potential to permanently immobilise CO_2 and/or influence the permeability of the rock and/or engineered materials);
- The presence of additional reservoirs above the primary reservoir that might act as secondary storage capacity.

The different processes that control the flux of CO_2 along a leakage path are, to some degree, coupled. For example, changes from higher density supercritical fluid to lower density gaseous CO_2 would influence the effective permeability of a particular pathway. For a particular pathway under a given pressure gradient, multiphase flux will tend to be slower than single phase flux. However, the phase changes are determined by the thermal gradient along the flow path, which in turn is influenced by the phase changes. If the CO_2 expands as a result of the decreasing pressure, there will be cooling (adiabatic cooling). An analysis of this particular coupling by Preuss (2005) showed that this kind of feedback between thermal effects and phase changes could result in the self-limiting of CO_2 fluxes.

Even though the precise duration of any CO_2 leakage cannot be estimated in the absence of site-specific information and details of operational methods, there is good reason to believe that the rate of any CO_2 leakage will diminish over time, even in the absence of mitigating actions. During leakage the pressure of the CO_2 remaining in the reservoir will fall, causing a decrease in leakage rate. Processes that tend to trap CO_2 permanently (e.g. carbonate mineral precipitation) are also progressive, meaning that over time there will tend to be a decreasing quantity of mobile CO_2 present in the subsurface. These processes can lead to increasing proportions of the CO_2 being trapped more securely and permanently, such that the potential for leakage and the amounts of leakage that could occur decrease with time, albeit on relatively long timescales for some geochemical processes. A progressive decrease in CO_2 emission rate over time has been observed at Crystal Geyser during the period of nearly 80 years for which the borehole has been deliberately left open as a tourist site (Shipton et al., 2004).

4 PROBABILITY OF LEAKAGE

In accordance with the EC Storage Directive (EC, 2009), before a proposed CO_2 storage project can be licensed to proceed, the developer of the project will need to provide regulators with sufficient evidence that the proposed storage site will not leak. Factors that might affect the probability of leakage will therefore need to be assessed at the site selection stage. Should the assessment conclude the probability of leakage to be significant, CO_2 storage will not proceed.

There is a large body of evidence to indicate that a CO_2 storage site can be appropriately chosen and operated to ensure that the probability of leakage will be very low. This evidence includes:

- observations at natural analogue sites (e.g. natural accumulations of CO_2 that have remained immobile for many millions of years; IEA, 2009);
- results from laboratory experiments (e.g. which have shown the integrity of caprocks to be maintained in the presence of CO_2; Bennion and Bachu, 2007);
- outputs from numerical simulations (e.g. using fully-coupled reaction-transport models to investigate caprock integrity; Johnson et al., 2004); and
- experience with pilot, demonstration and full industrial scale CO_2 storage projects (e.g. at Sleipner, offshore from Norway, Weyburn in Canada, In Salah in Algeria, Ketzin in Germany, Snohvit in Norway and the CO2CRC Otway Project in Victoria, Australia).

Once a site has been licensed and CO_2 storage has commenced, subsequent assessments of leakage probability would be made using data acquired during the project. The aim would be to build further confidence that the initial assessment of insignificant leakage probability is correct. If this initial assessment is shown to be incorrect, then mitigating actions must be taken. In this case, knowledge of the likely impacts is needed to implement mitigation plans effectively and inform discussions between the operator, regulators and other stakeholders aimed at deciding what mitigation should be undertaken.

The probability of leakage from any particular proposed CO_2 storage site will depend upon many inter-related factors. These factors must be assessed collectively to estimate the probability of leakage. In the absence of site-specific and project-specific information it is impossible to state, even for a particular kind of storage site, what may be the probability of leakage. This site-specific characterisation is therefore a fundamental requirement for development of safe storage projects.

At a particular storage site it will be possible to judge the probability of leakage through wells that are operated during CO_2 injection and monitoring, based on the extensive experience of well drilling and operation by the hydrocarbon industry. Wells that are operated during CO_2 injection and monitoring include those that are connected with CO_2 storage itself (the CO_2 injection wells and possibly monitoring wells and/or wells drilled to manage formation pressure).

In any case, if there is leakage from such wells, there is a good prospect that it could be mitigated rapidly and without there being significant long-term impacts to the environment. Other factors that need to be considered to establish whether or not wells might increase the probability of leakage include:

- the numbers of abandoned wells, which might remain following previous hydrocarbon exploration and production within the footprint of the plume of stored CO_2– all other factors being equal, the probability of leakage possibly increasing with:

  - increasing numbers of abandoned boreholes;
  - increasing age of abandoned boreholes, abandonment of older boreholes tending to have been done with less advanced seals and methods, and/or under less rigorous regulation than newer boreholes;
  - increasing maximum depths of boreholes, notably with increasing numbers of boreholes penetrating to the depth of the reservoir or deeper caprock;
- the reservoir pressures that will be attained during CO_2 injection, noting that higher pressures will tend to result in a greater probability of leakage only if they approach the fracturing pressure of the caprock or cause weak features in the rock to fail, such as by dilating a previously sealed impermeable fault plane;
- the heterogeneity of the caprock, for example the occurrence of relatively permeable rock layers within an otherwise impermeable caprock sequence, which might act as sections of an overall leakage pathway from a faulty well;
- the number of permeable faults which may act as additional pathways within the area covered by the plume of stored CO_2, although not all faults are permeable and many behave as seals.

Were leakage to occur through abandoned wells, once it has been identified, it is likely to be easier to mitigate than leakage through natural features of the rock, such as faults. This conclusion follows because a single well will be a single localised leakage pathway of known geometry, whereas a natural structure such as a fault will probably contain numerous leakage pathways. In addition, a well is a localised engineered (and hence relatively regular) feature, which probably can be re-engineered if necessary (e.g. by reaming) and sealed relatively easily. In contrast, natural structures such as faults generally will have much greater spatial extents and generally will be much more heterogeneous, making them difficult or impossible to seal.

5 LEAKAGE SCENARIOS

Hypothetical leakage scenarios enable developers of a CO_2 storage project to:

1. Illustrate to stakeholders, including regulators, that the consequences of unexpected CO_2 leakage are understood; and thereby
2. Enable stakeholders to understand where impacts are insignificant and in what circumstances mitigation would be required.
3. Develop mitigation plans
4. Develop efficient monitoring strategies

These scenarios are needed because regulations require the possible impacts of leakage to be discussed while at the same time demonstrating that leakage has not been detected; the scenarios make no *a priori* assumptions about leakage probability.

Each leakage scenario defined during the RISCS project consisted of general descriptions of a reference environment, including its climatic conditions and/or water depth and salinity (in the case of marine scenarios) and kinds of ecosystems that occur. The 'receptors', which are those components of a reference environment that could be impacted by any CO_2 that were to leak, include biota and groundwater aquifers that might be exploited for drinking water. The CO_2 leakage characteristics are defined in terms of the leakage pattern and consequential emission pattern (and quantity) at the surface of the solid earth, whether the CO_2 is a free phase or dissolved in water and the kind of dispersion of CO_2 after leaving the surface of the solid earth (in the case of aquatic environments).

5.1 Scale of impacts

Qualitatively, the impacts of leakage in these scenarios depend upon a number of factors, including the elevated concentrations of CO_2 that are attained at the location of any receptor and the temporal variations in these elevated concentrations, including the duration for which any particular elevated concentration is maintained. The nature of the receptor (e.g. whether a mobile or immobile organism, whether an animal with or without a calcified shell) and the stage in the lifecycle of a biological receptor at which exposure occurs can also significantly influence the scale of the impact. Consequently the season during which the receptor is exposed to CO_2 (in the case of biological receptors that show natural seasonal variations in growth and/or behaviour) is also an important factor. Other environmental stresses on the receptor prior to, or during, exposure to CO_2, such as climatic or pollution stresses, are also likely to be important.

The actual size of the impacted domain (surface area, or subsurface volume in the case of aquifers) at any particular time will depend upon a combination of the number and geometry of leakage paths, the dispersion of CO_2 within the impacted domain, the flux of CO_2, the duration of leakage and the weather or current conditions.

For a given flux and duration of leakage, a single borehole leaking directly to the land surface will impact a much smaller area of the surface than a fault that leaks directly to the land surface at multiple points along a length of kilometres. If a similar fault is overlain by unconsolidated sediment, CO_2 discharging from the fault into the sediment will tend to disperse as it travels through the sediment to the land surface. In this case, for a given flux and duration of leakage the impacted area of the surface will be larger than for the case where the fault leaks directly to the surface. If instead the fault terminates in a subsurface aquifer, then the impacted volume of the aquifer will increase as the duration of leakage increases for a given flux. Conversely for a given duration of leakage, the impacted volume of the aquifer will increase with increasing flux.

There is no simple correlation between the magnitude of the leakage flux and the impact that the flux may have. Impacts are mainly caused by high concentrations of CO_2, whether in the soil or sediment zone or the atmosphere or seawater, therefore the degree of dispersion of the CO_2 will significantly influence the impact of the leakage. Onshore, for emissions directly to the atmosphere, larger fluxes emitted at high velocity are likely to result in increased mixing with the ambient air and hence lower concentrations of CO_2. Numerical models of CO_2 leakage impacts on crops developed during the RISCS project predicted higher soil concentrations for a given leakage flux than was observed in field experiments. It appeared that a significant proportion of the injected CO_2 was travelling through high permeability pathways within the soil to the atmosphere and effectively bypassing the soil's matrix, thus reducing the CO_2 impact on the plants' roots. Such a bypass flow maybe more likely at higher flux rates and therefore soil concentrations will not necessarily increase with increased flux. Once in the canopy atmosphere, the bypass flux could impact the plants through increasing canopy concentrations or may be dispersed and not affect plant growth.

The particular scenarios that are most relevant to an actual site within a particular reference environment will depend upon the detailed characteristics of the site's geology and also upon the plans for CO_2 storage operations. These plans will include details of the number and design of boreholes to be used, the volumes of CO_2 to be stored, the rates at which CO_2 is to be injected and the overall scheduling of the storage project. For example, borehole leakage scenarios will be more relevant for sites where many boreholes have been drilled to the depth of the CO_2 storage reservoir, than for 'new' sites where there has been no history of deep drilling to reservoir depth.

5.2 Terrestrial leakage scenarios

The following scenarios were defined for leakage pathways in terrestrial environments:

- Normal Evolution Scenario (no leakage). This is expected to be the most likely scenario for the majority of storage sites where site characterisation and design have reduced the potential for leakage.
- Direct release to the atmosphere, via a well (high flux for a relatively short time period – e.g. days);
- Localised release to soils as a result of wells/faults/fractures, leading to high concentrations of CO_2 in the near surface;
- Localised release to soils as a result of wells/faults/fractures, leading to long-term low concentrations of CO_2 in the near surface;
- Localised release to freshwater lakes via fractures/faults;
- Diffuse releases to surface and near-surface systems;
- Localised release to aquifers that may be exploited as drinking or irrigation water resources; and
- Release to an urban environment.

In the above list, localised releases to the subsurface or aquifers from wells or fractures can be treated together, as the leakage patterns are similar. Whilst diffuse effects are noted for completeness, they are less likely to occur, or at least less likely to be associated with significant levels of impact. Features that are most likely to be associated with leakage include wells (for example following well seal failure) and faults and fractures (for example as a result of fault/fracture widening through induced or natural seismicity, or interaction of the storage complex with a fault that had not previously been mapped). In contrast diffusion through the rock matrix would be very slow, and would probably only reach the surface if it subsequently entered a more permeable pathway such as a fracture.

Although individual faults and fractures can be considered essentially planar features, in the event of leakage they are likely to lead to localised CO_2 releases to the atmosphere (essentially point sources), rather than more diffuse releases. Where a fault intersects the ground surface, these point sources are likely to have an approximately linear distribution along the length of the fault.

CO_2 that leaks along faults/fractures is likely to reach the atmosphere either where the fault/fracture intersects the ground surface, or through the rock matrix and/or unconsolidated deposits that intersect with but overlie the fault. The leakage of CO_2 through these media will occur via discontinuities, or through the matrix of the media concerned. Migration of the CO_2 through these relatively near-surface media above a fault will be accompanied by some dispersion and hence broadening of the zone through which CO_2 is eventually released to the atmosphere. However, zones of release will be relatively localised and a general diffuse release is much less likely to occur.

5.3 Marine leakage scenarios

The following scenarios were defined for leakage pathways in marine environments:

- Normal Evolution Scenario (no leakage);
- Localised direct release of free CO_2 via the sediment or directly to the water column above the seabed via a point source;
- Diffuse direct release of free CO_2 via the sediment or directly to the water column over a wide area;
- Localised release of CO_2-charged water through the sediment or directly to the water column via a point source; and
- Diffuse release of CO_2-charged water through the sediment and subsequently to the water column over a wide area.

The degree to which CO_2 dissolves in water before leaking from the seabed will determine whether or not a plume of dense CO_2-charged water forms. Hydrodynamic mixing and density variations due to CO_2 dissolution will control the pH profile that develops in the water column. Acidification of porewater in the sediment column beneath the seabed, as well as that of the water column above the seabed, is important in controlling impacts.

Where the existence of structures such as faults and fracture zones in the underlying rock control CO_2 movement, it is considered more likely that CO_2 or CO_2-charged water could be released as single emission points, or groups of emission points that are approximately aligned with one another (as considered for terrestrial environments).

A diffuse emission over a wide area, without any change in seabed topography, is also unlikely to develop in the event of leakage; more likely, pock marks would form within seabed sediments. However, the fact that such emissions have not been observed at natural analogue sites could reflect the difficulty of detecting this kind of emission, and so this possibility cannot be ruled out. If CO_2 dissolved in water within the sediment column below the seabed, the resulting dense, low-pH water might spread laterally over a wide area and without further dispersion could diffuse, albeit slowly, upwards to the seabed.

The kinds of subsurface leakage path that could give rise to these different patterns of emission at the seabed are similar to those considered for terrestrial environments, and leakage could potentially occur through a combination of different kinds of pathways.

5.4 Defining site-specific factors

While these scenarios illustrate the general factors that will need to be considered when assessing plausible leakage patterns and fluxes at an actual site, such an assessment would also need to include more detailed modelling of plausible leakage patterns using actual site data. Theoretical studies of possible CO_2 leakage, observations made at natural CO_2 seeps and experience of accidental CO_2 releases show that a very wide range of inter-related factors will control the scales of CO_2 leakage fluxes and impacted areas in each of the low-likelihood leakage scenarios.

Any impacts calculated for leakage scenarios need to be compared with the baseline provided by the 'no leakage' scenario. It may be that the receptors most likely to suffer impacts – e.g. terrestrial plants that are already stressed by climatic or poor soil conditions – are also sensitive to other potential environmental changes.

It should be borne in mind that should CO_2 leak from a storage complex, it could travel to the Earth's solid surface via multiple pathways (for example, via a failed borehole then a fault, then an aquifer). Thus, a given spatial pattern and flux of CO_2 emissions at the solid Earth's surface does not necessarily imply anything about the nature of the containment failure that caused CO_2 to leak from the storage complex in the first place.

The main differences between leakage in terrestrial and marine environments would arise from different CO_2 dispersion processes. Whereas relatively dense CO_2 could spread laterally within the unsaturated zone that is present above the water table in most terrestrial environments (excluding lakes and rivers); in marine environments, free CO_2 would not spread laterally in this way. Instead, dense CO_2-charged water produced by CO_2 dissolution would tend to spread laterally, below the seabed, or in the water column above it.

6 REFERENCE ENVIRONMENTS

The Guide aims to build confidence among stakeholders such that, if the suitability of a particular European CO_2 storage site was to be assessed in the future, the potential impacts of any CO_2 leakage, if it occurs, can be evaluated and understood adequately. A related aim is to provide guidance on *how* these potential impacts can be evaluated. Given the expected large range in environmental characteristics between individual sites both on- and off-shore, it is impractical to investigate all possible kinds of sites in a generic study of the kind undertaken in RISCS. Consequently, the approach taken was to research potential impacts within a few different kinds of environments (henceforth termed 'generic environments') that collectively contain all the important features and processes that might cause leaking CO_2, if present, to impact on sensitive domains above an actual storage site. It is likely that an actual CO_2 storage site will not be exactly like any of the generic environments. However, it is expected that the important features and processes that influence potential impacts within the actual storage site will occur within one or more of the generic environments. Consequently, by providing evidence to stakeholders that potential impacts within all the generic environments can be assessed adequately, the Guide will contribute to confidence among the stakeholders that potential impacts at the actual storage site can be assessed sufficiently. Similarly, based on experience gained by investigating and assessing potential impacts for the generic environments, techniques can be demonstrated that are appropriate for investigating and assessing potential impacts in any actual CO_2 storage site.

A small number of reference environments (Figure 4), including both marine and terrestrial examples have been defined (Table 1). The environments together explore a representative range of receptor classes within the two main broad categories, to give an indication of the range of features, events and processes that need to be considered when investigating potential impacts of CO_2 leakage.

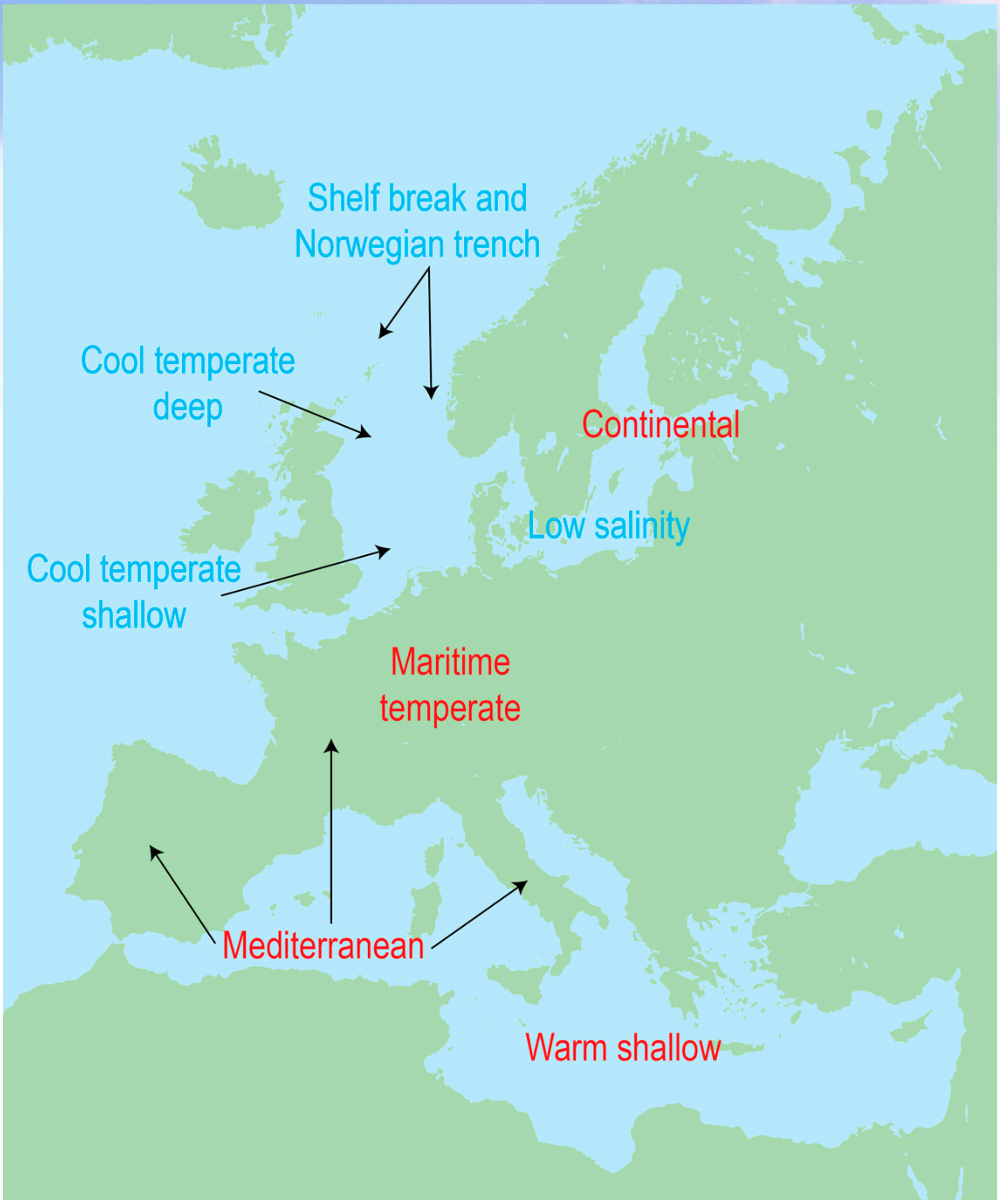

Figure 4 Reference environments defined to represent common ecosystems expected to occur over potential European storage sites.

Table 1 Reference environments defined in the Guide.

	Reference environments	Notes
Terrestrial	Maritime temperate	Representative of a northern central European, cool climate (e.g. UK and the Netherlands). The region is highly developed and has some of the world's highest population densities. Potential environmental risks from CO_2 leakage apply mainly to the root systems of agricultural crops, to soil microfauna or larger soil dwelling animals and to exploitable groundwater supplies.
	Continental	Climate associated with northern (but not Arctic) European continental land mass countries. The distribution of this environment corresponds broadly to the distribution of 'boreal forest' and extends as far north as the tree line. The environment is characterised by some of the lowest population densities in Europe. It also covers most of Sweden, Finland, and much of Norway.
	Mediterranean	Representative of warmer, more arid, southern European climates. The tree, bush and dwarf shrub dominated habitat types (forest, scrub and heath lands) occupy more than half of the region's landscape. Dense forests occur mostly in plantations or in natural forests under humid conditions by wetlands or in valleys.
	Generic urban	Specifically designed to explore potential impacts on humans should a storage system be located close to a large urban centre. At concentrations above 7% there is a significant danger in breathing, particularly where the concentration might increase in confined environments such as cellars. This reference environment is specifically defined to explore potential impacts on humans should a storage system be located close to a large urban centre. Detailed studies of the physiognomic effects of CO_2 are beyond the scope of this Guide and have not been considered in the RISCS project.
Marine	Cool, temperate, deep	Continental shelf remote from shoreline influences where the water depth is greater than 60 m, and typically over one hundred metres. Tides significantly influence mixing and currents but not water depth. The environment is not Arctic (no sea ice), but bottom water is cool (around 5°C). The moderately nutrient rich water is seasonally stratified, surface temperatures varying from around 4°C to around 15°C annually. Such an environment may be in the northern North Sea, or to the west of Norway south of the Arctic Circle.
	Cool, temperate, shallow	Land is relatively close and the water depth is a few tens of metres. A comparatively large tidal range could cause significant changes in water depth and strong mixing. Some seasonal stratification may occur but normally the water column is fully mixed. The temperature varies from around 4°C to around 15°C annually. Nutrient rich (eutrophic) water may be impacted by riverine water. Such a environment could be in the southern North Sea.
	Warm shallow	Land is relatively close and water is a few tens of metres deep. The tidal range is small. Variable seasonal runoff from adjacent land masses may be significant. The temperature is a minimum of 5°C at the seabed and varies annually from 6°C to 25 °C, with a mean of 10–12 °C, at the sea surface. Such a site could be in the Adriatic Sea.
	Low salinity (saline, but substantially lower than mean ocean salinity)	Land is relatively close and water is a few tens of metres deep. The tidal range is small. Water salinity is much lower than that of open ocean water (which is present in the other marine environments), but varies depending upon the proximity of the coast and open ocean. Biodiversity is much less than in the open-ocean. Such an environment would be in the Baltic Sea.

For each of these reference environments, key receptors can be identified. The potential impacts of elevated CO_2 exposure on some of these key receptors have been investigated for both terrestrial (**Table 2**) and marine (**Table 3**) reference environments.

Table 2 Terrestrial reference environments and key receptors. Those which are addressed in the Guide are identified by shaded cells.

	Receptor	Groundwater	Soil microbiology	Arable crops	Pasture
Reference terrestrial environments	Maritime temperate	▨	▨	▨	▨
	Continental			▨	▨
	Mediterranean	▨	▨	▨	▨
	Urban				

Table 3 Marine reference environments and key receptor species. Those which are addressed in the Guide are identified by shaded cells.

	Receptor	Annelid	Crustacea	Molluscs	Echinoderm	Phytoplankton	Microbes
Reference marine environments	Cool temperate deep	▨	▨	▨		▨	▨
	Cool temperate shallow		▨	▨	▨		
	Warm shallow		▨				▨
	Low salinity						

7 IMPACTS IN TERRESTRIAL ENVIRONMENTS

7.1 Background and context

The impacts of potential CO_2 leakage on any terrestrial site will be site specific and will depend on the geological context, previous history of the site and current land use, as well as the characteristics of storage, including the location of injection wells, the volume of stored CO_2 and the operational procedures employed.

7.1.1 Groundwaters

The potential impacts on shallow potable groundwater aquifers could apply in all terrestrial reference environments. Potential impacts could be twofold; firstly chemical reactions that could occur in the shallow aquifer should CO_2 leak into it and secondly the potential displacement or migration of deep brines into the aquifer as a result of pressurisation of the reservoir. Should CO_2 and brine migrate together, both processes could be combined. The potential impacts of brine displacement have not been specifically investigated in the RISCS project as the consequences of increases in salinity in groundwaters are well known from other work. The dissolution of CO_2 in the aquifer waters could result in acidification, water-rock reactions, and the potential release of elements (including trace metals) into the water. Depending on many complex, interacting processes (e.g. mineral dissolution and precipitation, elemental adsorption and desorption, and formation of ion complexes, all of which are a function of aquifer mineralogy and water chemistry, temperature and, to a lesser extent, pressure), elements could be liberated that may (or may not) impact water quality. The extent of the impact cannot be predicted in a generic sense as it depends on site-specific characteristics.

With brine displacement, high concentrations of various dissolved salts in a migrating brine could be mixed with the potable water that could locally reduce water quality, depending, again, on many interacting factors (e.g. the redox level of the intruding water versus that of the potable aquifer, brine leakage rate versus groundwater flow rate and aquifer mineralogy). Various other site specific factors will also affect the potential impact of CO_2 and/or brine leakage, such as confined versus unconfined aquifers, aquifer depth (i.e. pressure), groundwater extraction versus recharge rates, pumping well locations versus leakage location, aquifer heterogeneity (both mineralogy and permeability distribution), and the occurrence of other stressors (e.g. water production, anthropogenic contamination and saltwater intrusion).

Within this context four natural CO_2 sites were studied in the RISCS project: i) Florina (Greece), an industrially exploited CO_2 reservoir located in a stacked limestone-sandstone succession; ii) Latera (Italy), an extinct volcanic caldera with a high geothermal gradient where CO_2 is produced via thermo-metamorphic reactions in the underlying carbonates; iii) the San Vittorino Basin (Italy), an intra-montane basin surrounded by carbonate rocks of the central Apennine mountains where CO_2 produced by thermo-metamorphism is being emitted at surface together with groundwater (i.e. flowing springs); and (iv) Montmiral (France), where natural CO_2 accumulations in sandstones (capped by clays and marls) occur at depths of over 2000 m. These sites were studied to address the potential impact of both mechanisms described above, although focus was given more to in situ water-rock reactions in the aquifers themselves. It should be emphasised that these sites of naturally occurring elevated CO_2 are not potential CO_2 storage sites, since they are not located in areas that are geologically suitable.

7.1.2 Ecosystems

The potential impacts of CO_2 leakage on near surface ecosystems will depend on the characteristics of the land above the site including the geology, soil type, topography, climate and land use. They will also be influenced by the weather conditions, both preceding and prevailing, when leakage reaches the soil or escapes into the atmosphere. Factors such as soil moisture, permeability and cracking of dry soils will all influence the flux and concentrations of CO_2 in the soil. Preferential pathways through the soil are likely to lead to locally higher CO_2 concentrations where the impact of the leakage is potentially greatest. Lower permeability layers, or high moisture contents in the near surface, may impede gas escape and lead to a build up of CO_2 in the soil.

The flux of gas through the soil, and its concentration, are affected by the soil and air temperature, air pressure and wind speed and direction as well as soil moisture. These factors vary seasonally and with the passage of weather systems. The natural level and flux of CO_2 in the soil is also governed by these parameters and shows strong seasonal variability with maxima during the plant growing season when overall biological activity (especially plant respiration and photosynthesis) is greatest and minima in the winter. Thus the timing of leakage in this annual cycle can be important in determining the background level of CO_2 to which any leaked gas is added. During winter, frozen ground or snow cover can also affect soil gas contents and fluxes. Waterlogged ground may be common at this time of year, and in spring, especially where a thaw follows a hard winter, and can greatly impede CO_2 escape.

The timing of leakage will also be important in relation to the development stage reached by plants; young tender plants are likely to be affected more than mature specimens and the effects are likely to be greatest during the growing season compared with the more dormant winter months, at least in more temperate climes. In southern Europe in particular, hot dry summer conditions can lead to dieback in pasture vegetation and so the addition of CO_2 might have little impact on plants which have died back due to drought, though it could create larger impacts in plants that are becoming stressed through drought but yet to fully die back.

The RISCS project has included the study of impacts on both crops (arable and pasture) and soil microbes in both cool temperate and warmer Mediterranean terrestrial environments. Research encompassed both controlled injection experiments at sites in the UK and Norway, laboratory experiments in Norway and observations at sites of natural leakage in the Florina Basin in northern Greece. This has allowed a comparison of the impacts of newly introduced CO_2 in previously unaffected sites with sites, where the ecosystem has had a long time (years to thousands of years) to adapt to the presence of high concentrations of CO_2.

7.2 Baselines

An evaluation of the risks of leakage and their potential environmental impacts should be undertaken at each site because each will have specific characteristics, including the natural variation of the ecosystem. This can be achieved by undertaking baseline studies which include characterising the ecology of the surface and near-surface ecosystems. Such surveys may also contribute to required Environmental Impact Assessments. These surveys are applicable in all terrestrial reference environments but especially in the non-urban cases. Baseline studies need to cover the range of ecosystem and aquifer types within the project area and account for natural variability on different timescales (e.g. daily, seasonal, year on year). Results from the RISCS project suggest that the following should be included in baseline studies:

1. **Soil gas concentrations and fluxes.** The impacts of potential CO_2 leakages on ecosystems can only be evaluated if the baseline CO_2 soil gas concentrations and fluxes are available for any site. RISCS research has shown that CO_2 soil gas concentrations above 10% may impact on terrestrial ecosystems. Thus CO_2 soil gas concentrations above this concentration that were detected during the site characterisation phase would require further investigation to establish the cause. In some terrains with suitable access and relatively low relief, rapid surveys over large areas can be achieved with mobile atmospheric monitoring of CO_2 concentrations which could be supported by more detailed analyses of soil gas compositions and fluxes to atmosphere over identified areas of higher concentration.
2. **Plant surveys.** Differences in sensitivity in different species have been observed at all the RISCS project sites with grasses generally being more resilient than other plant types. Plant stress is detected where CO_2 concentrations are above 10% at 20–30 cm depth in the soil, although this concentration is within measured levels at depths of 60–90 cm in natural soils in some areas. Plant stress is manifested by discolouration of leaves (loss of chlorophyll). If exposure is stopped plants are likely to recover, but if exposure continues, plants are likely to die in less than four weeks. Additionally, poorly draining soils with high moisture content reduce CO_2 dispersal into the atmosphere. Thus baseline surveys should establish the land and agricultural use of a site, including the flora and soil type prior to any CO_2 injection. This would include any possible changes in crops in agricultural areas.
3. **Soil microbiology surveys.** Increased CO_2 concentrations have a complex impact on microbial populations which is difficult to interpret (Figure 5). Nevertheless, at sites where there has been prolonged exposure to high CO_2 concentrations, the microbial community has adapted to this environment with acidiphilic, anaerobic populations predominating. The RISCS project has not determined the significance of these changes with regard to soil fertility. Baseline studies could include an analysis of the microbial community present in the soil at a variety of depths so that any changes could be monitored in the event of leakage. Such analysis would be performed in areas of particular sensitivity, such as protected sites and would be undertaken once to establish baseline conditions, due to the expense of the surveys and the variable nature of microbial populations.
4. **Groundwaters.** A good understanding of an aquifer will require knowledge of the geology (lithology of the aquifer) and hydrogeology (flow and hydrodynamics) but also the 'baseline' conditions of mineralogy and water chemistry prior to CO_2 injection. This will help identify the potential impacts on the potable groundwater resource. Baseline monitoring of aquifers will be required in all reference environments where groundwaters are used, or could be used in the future, for fresh water supply. Some of this monitoring may be undertaken already if the aquifer is used to supply drinking water for example under the requirements of legislation such as the Water Framework Directive (EC, 2000).
    a. Baseline monitoring of a drinking water aquifer prior to deep injection is strongly recommended, with a wide range of parameters being measured in different areas and over different seasons to ensure a complete characterisation of the chemistry and spatial and temporal variability of the aquifer. This could include all carbonate system parameters, major and trace elements, dissolved gases and redox level. For example, work at the Florina site has shown seasonal variability of groundwater chemistry as a result of recharge rates in rainy versus dry periods of the year.

b. Mineralogical analyses of the aquifer are also desirable to aid in geochemical modelling and computer simulations of potential impacts, especially analyses of carbonate mineralogy for buffering capacity and of oxides for redox buffering and potential trace metal contents. The importance of site mineralogy was clearly shown at Latera and San Vittorino, where volcanic rock mineralogy at the former versus a carbonate mineralogy at the latter greatly influenced the level of impact and the specific changes in the water chemistry caused by the naturally-elevated CO_2. At San Vittorino, the greater buffering capacity of the carbonate lithologies reduced the potential changes in groundwater chemistry caused by the CO_2.

c. Specialised geochemical analyses can greatly aid interpretation of water rock interactions, as demonstrated at Montmiral. In shallow groundwaters at Montmiral, water-rock interactions were shown to have been caused by water in contact with a biogenic CO_2 soil reservoir. Lack of interaction with gaseous CO_2 of a deep origin was also confirmed by the absence of a $\delta^{18}O$ (the ratio of oxygen isotopes) shift towards more negative values as observed for example in the neighbouring Massif Central.

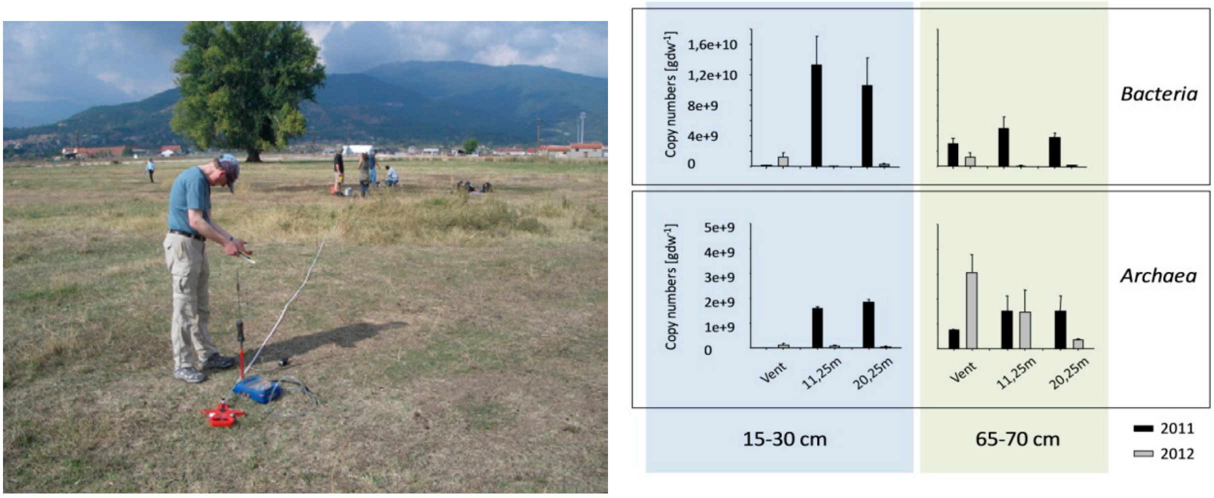

Figure 5 a) Measuring CO_2 content and flux of soil gas across a natural CO_2 vent near Florina, Greece. b) Impact of CO_2 on microbes near Florina, Greece. Numbers of bacteria and archaea were mostly lower at the gas vent but this was reversed by seasonal changes in 2012 at 65–70 cm

Accurate interpretation of the data from these baseline ecosystem studies will need to take into account other information including weather (such as temperature, precipitation and wind) and any other factors which might also impact on the health of the ecosystem.

Repeat baseline studies may need to be undertaken over a period of several years depending on regulatory demands and the seasonal variability at the site itself. Monitoring may be needed, for example, for between two and five years to sufficiently capture the expected range in natural variability. This monitoring does not need to delay the start of the project. Indeed, it may be prudent to undertake baseline surveys over long periods to determine changes resulting from other factors such as land-use changes and climatic variations. For some parameters, like soil gas concentrations and fluxes, continuous monitoring stations can be deployed to better define long-term (e.g. seasonal) variability at key locations. These can be used to extend baselines into the injection phase of a storage project, provided that no leakage occurs, and could help to identify underlying longer term trends.

Well-defined baselines are not only important in demonstrating an understanding of a site and its variability but also provide information that can be useful in assessing leakage allegations and claims of associated impacts as demonstrated by a recent example from Weyburn (Beaubien et al., 2013).

7.3 Potential impacts

7.3.1 Groundwaters

Impacts in groundwaters will be determined by a number of factors including the area of leakage, rate of CO_2 or CO_2-rich brine entering the aquifer, the groundwater flow rate, the mineralogy of the aquifer and its ability to mitigate changes to water chemistry.

Should monitoring find evidence of leakage into a potable aquifer, the work conducted in the RISCS project (on sites where natural CO_2 has been leaking or accumulating over geological time periods) can be used to infer the kinds of impacts that may be expected. Research at the four sites are examples of terrestrial Mediterranean environments (Figure 6), which are focussed on different aspects. The Latera and San Vittorino sites were examined at a very small scale to determine the spatial evolution of impact, the influence on different aquifer mineralogies, and possible differences between CO_2 + brine and CO_2-only leakage types. The Florina site was studied at the basin scale to look at potential regional effects and how impacts may vary in time as a result of different seasonal recharge rates. The Montmiral site was examined to compare deep reservoir brine chemistry and isotopes with that in shallow potable groundwater aquifers to study mixing processes, focussing on the potential for leakage of the brine upwards via faults or the deep boreholes drilled in the area.

Figure 6 Sites of RISCS groundwater CO_2 impact studies in France, Italy and Greece.

Analyses of natural CO_2-rich systems are extremely useful for determining how CO_2 migrates and reacts with groundwater and aquifer rocks in the subsurface, and the nature of the impacts when it leaks towards the surface. Although they do represent sites that have been exposed to naturally occurring emissions for very long time periods, and thus are quite unlike what might be expected from a potential CCS leak (which might be stopped shortly after its discovery), these sites help to fill the gap between short term laboratory experiments and theoretical modelling efforts. In particular, they allow the complex issues of scale, leakage pathways, heterogeneity, and interacting – and often competing – chemical reactions to be examined.

The distribution of leakage effects will strongly depend on factors such as leakage style (point or area), gas and/or brine leakage rate, groundwater flow rate, the presence of confined versus unconfined aquifers, and the aquifer mineralogy and chemistry. The carbonate-dominated aquifer materials buffered the pH decrease at San Vittorino to a minimum pH of 6 (Figure 7), compared to the less-reactive silicate mineralogy of sediments at Latera, where pH values down to 3.8 were observed. Furthermore, the composition of the gas stream can influence the nature of the impact, as the effect of pure CO_2 will be different from CO_2 which contains reduced acid gases like H_2S. For example, at Latera the presence of H_2S likely contributed to an additional lowering of the pH beyond that explained just by aquifer buffering capacity.

Groundwater flow direction and strength can strongly influence the shape of the impacted zone. At the San Vittorino site, although some impact was observed up gradient it was much reduced compared to that occurring down gradient (Figure 7). Brine displacement may induce anoxic conditions (i.e. where no free oxygen is present dissolved in the water) in an oxic aquifer.

The potential in situ release of trace metals will depend on aquifer mineralogy, with these elements occurring either as trace constituents of minerals that may be highly soluble (e.g. the carbonate minerals at San Vittorino) or as a potentially significant component of mineral phases that form a trace proportion of the rock that may be less soluble (e.g. arsenic in arsenopyrite, as is potentially occurring in the volcanic rocks at the Latera site).

Changes in chemical composition of the water along a flow path, and/or variations in mineralogy of the rocks through which flow occurs, can alter the attenuation of trace metal migration which is controlled by secondary precipitation of certain minerals in which the trace metals are included; or by adsorption onto mineral surfaces, such as clays or organic matter. Increases in the acidity of the water can cause release of trace metals to the point that precipitation of new minerals begins.

At both San Vittorino and Florina, increased Fe concentrations can be detected in groundwaters due to increasing CO_2 concentration and reduced pH values. Elevated concentrations of Mn were also observed at Florina. However, since Fe, Mn and other substances can also have elevated values in natural waters, changes in concentrations should be compared with variations in other indicators of elevated CO_2, as described above.

Springs can discharge CO_2-rich water without any impact on the health of humans or animals. Carbonated springs exist in San Vittorino and Florina and are used as drinking water sources. In Florina, naturally carbonated water is bottled and sold as sparkling spring water. This use of the water may be possible, however, owing to the carbonate lithology that occurs at both locations, as the source of potential trace metal contamination might be limited. In contrast, in terrains where the rocks have greater proportions of reactive minerals, as at Latera where the rocks are volcanic, there is the potential for more trace metal release. That said, the attenuation processes mentioned above will likely limit significant migration, while the kinetics involved in dissolution of these mineral phases might be sufficiently slow to minimise any impact if a leak is discovered quickly.

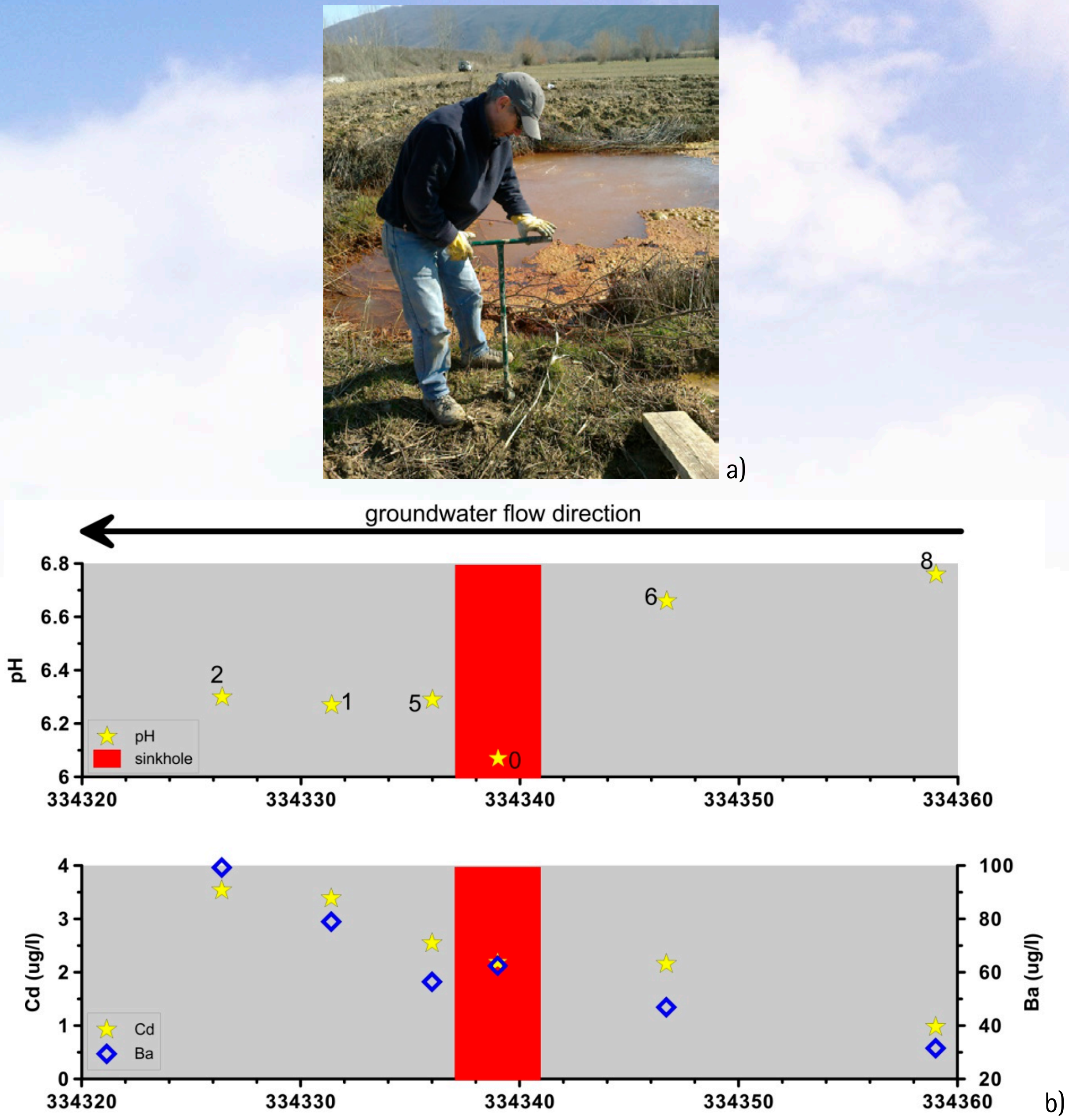

Figure 7 a) Augering a shallow borehole for groundwater sampling, San Vittorino, Italy. b) Results of groundwater CO_2 impacts, San Vittorino, Italy. The lower pH from CO_2 leakage at the sinkhole is associated with a rise in Cd and Ba. Cd gets close to drinking water limits (3-5 µg/l) but Ba is well below (700-2000 µg/l).

At Florina no significant negative groundwater impacts from elevated CO_2 concentrations were observed. There is no correlation between CO_2 concentration and dissolved metal concentrations, although a correlation between dissolved CO_2 and pH can be observed. However the possibility that CO_2-related leaching has resulted in previous release in metals has not been discounted.

At Florina, the ascent of CO_2 and of the groundwater with it, is not continuous but periodic. CO_2 concentrations vary substantially within the basin, reflecting the spatially and temporally variable flux of gas from depth. Hence, leakage may also be similarly spatially variable and episodic in rate.

7.3.2 Near surface ecosystems

Seasonal effects on plants and near-surface ecosystems, such as changes due to temperature, precipitation, and/or day length will impact plant growth and activity. Thus there is limited benefit to monitoring of such biological parameters in terrestrial ecosystems in the winter when growth is very limited because any impacts are unlikely to be detected, although near surface gas monitoring is often best in late autumn or winter when biological CO_2 production is at its lowest.

Plant response to increased CO_2 soil gas concentrations is very rapid. The threshold for observing responses appears to be at about 10% soil gas concentration at shallow depth (20–30 cm). Between 15–20% CO_2 at this depth, results indicate that broad-leafed plants become stressed within 7–14 days of exposure during the growing season and then die after a few weeks of continued exposure. However, plants with root systems that are well developed before exposure might be more resilient to subsequent increased CO_2 concentrations. For example, autumn-sown crops which were then exposed to CO_2 leakage in the following spring were less susceptible (Table 4).

Although CO_2 leakages have the potential to cause large decreases in yields from crops with short growing periods, such decreases are likely to have little economic impact because leakages are most likely to take place over small areas. Indeed, impacts may not be detected until harvest. This must be viewed in the context of other environmental stressors (e.g. weather extremes, disease and pests) which are likely to have greater overall impacts on crop yield. For well-established pasture, the impacts of CO_2 leakage on yields for animal feed might also be minimal, although they need to be evaluated carefully to establish whether there is a significant long-term (over several years) economic loss.

Table 4 Summary of CO_2 impacts on crops from ASGARD, UK field experiments, an example of a maritime temperate environment. Negative impacts (down arrows) were restricted to small areas.

	Oilseed rape (Spring)	Oilseed rape (Autumn)	Barley (Spring)	Barley (Autumn)	Beetroot
Plant / Stem no.	↔	↔	↓	↓	↔
Height	↓	↔	↓	↓	
Stem dry weight	↓	↔	↓	↓	
Pod / Grain no.	↓	↓	↓	↓	
Leaf dry weight	↓				↓

Microbial responses to increased CO_2 concentrations above ~20% at 20–30 cm depth are rapid with an increased activity rate as shown at ASGARD. Long term changes in the microbial community were only seen at Florina (Figure 5) and other European sites where there has been long-term natural leakage of CO_2. Such community adaptation was not seen at ASGARD over a period of 24 months.

Thus monitoring of the microbial population could provide early indications of increasing CO_2 on soil ecosystems and could also indicate where there has been long-term undetected exposure.

The RISCS project was not able to determine the significance of impacts of elevated CO_2 on soil fertility. This is because, in order to obtain a broad understanding of the impacts of elevated CO_2 in the near surface, the top 15 cm of soils, which is particularly important for fertility, were excluded in the studies. As impacts on plants with roots in the zone were observed (Figure 8), it is likely the microbes present will also be affected. This is a potential area of future research.

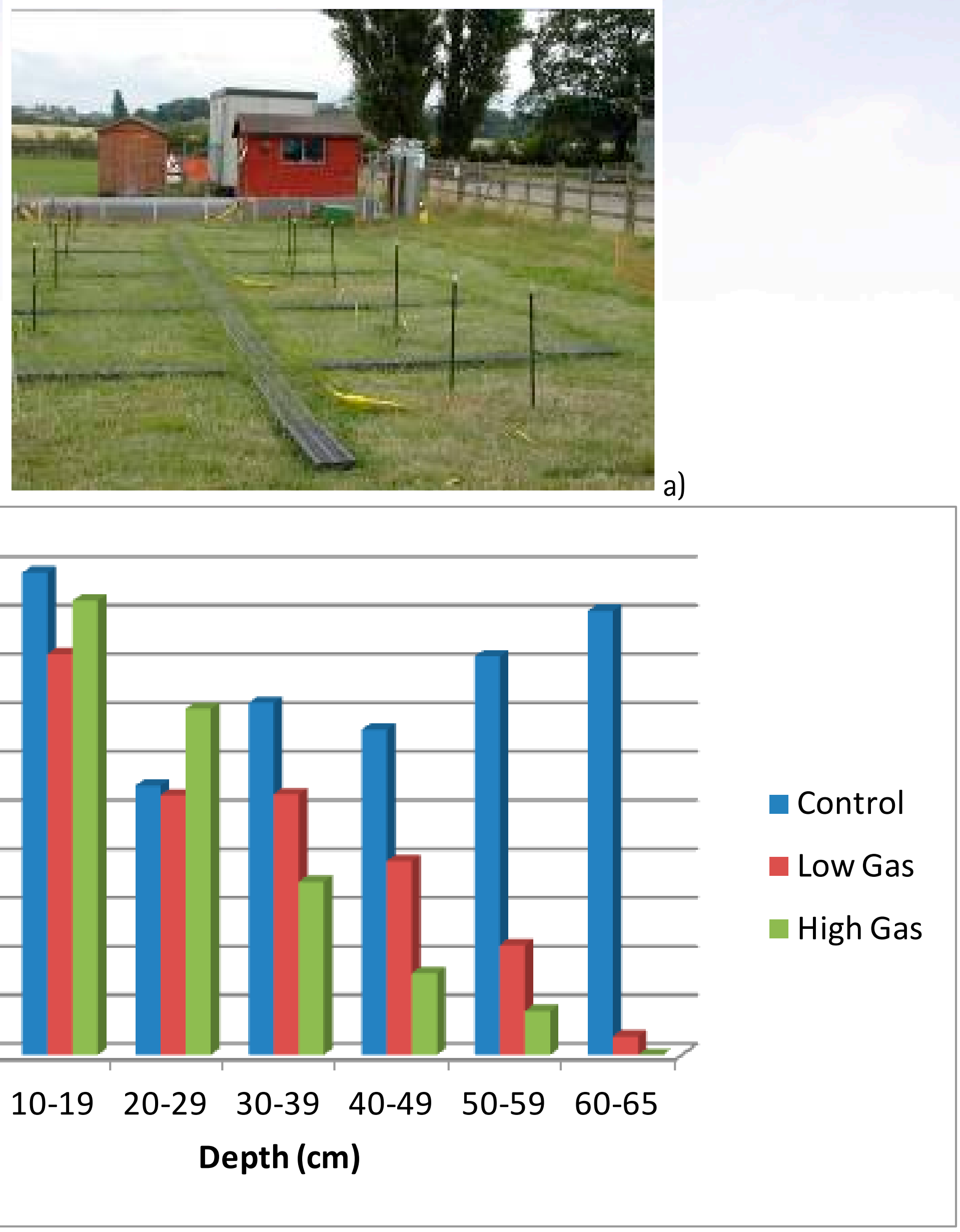

Figure 8 a) Experimental plots for examining CO_2 impacts, ASGARD near Nottingham, UK. b) Impact of CO_2 on root development of oilseed rape at ASGARD shows greatest impact on deeper roots but some enhancement at shallower depth.

Experiments conducted at the Grimsrud field laboratory, an example of a terrestrial continental environment and associated laboratory experiments simulated the impacts of a CO_2 leak on oats. Results showed that at the soil surface, the geometry of the leak seemed to be strongly related to the soil structure. Plant growth reduction, yellowing, purple discolouration, and reduced chlorophyll and canopy water contents were observed at the end of the growing season, where both soil and atmosphere were enriched in CO_2. The simulated leak had a strong impact on the soil CO_2 concentration but almost none on the atmospheric concentrations, suggesting that most of the impacts observed on plant development were due to high CO_2 concentration in the soil. In the canopy CO_2 seemed to be dispersed readily, even by gentle breezes, although there can be CO_2 build up under very still conditions. Such low air flow was more prevalent at night and especially just prior to sunrise.

The laboratory study performed in controlled conditions assessed the effect of high soil CO_2 concentrations on growth and photosynthesis parameters of different agricultural plant species. Results showed that plant growth and photosynthetic performance decrease with increasing root CO_2 concentration. The reduced plant growth and photosynthetic performance under high root CO_2 concentration is caused both by the direct toxicity of CO_2 and an indirect low soil O_2 concentration, resulting from replacement of soil air by CO_2. Differences in the tolerance to elevated root CO_2 concentration between oats and wheat could not be observed in the experiments. The sensitivity of plants to high root CO_2 concentration appears to depend on the size and/or physiological condition of the plants at the start of gas exposure.

7.3.3 Animals and humans

Impacts on animals (including humans) were not part of the RISCS project. The effects of elevated atmospheric CO_2 on humans when concentrations exceed certain thresholds are well known. Above 5–10% CO_2 can lead to unconsciousness and death, with symptoms such as headache, tiredness and dizziness at 1–5%. The hazard from leakage from CO_2 storage has recently been assessed and found to be lower than that arising from natural leakage of CO_2 in Italy. Natural seepage has caused animal and human deaths but at levels well below other socially accepted risks (Roberts et al., 2011). In the open air, the CO_2 concentration will depend on the leakage rate, the wind speed and direction and local topography. Continuous monitoring of atmospheric CO_2 suggests that the air is well mixed at relatively low wind speeds (5–6 ms^{-1} at 2 m above ground). Hence CO_2 will not reach hazardous levels except under very still conditions. Continuous monitoring at ASGARD for RISCS suggests that such conditions are more common at night and especially at daybreak. Under such low air flows CO_2 could build up in the atmosphere, particularly in hollows or valleys where it could accumulate because it is denser than air. The gas could also accumulate in basements if leakage occurred below buildings.

7.4 Monitoring and verification

As is widely recognised, multiple monitoring technologies are likely to be used to demonstrate site performance throughout the lifetime of a CO_2 storage project (pre-injection, injection, post-injection and closure periods). A range of monitoring tools is available and are continuously being improved (for example, see the IEAGHG Monitoring Selection Tool[3] for a comprehensive list of tools and their applications). Monitoring of the stored CO_2 is critical to ensure human and environmental safety and to conduct carbon credit audits. Additionally, monitoring could also contribute to the development of

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[3] http://ieaghg.org/ccs-resources/monitoring-selection-tool1

public confidence in any given storage project. Monitoring will be applicable in all reference environments.

Monitoring technologies should detect and provide early warning of any leakage that might require mitigating actions. They must be able to define the area of any CO_2 leakage and also provide an indication of the significance of this leakage on terrestrial ecosystems, as well as monitor the effectiveness of any remediation that may be implemented.

The RISCS project has demonstrated that the following factors should be considered when constructing and implementing a monitoring programme, which includes evaluations of the impacts of leakage on the terrestrial environment—specifically on plants, soil microbiology and potable groundwaters.

1. Any unexpected CO_2 leakage is most likely to be from small point sources, particularly arising from defective wells or associated with faults. This leakage would be most likely to occur during and immediately after the injection period. Both natural CO_2 emissions and those observed in injection experiments tend to occur over small surface areas (metres to tens of metres in scale). Therefore, given the size of storage sites, techniques must be selected to obtain a range of resolutions from rapid evaluation of a large area (kilometres in scale) to assessments capable of determining leakage on a metre scale. They must also be sensitive enough to determine increased CO_2 concentrations above the background concentrations determined during site characterisation. They also need to be able to discriminate the source of the CO_2 i.e. whether it arises from CO_2 storage or from other sources such as shallow biogenic processes. This can be achieved through an examination of the relationship between CO_2 and other gases such as oxygen and nitrogen, using isotope ratios or through tracers added to the injected CO_2. In some cases, low-level leakage has been apparent from such detailed methods even when not distinguishable from natural background using CO_2 concentration or flux measurements alone.
2. Reference sites, where no CO_2 injection is planned, could be useful in identifying impacts on terrestrial ecosystems due to factors other than CO_2 leakage which might also impact the storage site. However, this needs careful consideration to ensure the reference site remains relevant to the particular storage project throughout the project duration.
3. Soil gas concentrations above 10% at 20–30 cm depth start to impact on both plants and the soil microbiology. Such concentrations at normal soil gas sampling depths of 60–90 cm should trigger an inspection of the site. However, it may be that CO_2 concentrations below this level may be anomalously high at a specific site and so thresholds should be defined from the expected natural variability determined by the site-specific baseline surveys.
4. Monitoring must include techniques which can assess CO_2 leakage on surface and near-surface ecosystems and the RISCS project has used several methods that could be used or tailored for particular storage projects. Experimental and modelling studies have indicated that soil gas monitoring is particularly valuable (Figure 5). This is because plants and microbial soil ecosystems are more sensitive to increases in CO_2 concentrations in soils than to levels in the atmosphere, as the latter tend to be reduced rapidly by dispersion and mixing. However, it must be recognised that such monitoring will also need to assess any other potential causes of ecosystem stress in the environment. Consequently, a variety of techniques will have to be used together so that a full understanding can inform assessments.
5. It is likely that large areas may need to be monitored at any site, the size of which will be dependent on the particular storage project. Thus there is a need to utilise rapid survey

techniques to detect areas of concern. Consideration of continuous monitoring techniques e.g. soil gas concentration or flux measurements and/or atmospheric monitoring may also be needed where particular areas of concern are targeted, for example, near an injection well.

6. Ecosystem impacts can themselves potentially indicate the presence of leakage, although field experiments and numerical modelling in the RISCS project has shown that such impacts due to leaking CO_2 may be of a similar magnitude to those of other stressors. Hyperspectral remote sensing could be used to monitor changes in the reflectance spectra of the vegetation located above a CO_2 storage site. However, this method estimates the health of vegetation and might not be able to differentiate variation of health due to CO_2 leakage from that caused by other stressors e.g. extreme weather. Similarly, variations caused by changes in land use in farming areas may also be difficult to assess. Nevertheless, the method might be adapted to monitor larger areas and could be cost effective if, for example, satellite data can be used rather than special acquisition using aircraft. However, the data are not continuous and need processing which could be time consuming unless automated. The most appropriate times for this method are during the spring and summer in order to detect germination effects and changes in normal growth patterns. The method is less valuable in the autumn and winter when, for example, snow cover might prevent its use in some climates. Remote sensing imagery should be collected towards midday for greater sensitivity. Hyperspectral indexes such as the NDVI_{705} and the agricultural stress index seem to be particularly adapted to the detection of CO_2 leaks through plant stress.
7. Studies at the RISCS sites have shown that bio-indicators may be useful for determining the location of leakages. For example, *Polygonum* spp was a useful plant indicator of CO_2 vent zones at Florina (Figure 9) and at Laacher See. Leguminous plants, such as beans and clover, are also potential indicator species being sensitive to elevated CO_2 concentrations. The development of microbial bio-indicators for rapidly detecting elevated CO_2 in soils is also a potential area of research.
8. Where detailed tracking of CO_2 might be required, field trials undertaken in the RISCS project have indicated that isotopic monitoring can characterise the three-dimensional extent of the leak within the soil-atmosphere continuum, including the assimilation of leaking CO_2 by vegetation. In these experiments, isotopic analyses improved the detection and monitoring of the simulated leakage of geological CO_2, enabled the proportion of the flux that was due to injected CO_2 to be estimated and the characterisation of different zones of CO_2 transfer in soil. However, this was dependent on a clear isotopic contrast between the injected CO_2 and local biogenic CO_2. This might not be the case, for example, when the CO_2 is derived from the combustion of coal, which is itself formed from ancient plant material.

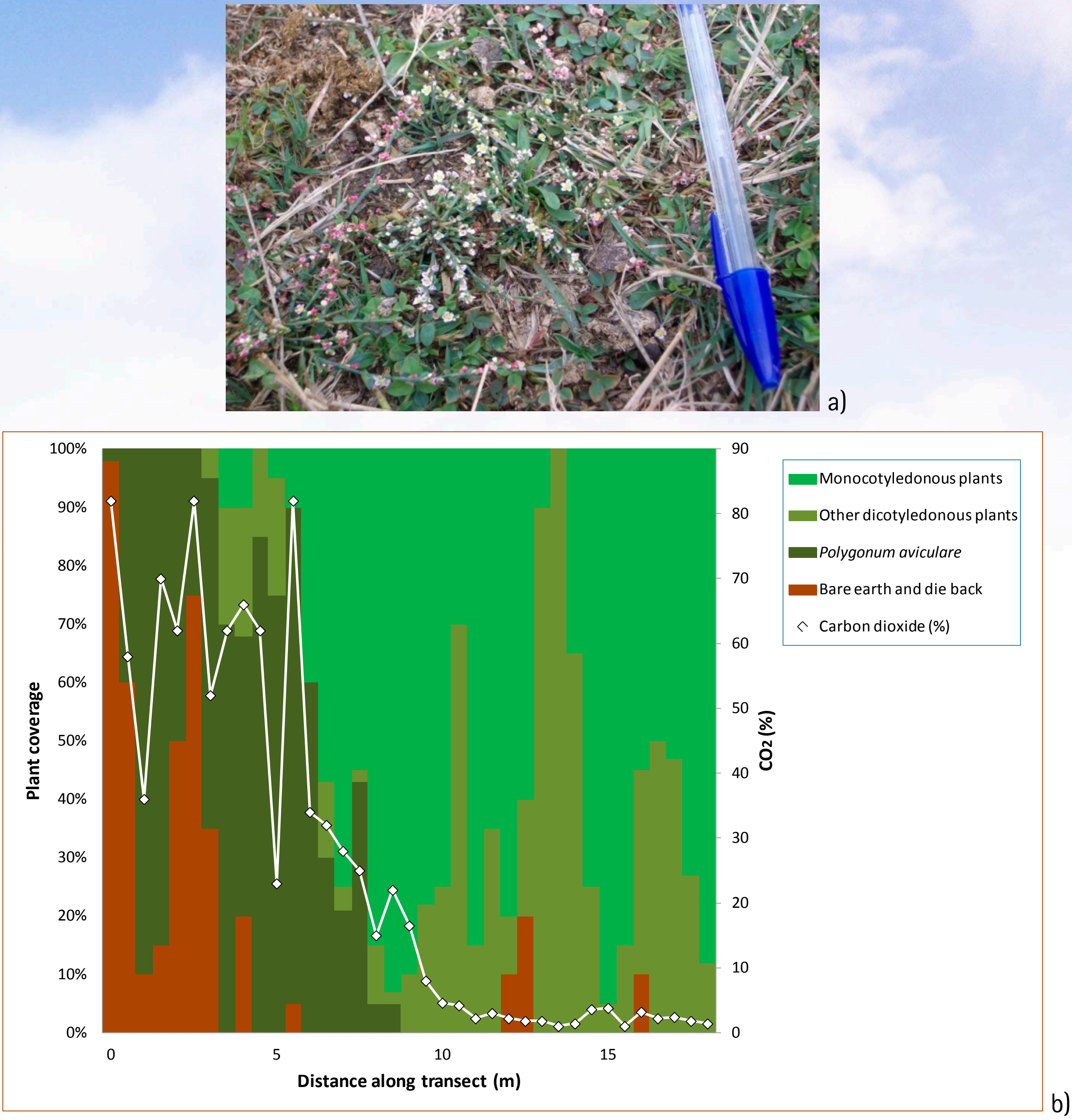

Figure 9 a) Plants present at different CO_2 levels, near Florina, Greece. *Polygonum aviculare* is tolerant of high CO_2 levels. b) Monocotyledonous (grasses) in general cope better at moderate CO_2 levels than dicotyledonous (Eudicotyledons) (broad leaved plants)

Through the work conducted in the RISCS project for the assessment of the possible environmental impact of naturally leaking CO_2 on groundwater quality, the following can be concluded:

1. Aquifer monitoring during CCS operations will require analysis of parameters that respond quickly to the addition of CO_2 (and/or brine) to maximise early warning. In addition these methods should be rapid, sensitive, and inexpensive. In this regard, field analysis (either manual or automatic) of conductivity and pH would be recommended, while carbonate

alkalinity analyses in the laboratory (as well as in situ) would also be extremely useful. Conductivity and pH analyses can be routinely and cheaply undertaken, if access to groundwaters is provided, e.g. via boreholes for public drinking water supply. These parameters were found to change significantly at all four of the analogue sites studied, and the first two provided an immediate, field-based assessment of impact during the sampling campaigns. Measurement of the dissolved gas concentrations could also be implemented, with, for example, the deployment of continuous monitoring probes that measure partial pressure of CO_2 (pCO_2).

2. Electrical resistivity tomography (ERT) could potentially be used above a shallow aquifer, as any significant increase in conductivity caused by CO_2-induced reactions or brine leakage would result in a measureable anomaly that could be used to define the spatial extent of the impacted zone.
3. If, during the monitoring period, there is indication or proof of leakage into an aquifer, samples will need to be analysed for major elements (to assess brine mixing and geochemical interactions), trace metals (such as As and Pb, which may be mobilised), and organic compounds that may be co-migrating. Examination of major and trace element concentrations and ratios, coupled with modelling, can also be used to determine whether an observed impact is due to in situ reactions with CO_2 or to mixing with leaking brine. The value of this approach was demonstrated at Florina where three water sampling campaigns were conducted to identify possible changes and define the general trends in water chemistry for the area.
4. Use of reference sites, where no CO_2 injection is planned, could be useful in identifying other impacts on groundwater and providing continued information on background variability. However, this needs careful consideration to ensure the reference site remains relevant to the particular storage project in terms of the chemistry and mineralogy of the reference versus studied aquifers. Work at the Florina site has shown that there will be seasonal effects on the chemistry of the groundwater. After prolonged rainfall elemental concentrations increased.
5. It is likely that large areas may need to be monitored, the size of which will be dependent on the particular storage project, but which may cover not only the footprint of the stored CO_2, but also at least some of the surrounding area. Thus there is a need to utilise rapid survey techniques to detect areas of concern. Consideration of continuous monitoring techniques, such as measurements of the dissolved and gas phase of CO_2, may also be needed where particular areas of concern are targeted, for example, near an injection well.

7.5 Remediation of terrestrial environments

Although remediation was not a specific part of the RISCS project, the following recommendations can be derived from the study, which are particularly relevant to non-urban reference environments. In addition, further possible options for remediation are included in Chapter 9. Plants appeared to recover quite rapidly after exposure to elevated CO_2. At ASGARD, 4 months after CO_2 injection ceased (and CO_2 concentrations were within normal limits), grasses had completely recovered in terms of biomass, but clover had not fully recovered. The pasture plots appeared to respond in a similar way but this requires further study. Recovery of crops will be dependent on various factors including the stage of development at onset of exposure, length of exposure and concentration of CO_2 in the soil. If exposure time is short, crops may resume growth following repair of any leak but yield may be reduced. Some crops are more susceptible to damage during the early stage of development and high soil concentrations of CO_2 at this stage may mean that no recovery of the plant is possible. Microbial recovery is difficult to interpret but RISCS project data suggest that microbial numbers do recover to baseline values.

The development of any remediation strategy will largely be based on economic considerations. It is probable that little can be done until the leakage has been halted. It is likely that lower crop yields will have to be accepted until this has occurred. Alternatively, replanting with grasses, as an alternative crop, could be feasible if CO_2 in soil gas is between 20 and 50% and if economically viable. However, demonstration of effective grass germination at these CO_2 concentrations would need to be established. If the leakage can be stopped rapidly, then a period of recovery may be necessary before replanting. As stated above, however, even if a leak were to occur it is expected that it would impact a very small area (e.g. 10x10 m), which would be negligible in the context of a cropped field of a few hectares.

Surface remediation of any leakages may be best achieved during fallow periods, when there are no crops in the fields, particularly following harvest because remediation may cause further damage to growing crops. When leakage has stopped, remediation of crop plants may simply be achieved by ploughing to aerate the soil followed by normal sowing procedures. For longer established pasture, remediation would also be better achieved during the winter after the growing period and any harvesting for animal fodder. However, careful consideration of the economic benefits of undertaking surface remediation would need to be made.

7.6 Site selection

Leakage from a storage site in a terrestrial environment will have a low probability, provided site selection and operation are carried out correctly following the requirements of the European Storage Directive (EC, 2009). The work carried out in the RISCS project identified no reasons why suitable storage sites could not be found within any of the generic environments. Site selection should include consideration of specially protected areas (e.g. Special Areas of Conservation or 'Natura 2000' sites (EC, 1992)). It would also be prudent to consider the possibility of CO_2 build up at the surface in the event of leakage, which, in terrestrial environments, would be influenced by a wide range of factors including topography, weather and soil moisture content. Thus, for example, open rural environments, where rapid mixing of any escaping CO_2 into the atmosphere could be expected, would be preferable to sheltered low-lying areas or urban environments where such mixing might be more limited and gas could concentrate in cellars or basements.

The RISCS project has investigated potential changes to groundwater chemistry as a result of long-term CO_2 leakage into near-surface aquifers, with the results being useful to determine risks based on different lithologies and geological settings. As these are natural sites, leakage is primarily related to faults. However, studies of these natural sites have provided generic evidence for the kinds of impacts that might occur around all the different kinds of leakage paths that will need to be considered when evaluating future CO_2 storage sites. Where a potable water aquifer overlies a CO_2 storage reservoir, the most important issues that must be addressed are potential gas and/or brine migration pathways (e.g. faults or boreholes), as well as the characteristics of the aquifer itself that may make it more or less vulnerable, such as the capacity of the aquifer to accommodate changes in groundwater chemistry caused by the introduction of the CO_2, existing or planned exploitation and other stressors. In addition, the scale of potential leaks is very important, ranging from point (e.g. well) or line (spot leakage along a fault) leakage for both gas and/or brine, to area leakage for brine only (e.g. up-dip displacement of saline pore water along an inclined aquifer due to increased injection pressure). The CO_2 in both localised and diffuse seeps could originate either as CO_2 that has been transported from depth as a free phase, or as CO_2 that has been transported in aqueous solution and then degassed at shallower depths. This scale will control the potential impact of a leak on groundwater supplies, with a point leak resulting in a plume that may have a very limited spatial impact to an aerial leak that could potentially affect a larger area. To further constrain these potential risks, detailed geological surveys, mapping, and the creation of 3D geological/structural representations are needed, and associated pressure, hydrogeological, and geochemical modelling must be undertaken during any site characterisation process.

7.7 Recommendations

- Ecosystem baseline surveys should be carried out at proposed storage sites to ascertain any changes resulting from leakage. These will also assist in Environmental Impact Assessments. It would also be beneficial if reference sites were similarly assessed and monitored so that any ecosystem changes attributed to CO_2 leakage can then be compared to changes at the control site.
- The significance of impacts from a credible leakage scenario on near surface ecosystems is expected to be very low, relative to other types of environmental damage such as those arising from climate change and extreme weather events. However, the significance of any leakage will depend on when it occurs (i.e. leakage during the growing season is likely to be more damaging than in winter) and its duration before detection and potential remediation. Additionally, marginal terrestrial environments, such as those with very short growing seasons, may be more sensitive to CO_2 leakage although this was not studied in the RISCS project. Consequently, it is important to take into account the context of leakage when assessing impacts on terrestrial ecosystems for a particular storage project.
- Storage projects should, as a minimum, undertake regular CO_2 soil gas evaluations at a variety of scales (metre to kilometre scale) and depths. It is not recommended to undertake ecosystem monitoring in the winter because ecosystems are much less active at this time. Initially, two to three surveys might be undertaken per year to define baselines although this will depend on land use.
- The RISCS project has shown that short term exposure to elevated CO_2 has no long-term effects for many crops. Affected crops should either be allowed to grow until harvesting or should be replanted. The decision on the approach will depend on economic considerations and the timing of leakage. However, recovery in pasture and after long-term exposure to elevated CO_2 concentrations is unclear and it is recommended that further research is undertaken to clarify these uncertainties.
- Further research should be undertaken to understand the effects of ecosystem changes on soil fertility arising from elevated CO_2 soil gas concentrations. Research into the potential use of bio-indicators as quick monitoring techniques should also be carried out.
- The significance of any leakage on groundwater resources will depend on many different site-specific factors, such as whether the aquifer is confined or unconfined, the aquifer material being pH or redox buffered, the mineralogy and the trace element content of the aquifer material, the balance between the flow rates of the aquifer groundwater and the leaking gas and/or brine, the time of year when the leak occurs (e.g. spring with high water table or autumn with low water table) and the leakage duration prior to it being discovered. Furthermore, whether an impact is deemed significant or not is to a very large degree a judgement for stakeholders based on local circumstances.

- In shallow aquifers, the RISCS project has shown that despite the very long term exposure of the studied groundwaters to gaseous CO_2 leakage, the impact is limited both in terms of spatial extent and water quality, but can be spatially and temporally variable. This is due to the interaction of various chemical and biochemical reactions that attenuate the mobility of any liberated or added elements, although again this will be site specific and will also depend on groundwater flow rates.
- The aquifer mineralogy can greatly influence the potential impact on groundwater, and impurities in the leaking CO_2 stream can also change the impact. Some impurities (for example hydrogen sulphide) may decrease pH to even lower levels and make the water more anoxic (decreasing the oxygen concentration).

8 IMPACTS IN MARINE ENVIRONMENTS

8.1 Background and context

As for the terrestrial environment, the heterogeneous nature of geology, marine unconsolidated sediments, water column hydrodynamics and biological communities implies that any given leakage event will be to a significant extent unique, although clearly governed by the same physical laws. In order to draw out useful generic understanding the RISCS project has looked in detail at three reference environments (shallow and deep cool temperate environments, typified by the southern and northern North Sea regions, and warm shallow typified by the Mediterranean fringes) whilst also acknowledging more uncommon environments such as the low salinity Baltic system. The RISCS project has used a combination of experiments (on both North Sea and Mediterranean species); observations of natural CO_2 seeps (Mediterranean); and modelling of leakage dispersion and impacts to assess the nature of possible impacts in these environments. The experimental approach included work on individual species (such as crabs and shrimps) and communities of organisms (e.g. a North Sea ecosystem, shell gravels and Mediterranean microbial assemblages). Experiments were conducted at different scales in mesocosms (tanks) ranging up to 1000 litres and in situ, in the deeper waters of a Norwegian fjord, using a benthic chamber lander. Observations were made around natural (volcanic) seeps of CO_2 near the island of Panarea in southern Italy (**Figure 10**). Modelling explored a range of leakage scenarios in a typical NW European shelf environment.

Setting aside the question of risk, understanding impacts in marine environments needs consideration of both the vulnerability of the biology and the area and/or volume of the environment affected by any given leakage scenario. Furthermore, the broader context is important as the marine system is extensively impacted by many other anthropogenic activities such as trawling and is highly likely to be impacted by climate change (e.g. ocean acidification) over extensive areas. A sensible risk assessment for CCS requires comparison with other ongoing and potential impacts.

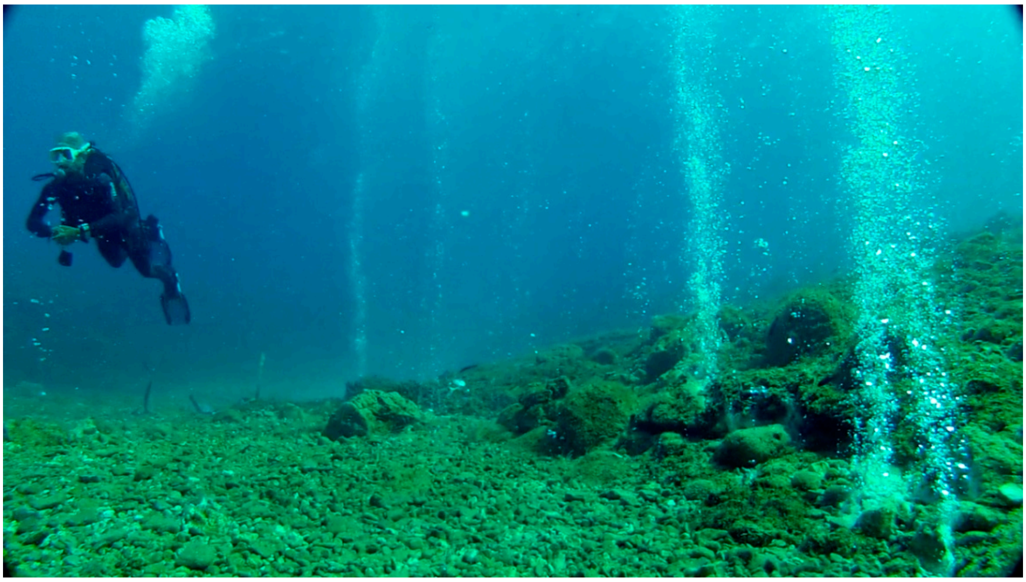

Figure 10 Investigating natural volcanic CO_2 leakage near Panarea, southern Italy

Apart from impact assessment, the second important requirement relates to monitoring. Monitoring of deep geology can effectively track significant accumulations of CO_2 but is unable to resolve smaller fluxes. Direct monitoring of the near surface environment provides further assurance and the possibility to quantify leakage, should it occur. The challenge which needs to be addressed is how to distinguish a leakage signal from the baseline, which due to a range of natural processes can show significant variability both spatially and over daily and seasonal cycles.

8.2 Baselines

8.2.1 CO_2 chemistry in the marine environment

CO_2 is a natural component of seawater, usually existing in equilibrium with the atmosphere, if integrated over an annual cycle. CO_2 is highly soluble in seawater; with solubility increasing with depth as pressure rises. CO_2 concentrations are most routinely referenced by either pH or pCO_2. The pH of surface seawater in the open sea usually lies in the range 8.0–8.3 and pCO_2 in the range 250–450 µatm, although there are many exceptions to this. Sediment systems have different chemical processes and restricted mixing in which pH may vary by over 1 pH unit within a very short distance of a few millimetres from the sea floor. Leaking CO_2 could theoretically reduce the local pH by as much as 2 pH units (equivalent to two orders of magnitude increase in acidity), though this would be in extreme circumstances.

The behaviour of carbon dioxide in sea water (known as the carbonate system) is well understood (**Figure 11**). When CO_2 dissolves in water it initially forms carbonic acid, which then disassociates into bicarbonate and hydrogen ions, the latter resulting in an increase in acidity measured as a decrease in pH. The extra hydrogen ions scavenge carbonate ions causing these to decrease. Such changes impact marine biogeochemical cycles and ecosystems as many biochemical and physiological processes are controlled by pH. Furthermore, bicarbonate and carbonate are substrates for some of the most fundamental marine processes such as photosynthesis and calcification. Calcification, the generation of hard shells by many types of marine flora and fauna, is inhibited by excess CO_2 in the system. Photosynthesis may be enhanced by excess CO_2, but for some species more than others, causing a change in community structure at the base of the food chain.

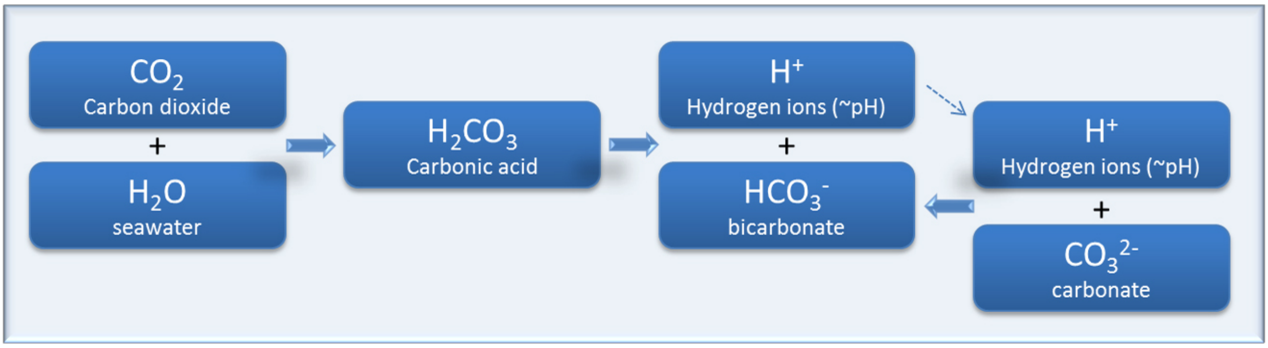

Figure 11 Schematic of the basic chemical reactions of carbon dioxide in seawater.

Over an annual cycle the acidity in seawater will vary by 0.2–1.0 pH units (typically 0.3–0.4 pH units in shelf seas, **Figure 12**). Note that pH is a log scale and a change of 1 unit represents an order of magnitude change in effective acidity/alkalinity. This variability is due to four main processes:

- The water temperature, which is much more variable over the annual cycle in relatively shallow shelf seas compared with the open ocean. Temperature affects the equilibrium state of the carbonate system (CO_2 in solution) and hence pH.
- Boundary conditions such as riverine flows and the Baltic input which have unique carbon signatures that derive from geology and land use. Locally these specific inputs can also change pH
- On seasonal scales exchange of CO_2 and O_2 with the atmosphere and oceanic water is also significant.
- The biological processes of respiration and photosynthesis which produce and take up CO_2 respectively. These processes vary both seasonally and over day-night cycles.

The natural variation in pH can also be significant over relatively small spatial and temporal scales, and in some cases diurnal signals can approach the magnitude of seasonal variability. Frontal systems and biological features such as blooms also give rise to significant spatial discontinuities. This variability is greatest in well-lit surface waters, where most of the primary production (photosynthesis) occurs. Primary production associated with benthic systems occurs only in shallow regions (<20 m) of relatively turbid waters like the North Sea but may occur at depths of up to 100 m in relatively clear waters (as found in some parts of the Mediterranean). At the benthic surface, where leakage signals are most likely to be apparent, the main biological process is respiration which can create locally significant increases in CO_2.

If leaked CO_2 appears at the sea floor in gaseous form it will be buoyant and form a rising bubble plume. Concurrently, as CO_2 is highly soluble in seawater, it will dissolve rapidly. The RISCS project has not explicitly researched bubble plume dynamics, but relying on published information we can be confident that bubble plumes will generally dissolve within 10 m of the sea floor. Seawater with a high concentration of dissolved CO_2 has a higher density and will tend to sink relative to 'normal' seawater. This effect is likely to create a plume of higher CO_2 concentration near the seabed over several tens to hundreds of metres from the source. As a result, most environmental impact is predicted to occur at the sea floor, to benthic communities and especially sessile, immobile biota.

Whilst the epicentre of a leak is likely to induce a pH significantly lower than found naturally, this might be confined to a small volume and be difficult to detect. The surrounding area affected by the leak will likely show deviations similar to that expected due to natural variability.

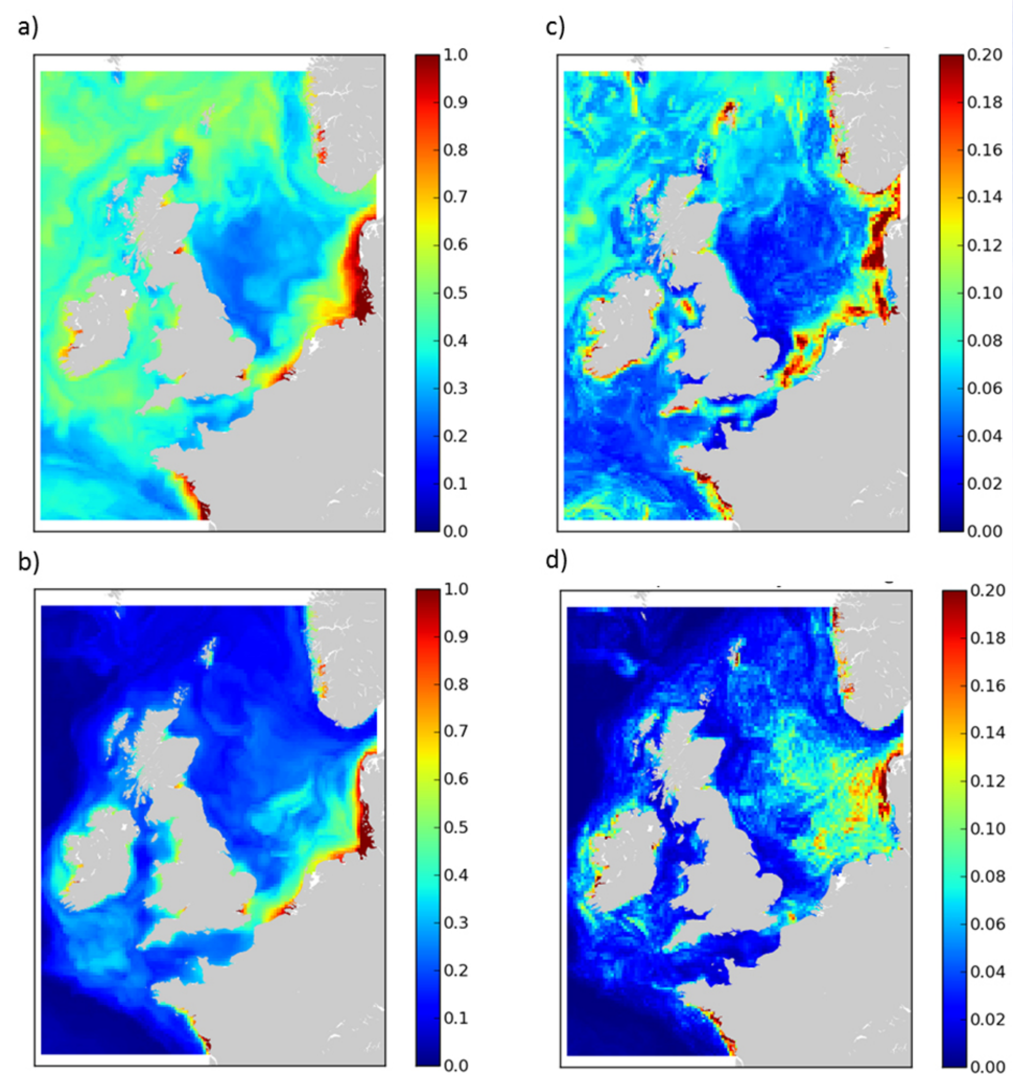

Figure 12 a, b) Annual range in daily mean pH derived from a model simulation (a surface, b, sea floor) c, d) Largest day on day change in pH recorded over a 15 year model simulation (c surface, d, sea floor).

8.3 Potential impacts

8.3.1 Biological sensitivities to high CO_2

It is essential for organisms to maintain their intercellular pH value within a certain range that allows physiological processes to function. However, as outlined in the previous section, pH also varies under natural conditions and organisms have the capability to cope with moderate pH changes in their environment. Mobile species, like fish, will avoid areas with unfavourable pH (and other) conditions, and therefore they will not be strongly impacted by a CO_2 leak. However, if a leak resulted in elevated CO_2 levels on the fish spawning grounds or nursery areas, avoidance of these could reduce the reproductive success of a fish population. Early life stages, especially those of calcifying species are amongst the most sensitive to the effects of elevated CO_2. This implies that the biological impact of a leak will be greatest during the reproductive season of these species (typically in early spring).

For many benthic sediment dwellers, because of strong natural gradients in pH, controlling internal levels of pH and CO_2 is an integral part of their physiology. Many infaunal organisms have developed physiological and/or behavioural mechanisms to cope with short-term variability in seawater carbonate chemistry (e.g. acid-base buffering, metabolic depression or changes in respiratory behaviour). However, these mechanisms are only effective within specific ranges of pH and pCO_2, and the largest changes in seawater chemistry predicted to occur in association with leakage events could swamp these mechanisms, resulting in significant impacts on organism health, activity and ultimately the survival of specific individuals. In addition, the mechanisms used by many organisms to cope with elevated CO_2 levels often come at a metabolic cost and need to be supported by either increased feeding or by diverting energy away from other physiological processes (e.g. growth or reproduction). This would mean that in situations where resources are limited, even small changes in seawater chemistry, if maintained for long enough, could result in negative effects on key ecological processes and a subsequent loss of either organism or population fitness.

Experiments in the RISCS project conducted on the decapod crabs, *Carcinus meanus* and *Carcinus aestuarii* have demonstrated that although exposure to elevated seawater pH caused substantial short-term changes in extracellular acid-base balance, these organisms were able to strongly regulate their physiology to cope with these impacts. These results are in agreement with a number of previous studies. Despite being relatively insensitive to elevated CO_2 in the short term, for *Carcinus aestuarii,* there is an additive negative effect when this species experiences both simultaneous increasing temperature and decreasing pH, which results in an increased mortality at higher temperatures indicating that elevated levels of CO_2 (hypercapnia) can reduce an organism's ability to perform and survive under elevated temperatures. Interestingly, these same experiments also indicate that when the crabs experience a sudden change of pH back to normal conditions, additional mortality occurs amongst crabs that until then seemed well adapted.

The shrimp *Palaemon elegans* showed greater sensitivity to reduced pH, independent of temperature, than the two species of crab. This was observed for populations from the Mediterranean and from the Western English Channel.

The larger the difference between the environmental and the organisms' optimum pH, the more energy it will need to maintain an acceptable intercellular pH value. As long as the organism is able to compensate for this energy loss by additional food uptake, it is likely to cope with a moderate shift in pH. This ability however is variable between species. For sea urchins, for example, it has been shown that parental adaptation to living at high CO_2 levels leads to reduced reproductive success.

Calcifying organisms like molluscs, corals and specific algae have been identified as especially vulnerable to acidification as these organisms need to produce calcified structures (shells, skeletons) to survive (Figure 13). Acidification lowers the aragonite and calcite saturation state of seawater, making carbonate ions less available for calcification, and increasing erosion of shells. Fully developed individuals are not directly affected by some outside erosion of the shell as long as it maintains its protective and structural function. Larval stages however, are very sensitive, particularly at the time when the foundation of the shell is produced. A reduction of 1 pH unit can therefore cause substantial mortality amongst mollusc larvae, as was shown in the outdoor mesocosm study performed within the RISCS project and confirmed by other research. However, these larvae are mobile and populations could recover quickly.

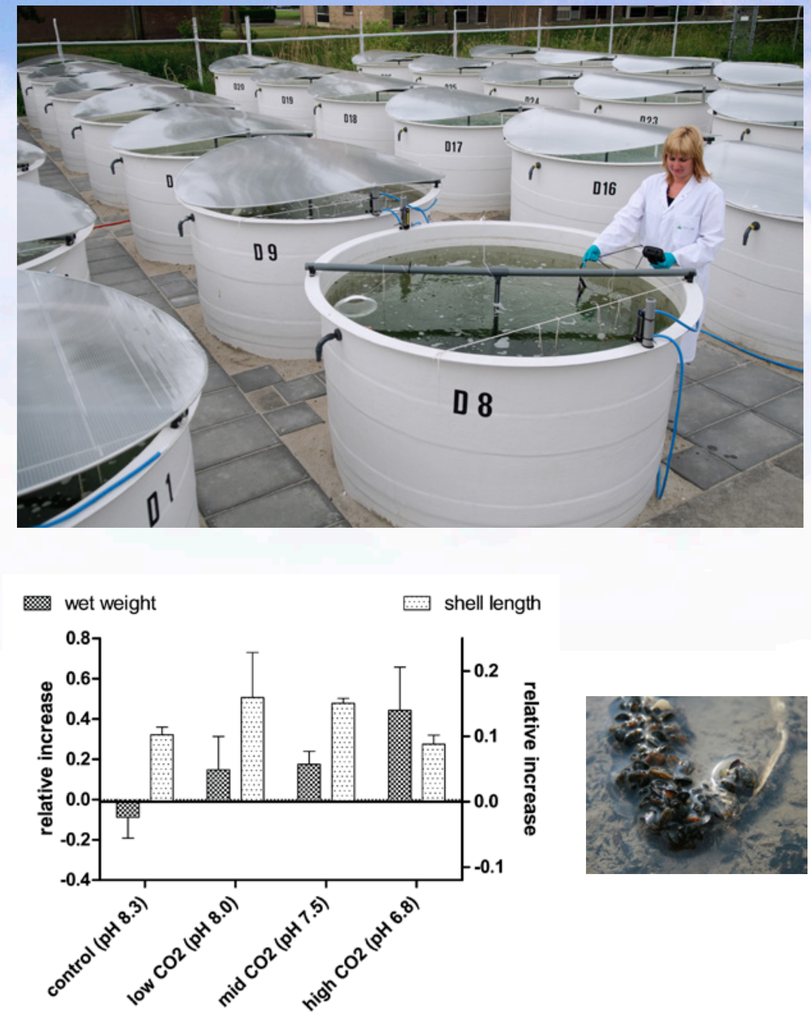

Figure 13 Effects of different CO_2 treatments on mussels from mesocosm experiments in the Netherlands. It is hypothesised that high CO_2 (low pH) stimulated primary production improving food availability for the mussels, which is reflected by increasing flesh weight. However, at the highest CO_2 concentrations shell growth cannot be maintained at the same level as seen at low and mid CO_2 concentrations.

In addition to these acidification effects, elevated CO_2 levels can also affect the respiration efficiency of aquatic animals. Although increased CO_2 concentrations do not directly lead to reduced concentrations of dissolved oxygen, the animals may experience suppressed excretion of CO_2 from the organisms' bodies at elevated CO_2 levels.

Finally CO_2 is the substrate for primary production. Hence, when other factors (essential elements and light) are not limiting, CO_2 addition can result in increased production of planktonic and benthic algae or macrophytes (Figure 14). In fact, this is the most striking observation in shallow Mediterranean natural CO_2 seeps, where seagrass meadows have replaced the normal community. However increased primary production associated with benthic systems can only occur in relatively shallow clear environments where sufficient light reaches the sea floor. Such a response would not be expected in much of the North Sea. Should production be enhanced, food availability for some species could increase. However the nature of the food supply will change as species have different abilities to utilise the extra substrate. Ultimately nutrient supply will limit extra production in most environments.

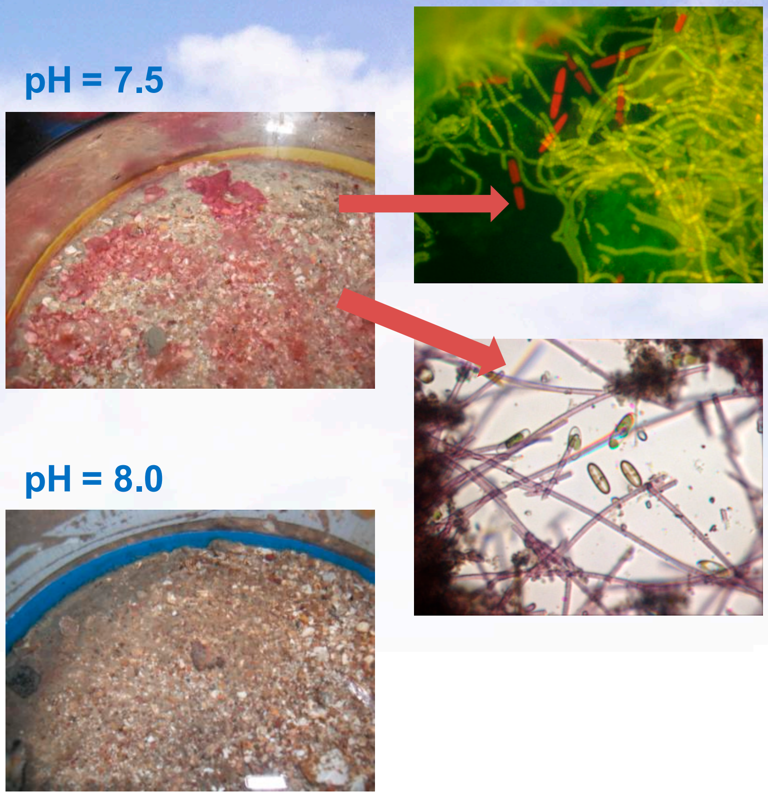

Figure 14 Results of CO_2 impacts from experiments on a shell gravel community in the UK. In moderate CO_2 treatments (pH 7.5 and 7.0) phytoplankton blooms were seen (also observed in Dutch experiments).

As not all species react in a similar way to elevated CO_2 concentrations, shifts in community structures can be expected when exposure lasts for longer periods. Logically these shifts will be characterised by the replacement of sensitive species with less sensitive ones, as has been shown in the studies that were conducted within the RISCS project with experimentally exposed microbial, zooplankton and benthic communities and also in field observations on macro algal, and coral communities.

The experimental results suggest that benthic marine communities from the cool temperate shallow marine and the warm shallow marine reference environments are able to withstand at least 10 weeks of exposure to elevated CO_2 concentrations, as long as the pH does not drop below 7.5 (Figure 15). Indeed preliminary model simulations indicate that short duration high exposures may be less harmful than long term moderate exposures; however this has not been tested experimentally. Planktonic communities might respond faster, but due to water currents and mixing exposure, these responses will be less persistent.

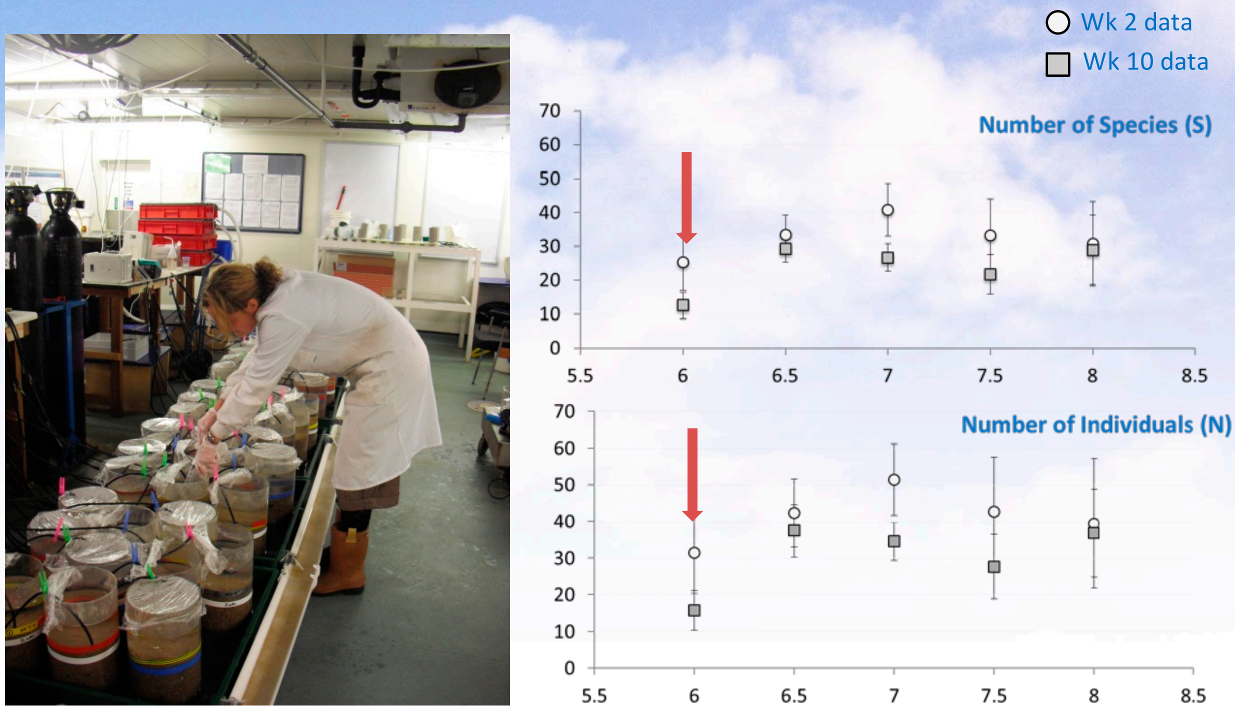

Figure 15 Results of CO_2 impacts from experiments on a shell gravel community in the UK. Significant impacts were only seen in the most extreme treatment (pH 6) after 10 weeks suggesting that they would be limited to a small area near the epicentre of a leak

The data from the RISCS experiments are in line with previous studies, suggesting that the generic impacts of CO_2 on marine invertebrate physiology are becoming clearer. In general, when marine invertebrate organisms are exposed to low pH and/or high CO_2 seawater, the primary physiological effect is a decrease in the pH or an 'acidosis' of the extracellular body fluids such as blood, haemolymph or ceolomic fluid. In some species this extracellular acidosis is fully compensated for, as levels of extracellular bicarbonate are increased by either active ion transport processes in the gills or through passive dissolution of a calcium carbonate shell or carapace. However, in other species from a variety of different taxa, studies have reported only partial, or no, compensation in the extracellular acid-base balance. Clearly some species are physiologically better equipped to cope with elevated levels of CO_2 than others, meaning that, depending on the duration of the leak, its volume, and dispersion, small-scale local extinctions and biodiversity loss could occur.

Experimental data suggests substantial differences in sensitivity between and within phyla (Vries et al., 2013). In general calcifying organisms like echinoderms, molluscs, corals and specific algae are more vulnerable, with fish and annelids having greater tolerance to hypercapnia and acidification (**Table 5**). These large differences in sensitivity could result in community changes after long term exposure to extreme seawater acidification, as sensitive species will be replaced by more tolerant groups. Such changes of communities were, for instance, observed in the planktonic and benthic communities in marine mesocosm studies (**Table 5**).

However, despite having identified these coarse taxonomic descriptors of potential vulnerability, variability in tolerance can exist between even closely related species, with this variability seemingly linked to key elements of an organism's lifestyle. Organisms that already exist in habitats, such as intertidal environments, which are regularly exposed to highly variable levels of CO_2, may be more likely to possess the physiological mechanisms necessary to cope with rapid changes in environmental conditions, than organisms from areas with more stable conditions, such as the polar oceans, deep sea or well oxygenated sands. It seems clear that the likelihood that a species will be lost from an area as a result of CO_2 leakage will be determined by both its phylogeny and its ecology. Ongoing research is already striving to identify key biological traits that can be used to assess CO_2 relative sensitivity in marine organisms.

Current understanding suggests that many of these traits will be associated with the way in which organisms use, partition and gather metabolic energy. This represents a fundamental advance in the understanding of the stresses associated with seawater hypercapnia and acidification. Previously it was assumed that all organisms which rely heavily on calcification would be negatively affected by seawater acidification, primarily due to the reduction in the saturation states of calcite or aragonite. However, recent research has shown that even within heavily calcifying taxa, there are large differences between the responses of similar species within the same taxonomic groups and even between populations or individuals from within the same species. One emerging explanation is that the response of individuals to elevated CO_2 is governed by the energy they have available to fuel the physiological responses needed to maintain acid-base balance and physiological function. If it is considered that organisms will need to actively elevate the pH (by removal of hydrogen ions) around the sites at which biogenic calcification takes place, it is easy to see that, if surrounded by seawater of reduced pH, this process will become energetically more demanding. Consequently, to maintain calcification rates, organisms will have to allocate more energy to this ion removal process. If energy (from food or from photosynthesis) is in short supply, this will mean that organisms will need to make a physiological 'choice'; do they maintain calcification at the expense of other important physiological processes (such as growth, reproduction, immune function) or do they tolerate reduced calcification? Either way, these organisms will be ecologically less fit than they would have been in a higher pH environment. This finding has significant implications for the survival of organisms during a leakage event. If organisms have access to sufficient resources then they will be able to employ the physiological mechanisms needed to survive short-term exposure to high levels of CO_2 and reduced seawater pH. This means that organisms and communities could potentially be better able to survive short-term leaks than previously thought. However, if leakage were to persist the increased energetic demand associated with living in a high CO_2 environment would inevitably lead to reduced growth, lower reproductive output and eventually death.

Evidence is emerging that suggests that a short duration but large perturbation event will be less harmful than a long duration moderate decrease in pH. The former may cause some mortality of weaker individuals, but vacated niches and resources would be quickly exploited during the recovery phase. Moderate exposure would place the whole community under stress, lowering efficiency and productivity for the duration of the event. In summary, any discussion of damaging thresholds must be moderated by consideration of the duration of exposure.

Table 5 Summary of impacts seen in Netherlands mesocosm experiments. Green = no impact; blue are positive impacts (e.g. fertilisation effects), yellow (slight) and red (strong) negative impacts

	Treatment	Control	Low CO_2	Mid CO_2	High CO_2
	pH (average)	8.3	8	7.5	6.8
	pCO_2 (µatm)	392	763	2566	15974
Grouping	**Species/Impact**				
Phytoplankton	Community Primary production	🟩	🟩	+	++
Zooplankton	Community Species diversity	🟩	-	-	--
Benthos	Community Species diversity	🟩	+	+	🟩
	Community Species abundance	🟩	🟩	🟩	--
Sponge	*Halichondria panicea* growth	🟩	🟩	-	--
Mollusc	Mussel (*Mytilus edulis*) shell length	🟩	+	+	🟩
Mollusc	Mussel (*Mytilus edulis*) flesh weight	🟩	+	+	++
Mollusc	Cockle (*Cerastoderma edule*) survival	🟩	🟩	🟩	(-)
Mollusc	Cockle (*Cerastoderma edule*) reproduction	🟩	-	--	--
Mollusc	*Periwinkle (*Litorina litorea*) growth survival*	🟩	🟩	🟩	🟩
Crustacean	*Acartia* sp. population development	🟩	🟩	+	--
Crustacean	*Eurytemora* sp. population development	🟩	🟩	🟩	+
Crustacean	Barnacles (*Balanus* sp & *Elminius* sp) settlement	🟩	🟩	🟩	🟥
Crustacean	Mud shrimp (*Corophium volutator*) population development	🟩	🟩	🟩	--
Annelids	*Ctenodrilus serratus*	🟩	🟩	-	-
Annelids	Lugworm (*Arenicola marina*)	🟩	🟩	🟩	🟩

8.3.2 Factors which affect the sensitivity of a marine environment to leaking CO_2

The scale of biological effects that can be expected as a consequence of leaking CO_2 depends on the local biological situation, such as the presence of sensitive species/life stages and food availability. In addition, physical circumstances can play a role. In the warm shallow marine reference environment (such as the Mediterranean), there is some indication that temperatures make a difference to the impact from elevated CO_2 exposure on some marine organisms such as crabs. However this was not observed in the cool temperate shallow marine environment (such as the North Sea). It should be recognised that temperature changes can also have an indirect effect on habitat and species, by altering the balance between components of the food chain.

Populations that are already living under less favourable conditions (such as food and nutrient shortage, lower oxygen levels, sub-optimal salinity or temperature) are likely to be more vulnerable to the impact of elevated CO_2 concentrations than populations experiencing optimal environmental conditions. This will also be the case for populations that are exposed to anthropogenic pollutants, especially since some dissolved heavy metals become more toxic at lower pH values due to their increased bioavailability.

Apart from the sensitivity of the ecosystem during the leak, the vulnerability of an environment is also determined by the capacity to recover after the leak has been stopped. Simulations suggest that once the CO_2 flux is ended recovery to normal CO_2 levels can be expected, typically within days in the pelagic system, although less is known about the benthic system. This implies that an area that has been negatively impacted by a CO_2 leak is available for re-colonisation soon after the leak has been stopped. Therefore if the area that is potentially affected by a CO_2 leak is relatively small, in most situations unaffected populations of the affected species will be present in the neighbourhood. The majority of the sessile marine species have a high reproductive potential, often with planktonic larval stages that are widely distributed by water currents. It may therefore be expected that recovery of an affected community can occur rather quickly, at least with respect to species diversity. Evidently, it will take longer for longer living species to recover to the original age structure of the population. However, impacts on habitat-creating organisms, like deep sea coral reefs, might affect the whole community that depends on the reef structure as a habitat. Hence, recovery strongly depends on the degree of connection with other populations. The more isolated populations are, the longer it will take them to recover after the CO_2 leakage has been stopped.

8.3.3 The physical scale of marine leakage scenarios

Dispersion of CO_2 plumes in seawater is a complex process. Initially highly buoyant gaseous CO_2 dissolves rapidly, forming potentially dense plumes of water containing higher concentrations of CO_2 that will tend to sink in the water column. Whilst local currents will determine the mean direction of a leakage plume, especially in cool temperate shallow and deep marine reference environments like the North Sea, tidal mixing is the main method of plume dispersion. Generally, tidal movement forces water masses in an elliptical pattern, accelerating dispersion. As shown below the resulting plume revolves around the leakage centre, with implications for both impacts and monitoring.

Model based studies indicate that dispersion can be relatively rapid so that only the neighbourhood of a leak event is likely to be strongly impacted (Figure 16), although this area could be metres or kilometres across, depending on the leakage rate. However, tides and currents will combine to make plume behaviour complex such that the CO_2 concentration and pH is prone to oscillate at any given point in space (Figure 17 and Figure 16). Deeper regions of shelf seas and most oceans stratify seasonally, i.e. when summer heating creates a warm less dense surface layer which does not mix with deeper waters. In such a case, any leaked CO_2 would be effectively trapped below the thermocline, with increased impacts on the benthic system.

Clearly any leakage event will be unique, and it is important to stress that the dispersion from any leak would depend on the flux rate, time of year, depth, tidal strength as well as local bathymetry, the phase nature of the flux and its distribution on the sea floor. We have taken the approach of analysing a selected number of evidence based scenarios that cover the spectrum of leak possibilities, to define the scale of potential impact and broadly assess the areas and volume affected.

We elected to develop a small number of exemplar scenarios based on the leakage scenarios identified in the RISCS project, set into a typical cool temperate marine reference environment. The scenarios investigated included, amongst others, a continuous release of 4 td^{-1}, a temporary leakage of 9000 t representing leakage from surface infrastructure and a continuous leakage of 1500 td^{-1}. For convenience, we have adapted a regional model of the SW English Channel for our purposes, rather than attempt to mimic a specific site that has been identified for storage. Our domain provides conditions that are typical of the NW European shelf in terms of tidal strength and hydrodynamic properties, so that the results can be considered qualitatively transferrable to other regions on the shelf. Bespoke simulations for specific storage sites will require detailed information on local conditions and the explicit design of an appropriate model domain. Such information is available, but would require some dedicated effort.

Previous work suggests that the environmental conditions will have a strong bearing on the evolution of a leak, therefore each scenario has been tested in a range of tidally driven mixing regimes. Damping input flow velocity at the model boundary has been used to produce a weak, medium and strong flow regime with mean current velocities of 0.10 ms^{-1}, 0.14 ms^{-1} and 0.17 ms^{-1}, respectively. These are typical of offshore North Sea conditions.

Figure 16 illustrates the evolution of three of the scenarios over the initial 10 day period illustrating the pH plume as experienced at the sea floor, presented as the change in pH from the background. The system response (**Figure 16**) follows the order of magnitude range of inputs and consequently only the 1500 td^{-1} (diffuse high) and 1 day release of 9000 T (pipeline rupture) scenarios produce pH changes that would have significant biogeochemical impacts. Both of the low end scenarios (the 4 td^{-1}, **Figure 16**a and 3 kg/d, not illustrated) do not produce a significant change in pH that is visible at the resolution of the model. It should be noted that significant pH changes would be seen at the very epicentre of the leak, but these would only penetrate a few metres from the source; the model resolution used is too large to resolve this detail.

The pipeline event (**Figure 16**b), whilst having an initially dramatic impact over an area of approximately 150 km^2, is relatively short lived. 72 hours after the event the plume has dispersed and no harmful CO_2 concentrations remain. An additional area of approximately 150 km^2 experiences changes in pH generally less than 0.3 units. Given the short duration of this exposure, it is likely that most organisms living at the borders of this exposed area will be able to cope with this pH shift which, as described above, lies within the range of natural variability. In areas of higher CO_2 concentrations, a stronger impact can be expected.

The high diffuse event (**Figure 16**c) produces a relatively constant low pH plume which would be ecologically harmful over an area approximating to 9 km^2. Beyond this region a tidally driven plume of moderately enhanced CO_2 circulates around the epicentre, resulting in an episodic exposure to low pH over an additional area of approximately 120 km^2. Most of the pH exposure in this zone is less than 0.3 units decrease for less than half of the time.

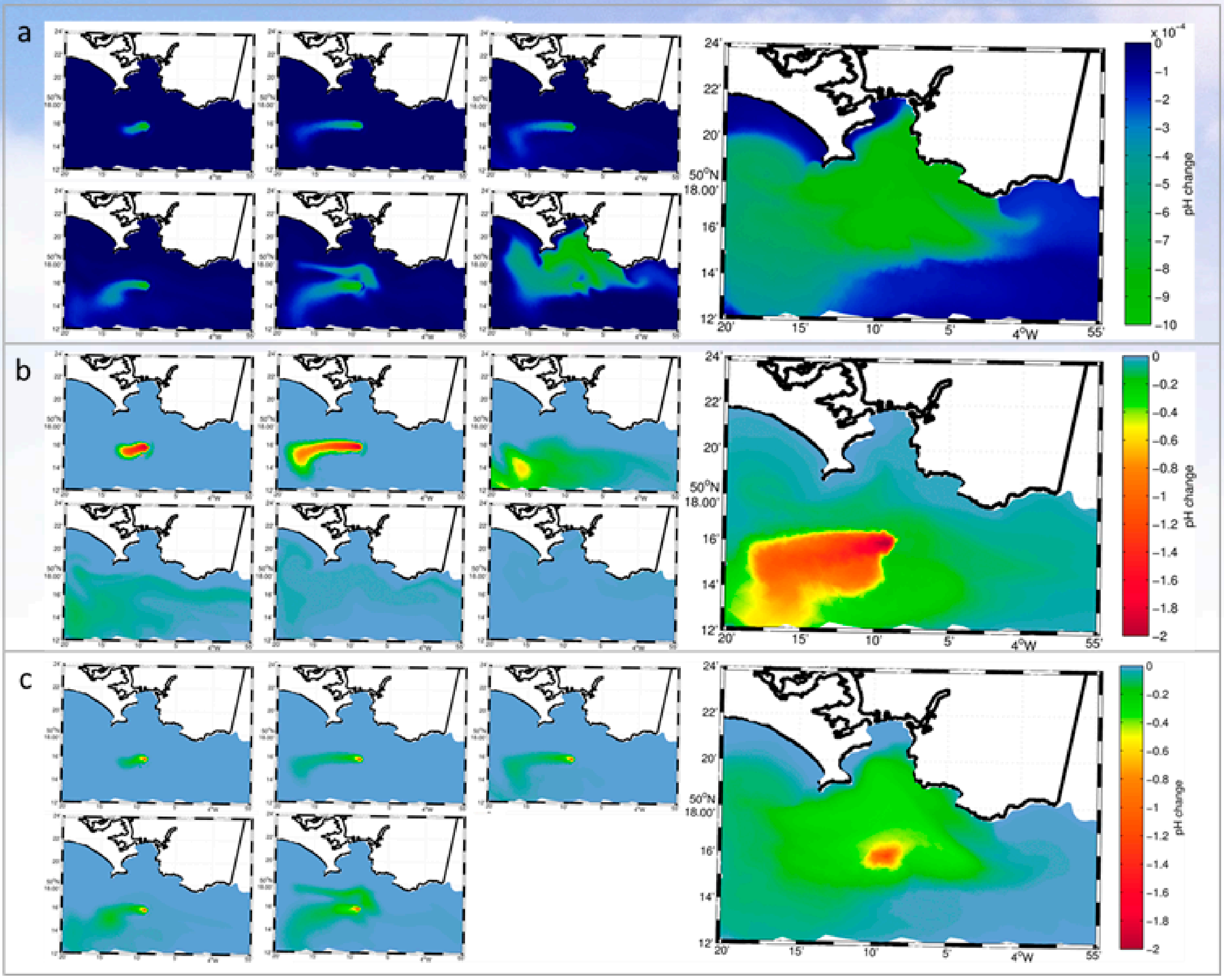

Figure 16 Modelled pH change from CO$_2$ leakage at the sea floor, a: continuous release of 4 td^{-1}, b: temporary leakage of 9000 t in total, c: continuous leakage of 1500 td^{-1}. Small figures: evolution at 6, 12, 36, 72, 120 and 240 hours. Large panel, maximum pH change during the simulation period. N.B. scales used in the top set of figures are several orders of magnitude smaller than the one used in the bottom two scales. Apart from the epicentre the impacted area changes over the tidal cycle.

What is clear from this limited set of simulations is that the relation between tidal mixing intensity and resulting shape of the CO$_2$ plume is highly complex, at least in this realisation. This suggests that naturally variable tidal cycles, coupled with the known geographical heterogeneity in tidal mixing strength will ensure that the location and timing of a leak event will be crucial in determining the dynamics of the resulting plume. Together with other factors that affect mixing, such as temperature and wind speed that are known to vary on small spatial and temporal timescales, this suggests that plume dynamics will be highly individual. Hence accurate predictions of plumes and development of monitoring strategies will require bespoke models to be set up to mimic the observed tidal regimes specific to a particular site of interest, rather than simplified generic applications. Observations at natural sites like Panarea show that conditions at individual sites vary quite markedly over time (**Figure 17**).

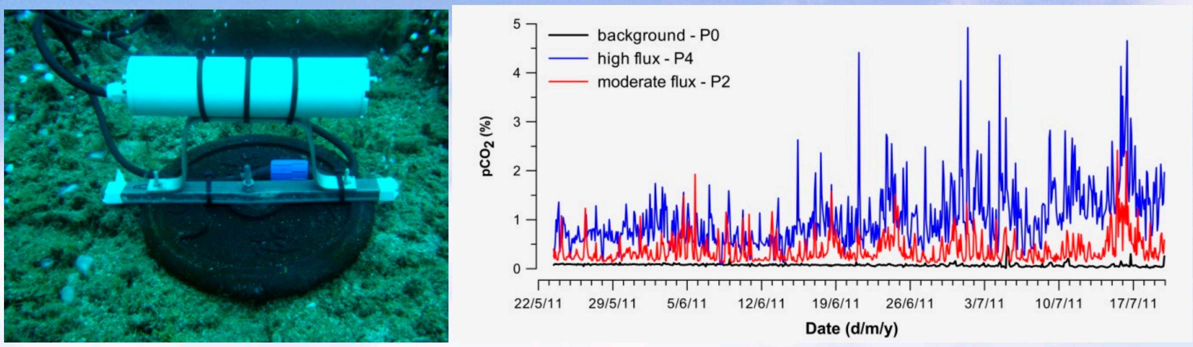

Figure 17 Continuous monitoring of pCO_2 near Panarea, southern Italy. Note the marked variation in CO_2 content at sites where the gas is escaping due to dispersion in the water column. Note also the background site, located only about 50 m from the high flux point, which shows very few (and small) anomalous peaks within a low and constant baseline.

Intensive water mixing in the area where the CO_2 is released will result in a wider area that is exposed to seawater with typically lower CO_2 concentrations than areas with less mixing or more stratification. This was illustrated during the seasonal sampling campaigns conducted at the natural CO_2 leaking site at Panarea, Italy (Figure 18). In deeper waters during summer, stratification of warm and cold water layers can occur, trapping the CO_2 enriched water near the bottom resulting in higher CO_2 concentrations than in non-stratified conditions. Other forms of stratification, such as those caused by salinity in fjords, which dominate much of the Norwegian coast, may also result in increased retention of CO_2 in the deeper waters. As the biological impact is rapidly reduced with increasing dilution, locations with intensive water mixing and little chance for stratification can thus be considered less sensitive to the impact of CO_2 leakage.

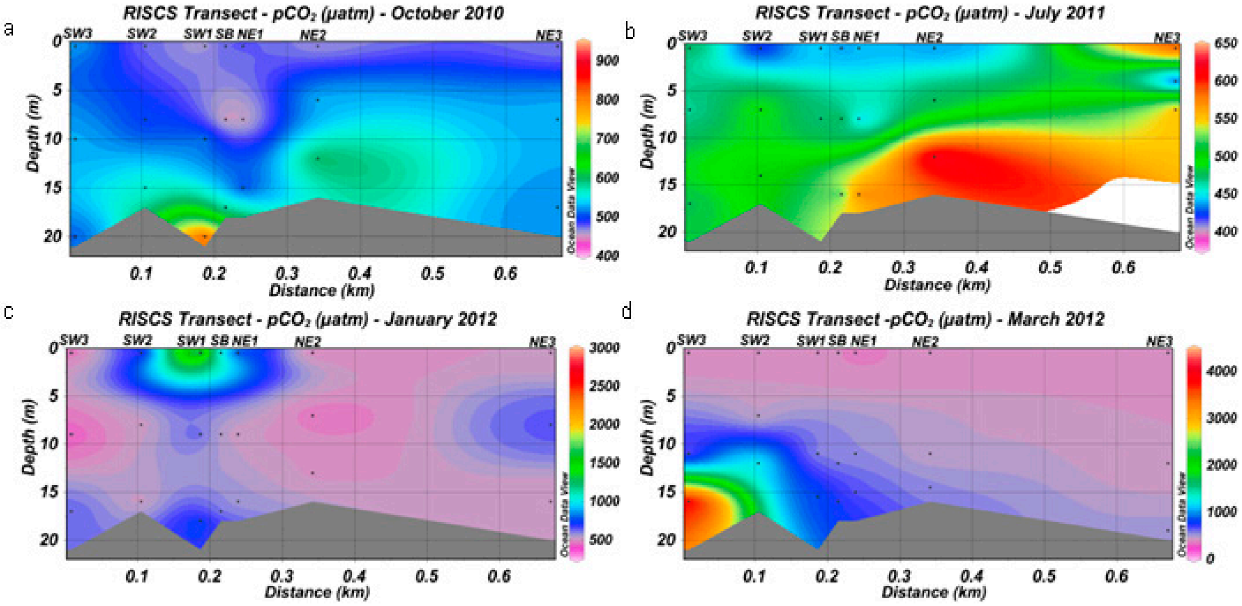

Figure 18 CO_2 levels in the vicinity of a volcanic seep (in micro atmospheres) along a transect near Panarea, southern Italy at different seasons. Note the seasonal variability with the highest levels seen in March 2012 when the dissolved gas occurred in higher concentrations within a cold dense layer of seawater lying below a warmer less dense surface layer. Note that the plots are produced at different scales.

Assessment of impacts arising from potential leakage should also consider the cumulative and combined effects of a CO_2 leak as an addition to the stress induced by other marine activities. Some areas likely to be the target of significant CO_2 storage activity, such as the North Sea, are also subject to other activities and its habitats are already considered by the UK Joint Nature Conservation Committee to be under stress.

8.4 Monitoring approaches in the marine environment

Whilst in the centre of a leak the pH decrease may be greater than occurs naturally, with increasing distance from the leakage point and as the CO_2 is dispersed, the resultant changes will be similar in magnitude to those expected under normal seasonal and diurnal cycles. Therefore the challenge of detecting leakage and its impacts is to have both a detailed understanding of baseline variability and the capability to detect small leakage features against this large and variable baseline.

Monitoring may have more effectiveness by co-measuring other environmental factors such as temperature and oxygen, enabling natural signals to be recognised and differentiated from leakage. For example, if an increase in CO_2 is accompanied by an equivalent decrease in oxygen then enhanced community respiration is the likely cause; if no oxygen decrease is measured then it is far less likely that a biological process is responsible and some external source of CO_2 can be suspected. The relationship between CO_2 and oxygen concentration varies seasonally and such information could also be used to inform the interpretation of CCS monitoring data. Similarly temperature has a significant impact on pH and pCO_2 and can be used as an indicator of natural physical dynamics that affect the carbonate system. Similarly, analysis of components that may be associated with co-migrating waters or brines may be used as tracers. For example, as demonstrated at Panarea, elevated silica concentrations may be associated with water-rock-gas reactions initiated by the leaking CO_2, while ammonia may be an indicator of a deeper, anoxic leaking porewater.

If monitoring of the potential scales of any leakage impact is to be efficient and effective then it is essential to quantify and understand the natural variability at all relevant scales in the region of interest. This will maximise the detectability of excess CO_2 whilst minimising the potential of false positives. However rapid dispersion will generally mitigate against extreme impacts. Due to the greater density of seawater saturated with CO_2, it is expected that the sea floor will be more exposed to CO_2 plumes than the water column or surface waters. Monitoring should therefore concentrate on measuring just above the sea floor, recognising the added difficulty of deploying instrumentation in this environment.

Detection of CO_2 bubble streams would be the most direct way to detect a leak and a number of technologies are being tested to provide integrated monitoring systems for bubble detection. However, leaks at low rates may not result in bubble streams, or the CO_2 may have dissolved in sediment pore waters before reaching the seabed, and therefore in these cases the most effective way to detect a CO_2 leak is by monitoring pH levels in the water close to the seabed.

Whilst monitoring biological processes or effects would theoretically also be possible, this is considered less reliable as an early warning for detection of an unknown leak. Biological data will be hard to interpret since biological variation can have many causes. Therefore, such observations should always be confirmed with additional evidence that the observed changes are indeed related to elevated CO_2 concentrations. As a minimum, the changes in the area potentially exposed to CO_2 should be compared with both baseline data collected over the storage area and the development in comparable reference areas. It is recommended that reference environments are defined, possibly as joint industry initiatives, against which environments above CO_2 storage operations would be compared. Seabed site specific direct monitoring should be a prerequisite for a licence, in order to follow article 17 of the Habitats Directive (EC, 1992), which includes the concept of Favourable Conservation Status of Natura 2000 sites, and the Marine Strategy Framework Directive (EC, 2008), which includes criteria for defining Good Environmental Status.

Biological indicators, which could be used as additional evidence of the nature of marine impacts from elevated CO_2 concentrations, include signs of erosion on bivalve and gastropod shells, increased primary production in the water column (Figure 14), reduced settlement of juvenile bivalves, and development of algal/cyano-bacterial mats on the sediment surface. However since none of these indicators is likely to occur without measurable changes in pH values, it is considered that pH monitoring is easier and more cost effective than detecting biological changes.

Detection of locally increased primary production via remote sensing is unlikely to provide a useful monitoring methodology, although the applicability of this option has not been fully investigated. There is likely to be a discontinuity between sea floor release and sea surface signal, due to horizontal mixing processes. Increases in primary production can also occur due to other natural factors and the potential for differentiating changes due to other factors would need to be investigated. In addition, such changes may take time to develop to the extent that they can be readily detected by remote sensing techniques.

Further biological monitoring is advised to determine the environmental impact in situations where a leak has been detected, and to follow recovery after the leakage has been stopped. The age structure of longer living calcifying species could give an indication of the duration of the leak before it was detected.

8.5 The potential for remediation of an affected ecosystem

Besides stopping the leak as soon as possible, little can be done to enhance recovery of the affected marine ecosystem in a substantial way. However, unless the ecosystem is particularly isolated, natural recovery can be expected to be quick for the benthic ecosystems that were studied within the RISCS project. To further help this natural recovery, bottom disturbing fishing techniques, such as bottom trawling and shellfish fisheries could be restricted for a time. In addition, further possible options for remediation are included in Chapter 9, primarily focussed on remediation of leakage in the geological environment in terrestrial sites.

8.6 Recommendations for subsea CO_2 storage and site selection

In site selection, the effect of an unforeseen CO_2 leak must be minimised as much as possible. This can be realised by selecting sites with the following characteristics, in addition to the primary requirement to have a geological store that will permanently retain the injected CO_2:

- Regions of unusually low mixing of the water column might be avoided where possible, both from the point of view of dispersing leakage and aiding recovery by colonisation.
- Regions with unusually heavy reliance on calcification as the basis of the ecosystem (e.g. cold water corals) or other unique and sensitive ecosystems should be avoided.
- The ecosystem should not be overly affected by other natural (e.g. low salinity, oxygen depletion, food shortage, etc.), or anthropogenic stressors (e.g. pollutants).

Once a site or region is identified for storage and the likely subterranean footprint of the reservoir complex known it is recommended that:

- The sites chosen for storage are subject to rigorous baseline surveys, drawing on existing data, models and if necessary new observations. This should include the analysis of the normal co-variance of CO_2, oxygen and temperature to aid monitoring interpretation.
- Bespoke simulations of leakage dispersal are made to identify optimal siting of monitoring equipment.
- An analysis of impact potential, based on the above, is developed. Assessment of impacts arising from potential leakage should also consider the cumulative and combined effects of a CO_2 leak as an addition to the stress induced by other marine activities. Some areas likely to be the target of significant CO_2 storage activity, such as the North Sea, are also subject to other activities and its habitats are already considered by the UK Joint Nature Conservation Committee to be under stress.

9 LEAKAGE MITIGATION

If a leak did occur, the following remedial actions (other than stopping the leak) could be undertaken to mitigate the impacts (Table 6). It is important to note that the corrective measures considered should be prioritised and ranked according to the assessed cost-effectiveness of their risk/uncertainty reducing effect. In some cases, leakage will not result in contamination of a sensitive receptor and may not require significant mitigation. In other cases, a mitigation technique may prove to be very costly or may result in other issues needing to be addressed, such as produced brines or waste materials requiring disposal.

Table 6 Mitigation options for geological CO_2 storage projects (IPCC, 2005; OSPAR, 2007; EC, 2009 and WRI, 2008).

Leakage scenario	Mitigation options	Terrestrial	Marine
Leakage through caprock failure, faults, fractures and spill points or up dip leakage	Intersect the leakage with extraction wells near the leak; Limit CO_2 injection rates and pressure build-up in specific wells or across the site, either temporarily or permanently; Reduce the reservoir pressure by extracting CO_2 or water from the storage reservoir or complex Reduce CO_2 injection pressure (e.g. by using lower injection rate, or more injection wells); Stop CO_2 injection to stabilise the project; Produce CO_2 from the storage reservoir/plume and either vent or re-inject in another site; Peripherally extract formation water or other fluids; Increase reservoir capacity and steer CO_2 in favourable directions by hydrofracturing (creating pathways to develop and access new compartments of the storage reservoir away from leakage areas; by expanding the storage container, the pressure will decrease); Extract CO_2 at or near an identified leakage point, zone or pathway; Seal regions where leakage occurs such as identified fault or caprock leakage pathways in limited areas by injecting low permeability materials; Increase pressure in formations upstream of CO_2 leakage, creating an hydraulic barrier (decreasing pressure gradient);	Yes	Yes
Leakage through active or abandoned wells	Repair leaking injection wells by squeezing cement behind the well casing to plug leaks behind the casing; Repair leaking injection wells with standard well recompletion techniques, such as replacing the injection tubing and packers, repairing damaged or collapsed casing; wellhead repair; Plug and abandon wells that cannot be repaired; Stop blow outs from injection or abandoned wells with standard techniques to 'kill' a well such as injecting a heavy mud into the well casing. If the wellhead is not accessible, a nearby well can be drilled to intercept the casing below the ground surface and 'kill' the well by pumping mud down the interception well; Stop injection;	Yes	Yes

Leakage into the vadose zone and accumulation in soil gas	Extract CO_2 from the vadose zone and soil gas by standard vapour extraction techniques from horizontal or vertical wells; Use caps or gas vapour barriers to stop or decrease surface fluxes. Pumping below the cap or vapour barrier could be used to deplete the accumulated CO_2 in the vadose zone; Pump CO_2 away from trenches or other low-lying areas, and either vent or reinject it in the subsurface; Employ passive remediation, such as diffusion and barometric pumping to slowly deplete isolated releases of CO_2 into the vadose zone; Irrigate and drain or apply alkaline supplements (such as lime) to remediate soils that have acidified because of CO_2 exposure; Where soil bacteria have been significantly damaged, it may be possible to inoculate the soil from an undamaged site; Depending on the timing of the leak, once it has ceased, plough the soil after harvest. This may be sufficient to remove residual effects; Create a hydraulic barrier by increasing reservoir pressure upstream of the leak; Install chemical sealant barriers to block leaks; Stop injection;	Yes	No
Accumulation of CO_2 in groundwater	Drill wells that intersect the accumulations in groundwater, and use them to extract the CO_2, either as free gas or dissolved in groundwater. The extracted CO_2 could be vented to the atmosphere or reinjected into a suitable storage site; Dissolve carbonate minerals in water, and extract it as a dissolved phase through a groundwater extraction well; Pump CO_2-contaminated groundwater to the surface, and aerate it to remove the CO_2. The groundwater could then either be used directly or reinjected back into the aquifer. If metals or other trace contaminants have been mobilised by acidification of the groundwater, 'pump-and-treat' methods can be used to remove them; Create hydraulic barriers to immobilise and contain any contaminants by appropriately placed injection and extraction wells; Employ passive methods that rely on natural biogeochemical processes; Create a hydraulic barrier by increasing reservoir pressure upstream of the leak; Install chemical sealant barriers to block leaks; Stop injection;	Yes	Unlikely

Accumulation of CO_2 in indoor environments with chronic low level leakage	Manage potential slow indoor releases with subsurface or subslab pressurization and subslab depressurization with venting, as air flow is induced through the near-building soil gas in order to disperse contaminants; Create a hydraulic barrier by increasing reservoir pressure upstream of the leak; Use fans to disperse CO_2, similar to radon fans; Stop injection;	Yes	No
Accumulation in surface water	Accumulation in shallow water is only likely where stratification of the water column occurs, i.e. some lakes and offshore in certain circumstances where thermal or salinity contrasts develop. Shallow surface water bodies that have significant turnover (shallow lakes) or turbulence (streams) will quickly release dissolved CO_2 back into the atmosphere; If impacted, active systems for venting gas accumulations in lakes have been developed and applied at Lakes Nyos and Monoun in Cameroon; Create a hydraulic barrier by increasing reservoir pressure upstream of the leak; Install chemical sealant barriers to block leaks; Stop injection;	Yes	Yes in very specific circumstances
Large releases of CO_2 to the atmosphere	Use large fans to rapidly dilute CO_2 to safe levels for releases inside a building or confined space (e.g. in a cellar or around a wellhead) or during periods of very low wind; Dilution from natural atmospheric mixing (wind) will rapidly dilute CO_2 from large releases over a large area; Install chemical sealant barriers to block leaks; Stop injection;	Yes	Yes but low likelihood of occurring. Could be applied but considered unnecessary in majority of cases.

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