Chapter 9. Seepage and leakage, effects and environmental impact

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Abstract
Carbon capture and storage (CCS) has been proposed as a key method to limit carbon dioxide emissions to the atmosphere whilst enabling the continued use of fossil fuel reserves. However a leakage of CO_2 from transport or storage could have environmental and safety implications. Monitoring of CCS systems is a further challenge, both to assure the public and, should leakage occur, to enable mitigation and verification. This chapter reviews the current state of knowledge regarding both environmental sensitivities and environmental (as opposed to geological) monitoring and outlines the challenges for research over the next few years. The current hypothesis is that significantly large leaks would be required to cause noticeable damage in the ecosystem. On land the primary concern is for undetected leaks to concentrate in topographical or built structures leading to health hazards. Monitoring of a geological leak in the marine system will be informed by the appropriate application of dispersion models and an understanding of baseline variability as well as the development of monitoring tools that can be efficiently deployed.

Keywords: Carbon capture and storage, environment, impacts, monitoring

1. Introduction

Carbon capture and storage (CCS) has the potential to remove a significant proportion of anthropogenically generated CO_2 and mitigate against the ensuing environmental and economic cost of climate change. At the same time concern about environmental and health impacts of leakage from CCS have, at least in part, curtailed several ambitions to develop CCS demonstration facilities, mainly in terrestrial settings. There is accordingly a need to understand and communicate the risks associated with long term geological storage and the potential impacts on the environment, economy and health and safety. This dialogue would also benefit from a contextual understanding, for example what are the probable consequences of not mitigating CO_2 emissions, how do potential CCS impacts compare with everyday anthropogenic impacts and what are the options for fulfilling energy requirements over the next several decades? Another essential requirement for the successful deployment of CCS is effective and trusted methods and strategies by which to monitor containment or leakage. This is likely to require not only development of specialised tools but an understanding of natural variability in CO_2 and related substances.

Understanding risk and consequence is a multi-faceted challenge. The risk can be defined partly as a geologic issue but must also factor in transport integrity and accident potential. Consequence analysis requires an understanding of geological migration and dispersal in soils, sediments, water and the atmosphere as well as comprehending the impacts on natural systems. Similarly monitoring techniques can be geophysical or based on shallow or surface physical, chemical and biological signals.

Several research projects are currently addressing many aspects of these challenges, but are hampered by a lack of direct observations. In this chapter, as well as reviewing the state of knowledge about impacts in both terrestrial and marine environments, and monitoring technologies, we review the utility of natural seep systems to elucidate what could happen if a leakage occurred and describe what future initiatives would facilitate further understanding in this area.

2. A generic approach to risks and impacts

When considering risk and potential impacts it is helpful to consider the Features, Events and Processes (FEPs) that could be significant. Analysing the system in this way helps to ensure that modelling studies represent everything that could be important, and ensure that field studies are designed to yield information where it is most needed. There are many slightly different formal definitions of these terms but fundamentally:

- A 'Feature' is a physical component of a system (a 'fault' could be a feature of the terrestrial system).
- An 'Event' is a process that influences the evolution of the system over a time period that is short compared to the time frame being considered (an earthquake might be considered to be a relevant 'event').
- A 'Process' is a dynamic interaction between 'Features', which may operate over any particular time interval of interest (dissolution of CO_2 in a near-surface might be considered be a relevant 'process').

An online generic FEP database (Maul et al. 2005; Walke et al., 2011) is freely accessible from the International Energy Agency (IEA) website (www.ieaghg.org). The database is generic, in that it is not specific to any particular storage concept or location. The FEPs included have been chosen for their relevance to the long-term safety and performance of the storage system after CO_2 injection has ceased, and the injection boreholes have been sealed.

3. Impacts and risks relating to the marine system

In aqueous media, CO_2 dissolves rapidly and dissociates into bicarbonate and hydrogen ions, the latter decreasing pH and combining with carbonate ions to form more bicarbonate. Hence any biological process that is dependent on bicarbonate or carbonate ions, or impacted by pH, is vulnerable to changes in CO_2 concentration. In brief, excess CO_2 in marine systems can enhance photosynthesis, inhibit the maintenance of carbonate based structures (e.g. shells and corals) and undermine many physiological processes that are sensitive to pH.

Dispersion of CO_2 plumes in seawater is a complex process. Initially highly buoyant gaseous CO_2 dissolves rapidly, forming potentially dense plumes of high CO_2 water that will tend to sink in the water column. Dispersal of plumes, especially in regions like the North Sea, will be strongly influenced by tidal mixing as well as residual currents. Model based studies (Blackford 2008; Chen et al 2005) indicate that dispersion can be relatively rapid so that only the epicentre of a leak event would be strongly impacted. However, tides and currents will combine to impart a complex dynamic in plume behaviour such that the CO_2 concentration and pH is prone to oscillate at any given point in space. Clearly any leak event will be unique, depending on flux rates, tidal state, currents and season.

Thus current evidence would suggest that if leaks were to occur they would tend to be localised and therefore more likely to impact upon those organisms that are unable to move away from the source of CO_2. In this respect, organisms that are restricted to a specific habitat or that have limited horizontal mobility are likely to receive the highest exposure. For the most part this would mean that sessile, benthic organisms are more likely to be affected by CO_2 leakage than mobile pelagic ones. In addition, it is predicted that rather than a rapid stream of CO_2 passing through the seafloor, leaks could take the form of a slow dispersive transport through the sediment. This would lead to an acidification of the sediment pore waters and a strong impact on sediment dwelling (infaunal) organisms. The formation of higher density plumes of CO_2 enriched seawater suggest that, in most types of potential leak, benthic organisms will be most heavily exposed to elevated levels of CO_2.

Unlike many other pollutants, CO_2 also occurs naturally, throughout the marine (and terrestrial) environment. In sediment systems in particular, large gradients in CO_2 can occur over very small spatial scales with marine organisms being exposed to changes in pH of over 1 unit (see Widdicombe et al., 2011, for a review). Consequently, controlling internal levels of pH and CO_2 is an integral part of marine organism physiology (see Portner 2008; Portner et al 2011) and many infaunal organisms have developed physiological and/or behavioural mechanisms designed 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 CO_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 survival. 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 (Blackford et al, 2010).

The effectiveness of physiological and behavioural mechanisms and the ability to assimilate and redistribute energy will vary between different taxa. This will naturally lead to a range of different tolerance levels between the species that make up the resident community (see Wicks & Roberts, 2011). For example, organisms that are dependent on heavily calcified structures may need to spend more energy on maintaining these structures than non-calcified species. Consequently, exposure to elevated CO_2 is likely to cause a shift from calcified to non-calcified organisms and, given the predominance of calcified groups in marine communities, this is likely to cause a decrease in species as well as functional diversity. This community level response has been seen in mesocosm experiments (Widdicombe et al 2009; Hale et al 2011) as well as studies conducted around natural CO_2 seeps (Hall-Spencer, 2008). These studies also demonstrate that changes to community structure and diversity following a leak cannot be predicted by assessing the tolerance of individual species in isolation and assuming these will hold true in a natural setting. For example, recent exposure experiments on natural communities have shown that, despite previously being shown to be negatively affected by exposure to elevated CO_2 (e.g. Thistle et al., 2007), the abundance of nematode worms increased under high CO_2 conditions (Widdicombe et al 2009; Hale et al 2011). The authors concluded that this increase in abundance was due to the nematodes being released from ecological pressures, such as competition or predation, due to the reduced abundance of other infaunal species in these high CO_2 treatments.

When considering the potential biological impacts of leakage it is also important to consider whether organisms are likely to be exposed to any other environmental stressors or pollutants, in addition to the elevated levels of CO_2 and changes in seawater chemistry. For example, as the CO_2 passes through the sediment it may act to liberate and transport other harmful substances such as methane, heavy metals and hydrogen sulphide. For CO_2 storage situated in or near oil or gas reservoirs, leaking CO_2 may also bring with it hydrocarbons and other drilling related pollutants. Currently there are few data published which quantify the potential interactions between CO_2 and these other pollutants. However, using evidence from the few studies that have been conducted, simultaneous exposure to both CO_2 and pollutants can be expected to exacerbate the biological impact of leakage (Widdicombe et al., submitted). Much more evidence exists with respect to the interactive effects of CO_2 and other environmental stressors, such a temperature, hypoxia and salinity. In many of the studies conducted to date, an organism's vulnerability to CO_2 is increased when exposure is combined with these other environmental stressors. In particular, an organism's window of thermal tolerance and its general level of aerobic performance can be drastically reduced by exposure to elevated levels of CO_2 (Pörtner & Farrell, 2008; Pörtner, 2010).

It is not just multi-cellular organisms that could be impacted by leakage; elevated levels of CO_2 have also been shown to have significant effects on the structure and function of sediment dwelling microbes, both bacteria and archea (Tait et al, submitted). This, in turn, will impact upon the key biogeochemical processes these microbes support, such as elemental cycling, primary production and waste degradation. In a recent study, Tait et al (submitted) showed that rates of ammonium oxidation can be significantly altered by high levels of CO_2, primarily through the differential effects of CO_2 on bacteria and archea. This study also demonstrated that the potential impact of leakage on nutrient cycling is likely to be governed by the nature of the microbial community already present at the leakage site. The direct impacts of CO_2 on microbes could be further exacerbated by changes in sediment mixing (bioturbation) performed by burrowing macrofauna. Bioturbation is a key process in structuring microbial communities (Laverock et al. 2011) and the nature and intensity is dependent on the types of bioturbators present and the levels at which each of these types are performing; both of which can be altered by elevated levels of CO_2. However, it should also be noted that not all microbes will be negatively impacted by leakage. Those organisms that consume CO_2 (e.g. cyanobacteria) or those that consume other substances that could be liberated by any leakage (e.g. methane or sulphide) may increase in function and activity.

In addition to sediment systems, there are other important benthic ecosystems that could be affected by leakage. In particular, those habitats which rely heavily on calcification for the provision of structural integrity could be badly impacted. These biogenic habitats (Figure 1) include coral reefs (warm water and cold water varieties), calcifying algae (such as the mearl beds) and large aggregations of molluscs (e.g. mussel beds). All of these habitats support high levels of associated biodiversity and could be vulnerable to exposure to high levels of CO_2. However, there are non-calcifying species that provide biogenic habitats (e.g. seagrasses) and these have been shown to flourish under high CO_2 conditions (e.g. Hall-Spencer et al 2008). Although, even in these habitats, whilst the key habitat providing species flourishes, the associated cryptic fauna is still negatively impacted and biodiversity is lost.

4. Impacts and risks relating to terrestrial systems.

In its gaseous phase, CO_2 is relatively unreactive, the main potential effects stem from impacts on photosynthesis – which may be positive at moderate levels, and its action as an asphyxiant, at high concentrations, preventing respiration. In this section consideration is given to the risks and potential impacts if CO_2 from a geological storage system were to return to the surface in a terrestrial environment

Of the eight categories of FEPs detailed in section 2, two directly relevant to the scope of this section:

- The 'Near-Surface Environment' category of FEPs is concerned with factors that can be important if sequestered CO_2 returns to the environment that is accessible by humans. This includes a sub-category for the terrestrial environment and human behaviour.
- The 'Impacts' category of FEPs is concerned with endpoints that could be of interest in an assessment of performance and safety. An example of a FEP entry in this category is shown in Figure 2.

4.1 CO_2 Transport in the Near-Surface Environment. When CO_2 enters the near-surface environment from the geosphere below, as it is denser than air it may 'pond' on top of the water table and migrate laterally, as illustrated in Figure 3. CO_2 will only break through at the surface when surface topography and the top of the CO_2 layer intersect, as is typically observed in local depressions and near rivers and springs, or where there are high localised fluxes of CO_2 from depth. There is the potential for the CO_2 to decrease the pH of potable waters and potentially mobilise certain contaminants, such as heavy metals, from solid phases in the rocks or sediments (e.g. Lu et al. 2010).

4.2 Potential Environmental Impacts. As discussed by West et al. (2005), although extensive physiological research is available, the environmental impacts of elevated CO_2 (whether through slow or catastrophic release) on terrestrial ecosystems are poorly understood. Essentially, respiratory physiology and pH control are the primary physiological mechanisms controlling responses in organisms to elevated CO_2 exposures. Information is available from a diverse research base including physiology, food preservation and botany; these data, however, are mostly from studies on organisms exposed to either slightly elevated concentrations of CO_2 or the high concentrations that give a lethal response.

Current research (for example the European Union project RISCS; Research into Impacts and Safety in CO_2 Storage; http://www.riscs-co2.eu/) aims to develop the knowledge base necessary to assess the potential impacts of leaks on near-surface ecosystems. As part of this project potential receptor classes have been defined for European terrestrial environments and these are summarised, together with potential impact mechanisms, in Table 1.

In a related study, Roberts et al (2011) quantifies the risk of human fatality at natural seeps onshore in Italy. This work demonstrated the relatively low risk of mortality even at largest seeps. However, these risks really describe the risk of mortality at a site where a seep has already been identified – not a newly emerging seep. Natural seeps in West Africa further confirm this (Smets et al, 2010) where most fatalities occur to travellers through a region who are unaware of the threat. This suggests that we can manage the risks of mortality at onshore storage sites by surface monitoring to identify any new seeps.

5. An ecosystem services description of economic impacts

The economic impacts of leakages, and the impacts of these leaks on society, are likely to be important determinants of whether CCS will be developed and make a contribution to climate change abatement strategies (van der Zwaan and Gerlagh, 2009). Understanding the economic and societal impacts of leaks can potentially be achieved through the assessment and valuation of ecosystem services. Ecosystem services are "the aspects of ecosystems utilised (actively or passively) to produce human well-being" (Fisher et al., 2009, p. 645). According to the Millennium Ecosystem Assessment (2003), they can be categorised into four broad functional groups (Table 2): *provisioning services*, which are the products we obtain from the environment, such as food, fuel wood and other natural resources; *regulating services*, which are the outputs of processes that regulate ecosystems, such as a regulated climate, clean water and air; *cultural services* which generate largely non-material benefits such as cultural diversity, knowledge systems and opportunities for leisure and recreation; and *supporting services* which are the processes and functions that underpin all the other ecosystem services, including nutrient cycling, primary productivity and the provision of habitat for other species. Due to concerns over double counting (e.g. Boyd and Banzhaf, 2007), ecosystem service valuation only focuses on provisioning, regulating and cultural services (because the value of supporting services are implicit in the value of all other services); however, understanding how leakages of stored CO_2 may affect supporting services is critical. Any change in supporting services will have implications for provisioning, regulating and cultural services. For example, many marine benthic organisms, soil organisms and organisms living in freshwater sediments are effective bioturbators, burying and transforming waste products within sediments, contributing to the levels of oxygenation in the sediments, the rate of decomposition of organic materials and the regeneration of nutrients. They may also form a food supply for other species. All of these processes are at the core of many ecosystem services that are valued by society for the contribution they make to human well-being. The relationships between these underlying processes and functions and ecosystem services though, are often poorly understood.

5.1 Provisioning services: The area impacted by an individual CO_2 leak in the marine environment is likely to be relatively small (Blackford et al., 2008). This suggests that the implications for marine food provision are likely to be minimal. Mobile marine organisms, such as commercially important fish species, will simply be able to avoid areas in which seawater acidity is likely to cause them some level of stress. Problems may only occur for mobile species if CO_2 leaks occur in important breeding or nursery grounds, as juvenile forms of some fish species have been shown to be sensitive to higher levels of seawater acidity (Munday et al., 2010; Munday et al., 2009). The implications for sessile organisms, such as shellfish, with close proximity to the leak may be more severe as seawater acidification is known to affect calcification, fertilisation success and development in some species (Fabry et al., 2008; Gazeau et al., 2007).

On land, the loss of CO_2 through soils from natural vents has been shown to lead to the death of trees (Farrar et al., 1995); early senescence and reduced photosynthetic capacity (Cook et al., 1998); and in an experimental situation, to reduced biomass production in pasture grass and poor germination in winter beans (Patil et al., 2010). If these findings can be extrapolated to other plants, and in particular food crops, then there may be implications for agriculture and food production; however, as with the marine environment, the area affected by a leak is likely to be relatively small.

In addition to the production of food, CCS may also have implications for the provision of freshwater. Although the CO_2 being stored may be relatively uncontaminated, it may interact with minerals and potential pollutants within the storage site that may enter freshwater supplies (Pires et al., 2011). CO_2 can cause the acidification of groundwater supplies, affecting the quality of drinking water obtained from them (van der Zwaan and Smekens, 2009).

5.2 Regulating services: Depending on the scale of the leak, the degassing of CO_2 from underground storage sites could potentially influence a number of regulating services. Section 2 discusses how acidification of seawater and seabed sediment can affect marine organisms responsible for bioturbation. Any loss of bioturbators may result in a reduction in the level of burial and storage of waste products in marine sediments, including organic matter (Solan et al., 2004). This may have implications for the control of waste and the regulation of climate, as less CO_2 and other pollutants are locked away and prevented from interacting with the environment. On land, any reduction in vegetation as a result of CO_2 leakages may also reduce the amount of CO_2 that is sequestered from the atmosphere and could potentially lead to a change in the hydrology of an area. Loss of vegetation cover is known to increase runoff, which can contribute to soil erosion (e.g. Bosch and Hewlett, 1982). However, the impacts of CO_2 leaks in both the marine and terrestrial environments are likely to be contained within relatively small areas; consequently the effects of leaks on these regulating processes which function at a global scale are likely to be minimal.

5.3 Cultural services: The benefits generated from cultural services are often non-material in nature and are related to individuals' beliefs and values. Any impacts of CO_2 leaks on these non-material benefits is likely to be closely related to the perceptions the public holds for CCS and hence their support for CCS projects. Most studies of public perceptions for CCS have indicated that the public have little knowledge of it (Huijts et al., 2007; Shackley et al., 2009). Consequently it is difficult to assess how a CO_2 leak might influence their values and beliefs; although it can be supposed to have a similar impact as other pollution incidents.

Another important cultural service is the opportunity the environment provides for leisure and recreation. CO_2 leaks are unlikely to have any effect on leisure and recreation, especially in the marine environment, due to the depth at which storage occurs and their distance from shore. The same is true for land-based activities, unless a leak occurs in a popular recreational site. Degassing of CO_2 from naturally occurring sources has been responsible for symptoms of asphyxia (Farrar et al., 1995) and death in people and animals (Roberts et al., 2011). This risk, however, is minimal and is much higher during other stages of the CCS process (Ha-Duong and Loisel, 2010) and from other activities, such as car accidents (Roberts et al., 2011)

The above discussion suggests that CCS site selection needs to be considered with reference to fish nursery habitats or shellfish beds, important agricultural ground and essential freshwater aquifers. Leaks, however, may not occur at the site of injection of CO_2 into the storage site, which implies a need for monitoring of storage sites to ensure any leaks are quickly identified and appropriately managed (e.g. to restrict access to areas affected by leak). The potential impacts of CO_2 leaks also need to be placed in context. Within the marine environment, fishing activities, in particular demersal trawling, may significantly alter marine benthic communities (Jennings and Kaiser, 1998), yet some areas of seabed (e.g. within the North Sea) are trawled more than once a year (Mills et al., 2007) and this has been the case for decades. The impacts of CO_2 leaks will be on a substantially smaller scale.

6. Monitoring and mitigation of storage sites

Strategies and technology for monitoring, measurement and verification (MMV) of offshore carbon capture storage sites will be largely determined by: (1) the nature and scale of the storage site, and (2) the status and need of the monitoring whether it be baseline surveys, verification of reservoir containment, or quantification of CO_2 leakage. Potential storage sites, comprising either depleted hydrocarbon reservoirs or saline aquifers, impart important limits on MMV strategies and technology. Here, given storage sites in the UK are predominantly offshore, we restrict discussion to marine environments, although the general principles outlined will apply to terrestrial environments as well. In the context of the North Sea, depleted reservoirs will typically have an aerial extent of 250-400 km^2, overlain with an ocean volume of the order of 25-40 km^3, have an array of cap seal penetrations (in the form of abandoned wells), and a cumulative storage capacity of >28 Gt of CO_2 sequestered by 2050. Saline aquifers will typically have an aerial extent of >22,000 km^2, overlain by an ocean volume of >2000 km^3, and a theoretical storage capacity exceeding 50 Gt of CO_2 (Senior, 2010). Such storage options lead to potential leakage scenarios ranging from high discharge (e.g. >200 tonnes d^{-1}) point source leakage (due to acute well-casing leakage or hydro-fracturing of a seal cap) in a relatively small depleted reservoir site, through to low discharge (e.g. <20 tonnes d^{-1}), dispersed source discharges from an extensive saline aquifer system. Such a continuum of leakage scenarios necessitates diverse, and responsively staged monitoring.

Current and proposed regulatory monitoring practice (EU Carbon Capture Storage Directive 2009) places significant emphasis on "deep" geophysical monitoring of the reservoir containment formation, integrity of the capping seal, and migration of CO_2 within the reservoir, typically at sub-seafloor depths of 800 – 2000 m. As demonstrated at the Sleipner storage site, repeat seismic reflection surveys (termed "4D" seismic) have proven to be an excellent method of intermittently imaging progressive dispersion of CO_2 within the reservoir (Chadwick et al 2009), where differences in reflector amplitude and velocity "pushdown" (e.g., Shi et al., 2007) are interpreted as CO_2 fluid within intra-reservoir beds. Other geophysical techniques including passive micro-seismicity recording, seafloor gravimetry, controlled source electromagnetics, and even bore-hole or arrayed bore-hole electrical resistivity tomography and electromagnetic monitoring have been proposed with varying assessments of cost and applicability. All these methods rely on changes of a geophysical parameter due to varying saturation with supercritical CO_2, whether it be acoustic impedance, electrical resistivity, or rock density, being used either qualitatively to image CO_2 migration, or quantitatively inverted into predicted CO_2 volumes. The latter is predicated on knowing the quantitative relationship between CO_2 saturation and change in the geophysical parameter. Whether such geophysical inversions will be sufficiently sensitive to determine volumes of potential CO_2 loss from the containment formation for the purposes of regulation and carbon emission trading is an open question.

If CO_2 leakage occurs from the containment formation (Figure 4), monitoring at the seafloor and shallowest sub-surface provides two additional significant opportunities for monitoring of offshore carbon capture storage sites. The first is that in many circumstances it is probable that initially pre-cursory fluids will be emitted at the seafloor before CO_2 due to the buoyancy pressure of CO_2 displacing stratigraphically higher fluids. Such pre-cursory fluids would include displaced formation brines and reduced pore fluids within unconsolidated, shallow sub-seafloor sediments. Both brines and reduced pore fluids have characteristic chemical signatures, with the former having elevated temperature and salinity, and the latter having higher Mn, ferrous Fe, acidity, H_2S, and lower dissolved oxygen. The second significant monitoring opportunity lies in the fact that the seafloor, and to a lesser extent the overlying ocean, provide a site for more direct and quantitatively explicit measurement of CO_2 flux (both as free gas and dissolved phases) that is potentially more sensitive for measurement and verification of CO_2 leakage. Physical and chemical signatures of CO_2 loss from the seafloor, either as direct CO_2 measurement, a decrease in pH, or emission of gas bubbles, are arguably more tractable both in the sense of making the observation and understanding its relationship to CO_2 volume loss.

Such monitoring opportunities of the seafloor and overlying ocean are stimulating considerable research of potential physical and chemical processes that would signify CO_2 leakage. Physical techniques are principally developing around passive and active acoustic bubble detection that would resolve the free gas leakage. Passive detection uses hydrophones to acoustically detect bubble oscillation and expansion during ascent from the seafloor, while active sonar record the acoustic back-scatter response of ascending gas bubbles. Theoretical considerations demonstrate that both passive and active multi-frequency acoustic data can be inverted to determine bubble size populations (Leighton and White, 2011), which if combined with bubble ascent velocity could yield a gas flux, though it is known that at least for methane bubbles, both gas and any surface skin hydrate compositions can change during ascent (e.g., Greinert et al 2006). Similarly, high-frequency, broad band 400 Hz – 24 kHz seismic profiling may provide a method to image shallow, CO_2-charged sediments. Chemical techniques principally determine changes in marine carbonate chemistry (e.g., CO_2 directly or pH) or pre-cursory saline or reduced pore-fluid signatures described above.

These chemical and physical techniques require the development of both new instruments and sensors, and "underwater platforms" capable of low-cost, long-term, and sustained observing with delayed or real-time data telemetry. For chemical sensors, newly developed techniques in solid state optical-transistor (e.g., Garcia and Masson, 2004) and microfluidic-reagent reaction sensors (e.g., Floquet et al., in press) provide the opportunity to observe a number of important chemical parameters. Improvements in limits of detection, and correction for pressure and temperature changes, now hearld an emerging capability to undertake sustained in situ monitoring. Typically limits of detection for dissolved Fe and Mn are nM, methane 0.2 nM, salinity 0.00001 psu, temeprature 0.005°C, and for pH is currently 0.005-0.003 pH unit, but could be improved to 0.0005 pH unit in the near future. Similarly, a CO_2 sensor with a detection limit of ~3 ppm is possible using microfluidic techniques. In parallel, the development of "underwater platforms" both as seafloor observatories (e.g., Bagley et al., 2007) or mobile autonomous underwater vehicles (AUV's) (e.g., McPhail, 2009) and gliders are developing the necessary capability from which to deploy sensors for long-term deployment. New AUV developments include vehicles that are capable of being deployed for up six months that provide the prospect of surveying large seafloor areas and ocean volumes at storage sites with minimal ship support. These combined sensors and vehicle developments are also stimulating interest in using natural analogue CO_2 seep sites (e.g., Caramanna et al., 2011) or existing North Sea storage sites as "test beds" for trial deployment of these emerging monitoring technologies. Effective chemical monitoring will also depend on understanding spatial and temporal scales and causality of natural variability and it is probable that multi-variate monitoring would be more effective in identifying irregularities than high precision uni-variate techniques.

Identifying effective biological tools for monitoring the marine environment above any geological CCS facility, in order to identify sites of CO_2 leakage, is not straight-forward. The horizontal extent of many potential geological reservoirs means that CCS monitoring programmes will need to cover far larger areas than existing programmes, such as those used to assess the impact of oil and gas extraction. So, whilst many marine organisms and processes are impacted by exposure to elevated levels of CO_2, their use in monitoring may be restricted by the speed at which appropriate biological data can be gathered and the limited spatial extent to which specific biological observations apply. With this in mind, wide-scale observations of the seafloor using AUV mounted cameras may provide the most potential for identifying effective biological monitoring with recent experiments showing two main biological responses visible at the sediment surface (Figure 5). Firstly, elevated levels of CO_2 may promote the growth of microbial mats by fertilising CO_2 limited bacteria (e.g. cyanobacteria, Figure 5A) or by liberating other substances (e.g. methane or sulphide) that could stimulate the growth of specific microbial groups. Secondly, reduced pore-water pH levels could drive infaunal organisms onto the sediment surface (Figure 5B) and in extreme cases result in large-scale mortality (Figure 5C). Whilst the application of biological monitoring tools in identifying CO_2 leakage appears limited, the use of biological observations in monitoring environmental recovery after a leak provides far more opportunity. In this activity a number of traditional tools could be applied including the assessment of macrofaunal community structure and diversity and the use of bioassays that quantify organism immune function and general health status.

7. The role of natural analogue sites and artificial experiments

Natural analogues for CO_2 storage can provide useful information on the processes that are important for the migration and storage of CO_2 as well as for testing monitoring strategies (Pearce et al., 2004; Holloway et al., 2005). The IPCC Special Report on Carbon Dioxide Capture and Storage (IPCC, 2005) includes a review of natural CO_2 accumulations, supplying information on migration mechanisms and potential impacts of leakage. Concentrations and fluxes of CO_2 in natural 'baseline' environments and in sites where CO_2 leakages occur naturally vary over a wide range (see, for example, West et al., 2005). Onshore concentrations can vary from <0.1% to ~95% of the total gas in soils.

The European Commission (2011) considers that CO_2 stored by man at depth in geological reservoirs could potentially find its way into 3 different spatial regimes

i. ***Primary storage site*** and seal at ~1km depth within which CO_2 is expected to be securely stored.
ii. ***Secondary containment formations*** which are defined by secondary seals and reservoirs that may contain the CO_2. If present these overlying formations may provide a natural self-remediation in case the plume migrates beyond the primary seal.
iii. ***The surrounding environment.*** Migration of CO_2 above the secondary containment formations into the shallow subsurface would be termed leakage and incur a financial penalty. Should CO_2 leak into the surface environment the operation would come

under scrutiny from further environmental legislation. It is the responsibility of the store operators to ensure that their store, injection strategy and monitoring strategy is designed such that there is minimal risk of CO_2 escaping the secondary confinement into the shallow subsurface and surface environment.

Natural CO_2 seeps occur both onshore and offshore. The CO_2 emerging from the onshore seeps has typically been identified as derived from volcanism, metamorphism (such as may be occurring at depth beneath active mountain belts) and degassing from the mantle, whilst offshore seeps are predominantly associated with volcanism. As well as natural CO_2 seeps, a large number of natural CO_2 fields have been discovered which have been exploited to, for example, produce CO_2 for carbonated water or enhanced oil recovery (EOR). Typically, these were discovered in the search for hydrocarbon resources (Bonini 2009; Chiodini et al 2010). Studying natural CO_2 stores (natural CO_2 fields) and seeps allows us to explore factors important to storage security and may help in understanding the size and nature of potential migration paths through the deep and shallow subsurface. Thus study of natural analogues for both geological storage and migration of CO_2 to the ground surface or seabed can make a significant contribution to reducing the risks of leakage from anthropogenic stores. As an example of the former, there is geological evidence that some 215 million tonnes of natural carbon dioxide has been stored in the Pisgah Anticline, Mississippi since late Cretaceous times, some 65 million years ago (Studlick, et al. 1990). Study of the structure of the natural geological trap in which this CO_2 is found, and the cap rocks above the reservoir, could yield important information about long-term sealing capacity. Natural analogues can also tell us about CO_2 leakage pathways and the effects of CO_2 emerging from the ground surface or seabed on the environment. Fault related CO_2 seeps near Green River, Utah, provide a good example of pathway evolution and variable flow through time. At this location U-Th dating of numerous fossilized travertine deposits show that CO_2 leakage location has repeatedly switched km distances over 100,000 year time scales and that the volume of emitted CO_2 have varied throughout time (Burnside et al 2012). Natural offshore seeps at Panarea, Italy allow monitoring of the effects of dissolving bubbles of CO_2 on the pH of seawater in their immediate vicinity, and the resulting effects on biota.

Onshore seeps include, for example, springs and streams of carbonated water, bubbling pools of water or mud (e.g. Figure 6A and B), and diffuse seeps through soil (e.g. Figure 6C). Flux rates at natural CO_2 seeps vary over orders of magnitudes. For example, at the Pululahua Caldera in Ecuador the mean flux is 3.1×10^{-2} T m^{-2} yr^{-1} (Padron et al 2008; Figure 7A), whilst at the Mefite d'Ansanto site (Figure 6A), the CO_2 flux rate is ~100 tonnes T m^{-2} yr^{-1} (Chiodini et al 2010; Figure 7A). Since the emerging CO_2 is denser than air, at this location it travels downslope into the river channel; it has killed off vegetation in the area immediately around the seep and an impact on the vegetation can be seen for some distance downstream.

Although seep rates at natural analogue sites are measureable, it is important to bear in mind that because of the highly variable geology and, in many cases the active volcanic processes that generate the CO_2, these measured fluxes may be highly site-specific and may vary through time. This makes it difficult to make inferences about seep rates at potential anthropogenic storage sites.

The potential effects of such seeps on human health and the environment are clearly potentially important analogies. It is worth noting that the area around the Mefite seep is well populated and people are currently living within 100m. It is the build-up of relatively high concentrations of CO_2 in air that poses a threat to human or animal life rather than the flux through the ground. In this context, if a dry seep such as that in Figure 6C emerged within the basement of a building, there could be a risk of asphyxiation that could otherwise be difficult to detect without proactive monitoring, even if the flux from the seep was relatively low, because of the confined environment. Conversely, as long as seeping CO_2 is dispersed and mixes with the ambient air instead of being allowed to build up, the risks should be minimal.

Another onshore example of benefit derived from studying a natural analogue site is given by the Latera site in Italy (Annunziatellis et al., 2008). In this volcanic area CO_2 migration pathways are restricted at depth to relatively narrow vertical zones associated with faults and/or intersections of faults. 'Channelling' occurs along the pathway of highest permeability, so that the 'pipes' will not necessarily be straight, but weave in two or three dimensions within the fault. Above these faults, transport in the near-surface terrestrial environment is determined by the properties of heterogeneous layers of alluvium and various volcanic products. This heterogeneity results in the near-surface vents that range in diameter from about 10 to 80 m. CO_2 fluxes across vents that cause substantial plant loss are typically in the range 0.2 to 1.8 kg CO_2 m^{-2} d^{-1} (Beaubien et al., 2008). The key features of a detailed study of a single vent at the site were reproduced by mathematical models, as described by Maul et al. (2009).

Active offshore seeps have generally been identified by the observation of bubbles of CO_2 rising within the water column; some palaeo-seeps may be identified by pock marks on the sea bed and/or gas chimneys imaged rising to the seabed. Typically, measured flux rates are comparable to those of onshore seeps, however none have been documented with a flux rate as high as Mefite. Leakage rates measured on individual point seeps at Panarea (offshore from the Aeolian Islands, Italy) are typically between 10-100 T yr^{-1}. What is less clear is whether there is an offshore analogy for the more diffuse onshore seeps. For example, in an offshore setting is seems likely that low fluxes of migrating CO_2 might dissolve within any shallow sediment layer that might be present and CO_2 rich water might be displaced into the seawater column. Such a seep might not be detectable by monitoring for bubbles – and hence there is a potential for an absence of evidence for low rate seeps offshore. One example of this is the Juist Salt Dome in the Southern German North Sea where there are no visible signs of seepage even though CO_2 levels are locally 10-20 and in one case 53 times greater than background (McGinnis et al. 2011).

Few natural offshore CO_2 seeps have been studied in detail. Consequently there is a need for field scale experiments which can characterise the impacts, both chemically and biologically of new seeps. Kirk (2011) listed some of the questions about offshore seeps that could be potentially valuable in terms of understanding the physical, chemical and biological interaction between CO_2 leakage and the sea floor / sea water environment including:

- How much of the CO_2 being released is dissolving in the seabed sediment layer immediately below the seabed itself?
- What pH changes result?
- What is the impact of a new seep on benthic marine organisms?
- How much geochemical interaction is there between naturally seeping CO_2 and sediments?
- What level of accuracy of seepage quantification can be achieved offshore, especially below easily diveable depths? For example will it be possible to account for all of the CO_2 potentially leaking from an offshore CO_2 storage site by direct measurements (bubbles, dissolution etc.)?
- What would a comprehensive offshore seabed leakage detection and measurement system look like and cost?
- Is there any realistic prospect of remediating or mitigating a leak at the seabed from an offshore CO_2 storage site?
- Would an offshore leak naturally decay and if so over what kind of time period?

It is informative to compare shallow-water CO_2 seep analogues with water and gas emissions at mid-ocean ridges, particularly associated with black smokers and hydrothermal vents

(Wankel et al. 2011). By mass, the emissions from the latter are typically composed of 94.1% $CO_{2(aq)}$, 5.8% CH_4 and 0.1% H_2. The large and small focused seeps recorded annual $CO_{2(aq)}$ emission rates very similar to those from the shallow-water free CO_2 seeps at Panarea (Figure 7c). These sites also provide evidence that CO_2 can leak from the sea floor in an aqueous phase – although the hydrothermal regime at an engineered CO_2 storage site would be considerably different to the mid-ocean ridge setting.

Natural analogues may provide an idea of the long-term effects that could be expected in the event of leakage from a geological storage site. By their nature, natural analogues are mature systems in which CO_2 has either remained trapped in the subsurface at depth (~km to 100s m) or it is leaking through an established seep. We can therefore consider their spatial extent of CO_2 in the subsurface to be relatively constant. There is rarely monitoring of systematic changes in seep rate through time except where human intervention has impinged on the integrity of natural stores. One natural analogue that has showed variation in flow rate is Panarea which has been known to increase CO_2 activity in reponse to increased geothermal activity (Caramana et al 2011). The last know event occurred in November 2002 when 'a series of underwater gas explosions' lead to an abrupt increase in the volume of emitted fluids. It has been estimated that one of the most active vents emitted 54 t/day of CO_2 for nearly 2 months.

Natural analogues can be used to test different monitoring techniques both at storage depths (3km-500m), shallow depths (~500m to surface) and fluxes out of the surface – but these are images of a long lived store and/or seep. However, the monitoring of a newly forming seepage pathway requires modern analogues that experience breakthrough of CO_2 for the first time. We have not identified analogues of such evolving systems that are required to assess the performance of monitoring techniques by tracking the unintended migration of CO_2. The physical limitations of different monitoring techniques make them appropriate for monitoring different parts of the systems so an effective monitoring strategy will need a range of tools capable of monitoring across the whole depth range. Triggers typically form an integral part of any monitoring strategy: for example, when a measured parameter departs from an acceptable range this may trigger new monitoring activities aimed at obtaining further information as to the reason for the observed anomaly.

Research is underway at several experimental locations to investigate the shorter term effects of CO_2 on terrestrial ecosystems and marine test sites are under development. An example is the ASGARD (Artificial Soil Gassing and Response Detection) field site at the University of Nottingham. The impacts of a controlled injection of CO_2 on soil microbiology, soil geochemistry and the range and health of plants growing at the surface are being studied; some early results from this work are described by West et al. (2009). In these types of experiments it is as yet difficult to determine which biogeochemical processes contribute to the observed impacts.

8. Challenges and emerging trends

The EU Directive on Geological Storage of CO_2 states that

> *"The operator ...... must monitor continuously all aspects of the CO_2 flow and the surrounding storage complex, ... and respond with corrective measures to any leakages or "irregularities" that occur"*

In addition, guidelines ask:

> *"Have all vulnerable domains surrounding the targeted storage sites ... been identified? Has relevant environmental data required for screening been acquired and reviewed?"*

The ensuing research challenges are clear. Firstly methods of monitoring that are efficient and effective need to be developed. Whilst primary monitoring will logically be focussed around the geological storage zone and within transport mechanisms, for geological leaks, quantifying leakage (and subsequent penalties) will be far more tractable using surface based methods. This will be complicated by the potential for horizontal movement within geological structures and strong mixing and dispersion potential in the atmospheric and marine systems. In this latter respect hydrodynamic models are vital predictors of dispersion and thus vital for the design of appropriate monitoring strategies.

A second challenge is to define "irregularities". Natural systems are dynamic and vary on multiple spatial and temporal scales. Understanding this dynamic baseline is vital not just for monitoring but also to ensure that irregularities are correctly attributed to their cause.

A third challenge is to assess if any vulnerable domains exist and in general be aware of the economic value of the environment so that risk assessment can be carried out in as quantitative way as possible. Understanding the potential damage that a leak from CCS storage might cause and how this relates to the ecological value of the wider region and impacts from other anthropogenic activities, especially climate change will promote a coherent and informed assessment of risks and management. In turn this is again dependant on understanding dispersion and the spatial extent of potential impact. If CCS is to be an effective and accepted climate change abatement strategy, the implications of CCS and CO_2 leaks need to be better communicated to the public.

This chapter has outlined the current status of research with respect to impacts, valuation, monitoring and the utility of natural analogue sites. In particular the concept of ecosystem services can be useful in exploring the potential impacts of CO_2 leaks on society, but if meaningful assessments are to be made then better understanding is needed of the links between biodiversity, ecosystem process and function, and ecosystem services in a context that encompasses the multiple uses and stressors of the natural environment.
Finally whilst the research effort is currently buoyant, a remaining challenge is to ensure that the scientific knowledge gained is transferred to the emerging regulatory mechanisms coherently and comprehensively so that the widest range of stakeholders can have confidence in the operation of CCS demonstration programmes over the next decade.

9. Sources of further information.

A number of projects are currently undertaking research into environmental impacts of CCS, a by no means exhaustive list is:

- **RISCS (Impacts and safety of CO_2 Storage)** http://www.riscs-co2.eu/
- **ECO_2 (Carbon storage and the marine environment)** http://www.eco2-project.eu/home.html
- **QICS (Quantifying Ecosystem Impacts of Carbon Storage)** http://www.bgs.ac.uk/qics/home.html

A number of reports have detailed the issues and challenges for CCS, these include: The Intergovernmental panel on Climate Change released a report on CCS 'CCS, IPCC Special Report, Working Group III, September 2005.', which is available from Cambridge University Press (http://www.cambridge.org/ipcc), The Edinburgh Building, Shaftesbury Road, Cambridge, CB2 2RU England.

A readable description of the chemistry and ecological implications of adding CO_2 to marine systems, in the context of ocean acidification can be found in the Royal Society report of 2005 by Prof John Raven et al: 'Ocean acidification due to increasing atmospheric carbon dioxide' (Royal Society 2005). This can be downloaded from: http://royalsociety.org/document.asp?id=3249.

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References

Annunziatellis, A., Beaubien, S.E., Bigi, S., Ciotoli, G., Coltella, M., and Lombardi, S., 2008, Gas migration along fault systems and through the vadose zone in the Latera caldera (central Italy): Implications for CO2 geological storage: International Journal of Greenhouse Gas Control, v. 2, p. 353-372.

Bagley, P.M., Smith, K.L., Bett, B., Priede, I.G., Rowe, G., Clarke, J., Walls, A., 2007. Deep-ocean Environmental Long-term Observatory System (DELOS):- Long-term (25 year) monitoring of the deep-ocean animal community in the vicinity of offshore hydrocarbon operations. *OCEANS 2007 - Europe*, pp.1-5, 18-21 June 2007 doi: 10.1109/OCEANSE.2007.4302250

Beaubien S E, Ciotoli G, Coombs P, Dictor M C, Krüger M, Lombardi S, Pearce J M. and West J M (2008). The Impact of a Naturally Occurring CO_2 Gas Vent on the Shallow Ecosystem and Soil Chemistry of a Mediterranean Pasture (Latera, Italy). International Journal of Greenhouse Gas Control, 2 (3), 373-387.

Blackford, J.C., Jones, N., Proctor, R., Holt, J., 2008. Regional scale impacts of distinct CO_2 additions in the North Sea. Marine Pollution Bulletin 56, 1461-1468.

Blackford J, Chen B, Widdicombe S, Lowe DM (2010) Marine environmental risks of CO_2 sequestration. In: Maroto-Valer M (Ed.) *Developments and innovation in carbon dioxide (CO_2) capture and storage technology*. Woodhead,

Bonini, M. 2009, Structural controls on a carbon dioxide-driven mud volcano field in the Northern Apennines (Pieve Santo Stefano, Italy): Relations with pre-existing steep discontinuities and seismicity. Journal of Structural Geology v 31(1), p 44-54.

Bosch, J.M., Hewlett, J.D., 1982. A review of catchment experiments to determine the effect of vegetation changes on water yield and evapotranspiration. Journal of Hydrology 55, 3-23.

Boyd, J., Banzhaf, S., 2007. What are ecosystem services? The need for standardized environmental accounting units. Ecological Economics 63, 616-626.

Burnside, N.M., Shipton, Z.K., Dockrill, B., Ellam, R.E., 2012. 400,000 years of of natural and man-made leakage from an analogue for engineered storage of CO_2. Tectonic Studies Group Annual Meeting 2012, Our Dynamic Earth, Edinburgh.

Caramanna, G., Voltattorni, N., and Maroto-Valer, M.M., 2011, Is Panarea Island (Italy) a valid and cost-effective natural laboratory for the development of detection and monitoring techniques for submarine CO2 seepage?: Greenhouse Gases: Science and Technology, v. 1, p. 200-210.

Chadwick, R.A., Noy, D., Arts, R., Eiken, O., 2009. Latest time-lapse seismic data from Sleipner yield new insights into CO_2 plume development. *Energy Procedia 1*, 2103-2110.

Chen, B; Song, Y.; Nishio, M.; Someya, S.; Akai, M. 2005. Modeling near-field dispersion from direct injection of carbon dioxide into the ocean. Journal of Geophysical Research, 110, C09S15.

Chiodini, G., Granieri, D., Avino, R., Caliro, S., Costa, A., Minopoli, C., and Vilardo, G., 2010, Non-volcanic CO2 Earth degassing: Case of Mefite d'Ansanto (southern Apennines), Italy: Geophys. Res. Lett., v. 37, p. L11303.

Cook, A.C., Tissue, D.T., Roberts, S.W., Oechel, W.C., 1998. Effects of long-term elevated [CO2] from natural CO2 springs on Nardus stricta: photosynthesis, biochemistry, growth and phenology. Plant, Cell & Environment 21, 417-425.

EU Carbon Capture Storage Directive 2009, Directive 2009/31/EC of the European Parliament and of the Council of 23 April 2009 on the geological storage of carbon dioxide and amending Council

Directive 85/337/EEC, European Parliament and Council Directives 2000/60/EC, 2001/80/EC, 2004/35/EC, 2006/12/EC, 2008/1/EC and Regulation (EC) No 1013/2006.

Fabry, V.J., Seibel, B.A., Feely, R.A., Orr, J.C., 2008. Impacts of ocean acidification on marine fauna and ecosystem processes. ICES Journal of Marine Science 65, 414–432.

Farrar, C.D., Sorey, M.L., Evans, W.C., Howle, J.F., Kerr, B.D., Kennedy, B.M., King, C.Y., Southon, J.R., 1995. Forest-killing diffuse CO_2 emission at Mammoth Mountain as a sign of magmatic unrest. Nature 376, 675-678.

Fisher, B., Turner, R.K., Morling, P., 2009. Defining and classifying ecosystem services for decision making. Ecological Economics 68, 643-653.

Floquet, C. F. A., V. J. Sieben, A. Milani, E. P. Joly, I. R. G. Ogilvie, H. Morgan, and M. C. Mowlem, in press. Nanomolar detection with high sensitivity microfluidic absorption cells manufactured in tinted PMMA for chemical analysis, *Talanta*.

Garcia, M.L., Masson, M., 2004. Environmental and geologic application of solid-state methane sensors. *Environmental Geology 46*, 1059–1063.

Gazeau, F., Quiblier, C., Janse, J.M., Gattuso, J.-P., Middleburg, J.J., Heip, C.H.R., 2007. Impact of elevated CO_2 on shelfish calcification. Geophysical Research Letters 34, L07603.

Greinert, J., Artemov, Y., Egorov, V., De Batist, M., McGinnis, D., 2006. 1300-m-high rising bubbles from mud volcanoes at 2080 0;m in the Black Sea: Hydroacoustic characteristics and temporal variability, *Earth and Planetary Science Letters, 244*, 1-15, doi: 10.1016/j.epsl.2006.02.011.

Ha-Duong, M., Loisel, R., 2010. Expected fatalities for one wedge of CCS mitigation: actuarial risk assessment of carbon capture and storage at the global scale in 2050, Centre International de Recherches sur l'Environnement et le Developpement, Nogent sure Marne.

Hale R, Calosi P, McNeill CL, Mieszkowska N, Widdicombe S (2011) Predicted levels of future ocean acidification and temperature rise could alter community structure and biodiversity in marine benthic communities. *Oikos* 120: 661-674.

Hall-Spencer J, Rodolfo-Metalpa R, Martin S (2008) Volcanic carbon dioxide vents show ecosystem effects of ocean acidification. *Nature* 454: 96-99.

Holloway S, Pearce J M, Ohsumi T and Hards V L (2005). A Review of Natural CO_2 Occurrences and their Relevance to CO_2 Storage. International Energy Agency Greenhouse Gas R&D Programme Report 05/08, 124 pp.

Huijts, N.M.A., Midden, C.J.H., Meijnders, A.L., 2007. Social acceptance of carbon dioxide storage. Energy Policy 35, 2780-2789.

IPCC (2005). Carbon Dioxide Capture and Storage. A Special Report of Working Group III of the Intergovernmental Panel on Climate Change. Cambridge University Press,Cambridge, United Kingdom and New York, NY, USA, 442 pp. Details are available at: http://www.cambridge.org/uk/earthsciences/climatechange/.

Jennings, S., Kaiser, M.J., 1998. The effects of fishing on marine ecosystems. Advances in Marine Biology 34, 201-212, 212a, 213-266, 266a, 268-352.

Kirk, K. (2011) Natural CO2 flux literature review for the QICS project, British Geological Survey Commissioned Report, CR/11/005. 38pp.

Laverock B, Gilbert JA, Tait K, Osborn AM, Widdicombe S (2011) Bioturbation: impact on the marine nitrogen cycle. *Biochemical Society Transactions* 39: 315-320.

Leighton, T. G., White, P. R., 2011. Quantification of undersea gas leaks from carbon capture and storage facilities, from pipelines and from methane seeps, by their acoustic emissions. Proceedings of the Royal Society A; DOI: 10.1098/rspa.2011.0221

Lu J, Partin J W, Hovorka S D and Wong C. 2010. Potential risks to freshwater resources as a result of leakage from CO_2 geological storage: a batch-reaction experiment. Environmental Earth Sciences, 60, 335-348.

Maul P R, Savage D, Benbow S J, Walke R.C, Bruin R, Pearce J, Thorne M C and West J M (2005). Development of a FEP Database for the Geological Storage of Carbon Dioxide. In: Wilson M, Morris T, Gale J, Thambimithu K (Eds.), Proceedings of the Seventh International Conference on Greenhouse Gas Control Technologies, vol. 1, Vancouver, Canada, pp. 701-710.

Maul P R, Beaubien S E, Bond A E, Limer L M C, Lombardi S, Pearce J, Thorne M C and West J M (2009). Modelling the Fate of Carbon Dioxide in the Near-Surface Environment at the Latera Natural Analogue Site. Energy Procedia, 1 (1), 1879-1885.

McGinnis D F, Schmidt M, DelSontro T, Themann S, Rovelli L, Reitz A and Linke P (2011). Discovery of a natural CO2 seep in the German North Sea: Implications for shallow dissolved gas and seep detection. Journal of Geophysical Research, vol 116, 12pp.

McPhail, S., 2009. Autosub6000: A deep diving long range AUV, *Journal of Bionic Engineering*, 6: 55-62, doi: 10.1016/S1672-6529(08)60095-5.

Millennium Ecosystem Assessment, 2003. Ecosystems and Human Well-being: A Framework for Assessment. Island Press, Washington DC.

Mills, C.M., Townsend, S.E., Jennings, S., Eastwood, P.D., Houghton, C.A., 2007. Estimating high resolution trawl fishing effort from satellite-based vessel monitoring system data. ICES Journal of Marine Science 64, 248-255.

Munday, P.L., Dixson, D.L., McCormick, M.I., Meekan, M., Ferrari, M.C.O., Chivers, D.P., 2010. Replenishment of fish populations is threatened by ocean acidification. Proceedings of the National Academy of Science of the United States of America 107, 12930-12934.

Munday, P.L., Donelson, J.M., Dixson, D.L., Endo, G.G.K., 2009. Effects of ocean acidification on the early life history of a tropical marine fish. Proceedings of the Royal Society B 276, 3275-3283.

Padrón, E., Hernández, P.A., Toulkeridis, T., Pérez, N.M., Marrero, R., Melián, G., Virgili, G., and Notsu, K., 2008, Diffuse CO2 emission rate from Pululahua and the lake-filled Cuicocha calderas, Ecuador: *Journal of Volcanology and Geothermal Research*, v. 176, p. 163-169.

Patil, R.H., Colls, J.J., Steven, M.D., 2010. Effects of CO_2 gas leaks from geological storage sites on agro-ecosystems. Energy 35, 4587-4591.

Pearce J M, Czernichowski-Lauriol I, Lombardi S, Brune S, Nador A, Baker J, Pauwels H, Hatziyannis G, Beaubien S and Faber E (2004). A Review of Natural CO_2 Accumulations in Europe as Analogues for Geological Sequestration. In: Baines S and Worden R J (Eds.), Geological Storage of Carbon Dioxide, vol. 233 Geological Society of London, pp. 29–41. (Special Publication).

Pires, J.C.M., Matins, F.G., Alvim-Ferraz, M.C.M., Simões, M., 2011. Recent developments on carbon capture and storage: an overview. Chemical Engineering Research and Design 89, 1446-1460.

Pörtner HO (2008) Ecosystem effects of ocean acidification in times of ocean warming: a physiologist's view. *Marine Ecology Progress Series* 373: 203-217.

Pörtner HO (2010) Oxygen- and capacity-limitation of thermal tolerance: a matrix for integrating climate-related stressor effects in marine ecosystems. *Journal of Experimental Biology* 213: 881-893.

Pörtner HO, Farrell AP (2008) Physiology and Climate Change. *Science* 322: 690-692.

Pörtner HO, Gutowska M, Ishimatsu A, Lucassen M, Melzner F, Seibel B (2011) Effects of ocean acidification on nektonic organisms. In: Gattuso J-P & Hansson L (Eds.), *Ocean Acidification*, Oxford University Press. pp. 154-175.

Roberts, J.J., Wood, R.A., Haszeldine, R.S., 2011. Assessing the health risks of natural CO_2 seeps in Italy. Proceedings of the National Academy of Science of the United States of America. DOI: 10.1073/pnas.1018590108

Royal Society: Raven, J., Caldeira, K., Elderfield, H.,Hough-Guldberg, O., Liss, P., Riebesell, U.,Shepherd, J., Turley, C.M., Watson, A., 2005. Ocean acidification due to increasingatmospheric carbon dioxide. The Royal Society Policy Document 12/05, 68.

Senior, B., 2010. CO2 Storage in the UK - Industry Potential. Department of Energy & Climate Change, URN 10D/512.

Shackley, S., Reiner, D., Upham, P., de Coninck, H., Sigurthorsson, G., Anderson, J., 2009. The acceptability of CO_2 capture and storage (CCS) in Europe: An assessment of the key determining factors: Part 2. The social acceptability of CCS and the wider impacts and repercussions of its implementation. International Journal of Greenhouse Gas Control 3, 344-356.

Shi, J-Q., Xue, Z., Durucan, S., 2007. Seismic monitoring and modeling of supercritical CO_2 injection into a water-saturated sandstone: Interpretation of P-wave velocity data. *International Journal of Greenhouse Gas Control 1*, 473-480.

Smets B, Tedesco D, Kervyn F, Kies A, Vaselli O, Yalire MM (2010) Dry gas vents (''mazuku'') in Goma region (North-Kivu, Democratic Republic of Congo): Formation and risk assessment. Journal of African Earth Sciences 58: 787–798

Solan, M., Cardinale, B.J., Downing, A.L., Engelhardt, K.A.M., Ruesink, J.L., Srivastava, D.S., 2004. Extinction and ecosystem function in the marine benthos. Science 306, 1177-1180.

Studlick JRJ, Shew RD, Basye GL, Ray JR (1990) A Giant Carbon Dioxide Accumulation in the Norphlet Formation, Pisgah Anticline, Mississippi. in: J.H. Barwis, J.G. McPherson & J.R. Studlick (Editors) Sandstone Petroleum Reservoirs, Springer-Verlag, New York, 181-203.

Tait K, Laverock B & Widdicombe S (2012) Response of an arctic sediment ammonia oxidising community to increased pCO_2. *ISME Journal* submitted.

Tassi, F., Capaccioni, B., Caramanna, G., Cinti, D., Montegrossi, G., Pizzino, L., Quattrocchi, F., and Vaselli, O., 2009, Low-pH waters discharging from submarine vents at Panarea Island (Aeolian Islands, southern Italy) after the 2002 gas blast: Origin of hydrothermal fluids and implications for volcanic surveillance: *Applied Geochemistry*, 24, 246-254.

Thistle D, Sedlacek L, Carman KR, Fleeger JW, Brewer PG, Barry JP (2007) Exposure to carbon dioxide-rich seawater is stressful for some deep-sea species : an insitu, behavioral study. *Marine Ecology Progress Series* 340: 9-16.

van der Zwaan, B., Gerlagh, R., 2009. Economics of geological CO_2 storage and leakage. Climatic Change 93, 285-309.

van der Zwaan, B., Smekens, K., 2009. CO_2 Capture and Storage with Leakage in an Energy-Climate Model. Environmental Modeling and Assessment 14, 135-148.

Walke R, Metcalfe R, Limer L, Maul P, Paulley A and Savage D (2011). Experience of the Application of a Database of generic Features Evenets and Procesees (FEPs) Targeted at Geological Storage. Energy Procedia volume 4 2011, 4059-4066.

Wankel, S.D., Germanovich, L.N., Lilley, M.D., Genc, G., DiPerna, C.J., Bradley, A.S., Olson, E.J., and Girguis, P.R., 2011, Influence of subsurface biosphere on geochemical fluxes from diffuse hydrothermal fluids: *Nature Geosci*, 4, 461-468.

West J M, Pearce J M, Bentham M and Maul P R (2005). Issue Profile: Environmental Issues and the Geological Storage of CO_2. Eur. Environ. 15, 250–259.

West J M, Pearce J M, Coombs P, Ford J R, Scheib C, Colls J J, Smith K L and Steven M D (2009). The Impact of Controlled Injection of CO_2 on the Soil Ecosystem and Chemistry of an English Lowland Pasture. Energy Procedia volume 1 issue 1 2009, 1863-1870.

Wicks LC, Roberts JM (2011) Benthic invertebrates in a high-CO_2 world. *Oceanography and Marine Biology Annual Review*.

Widdicombe S, Lowe DM, Pope ND, Langston W, McEvoy A (submitted) The impact of CO_2 acidified seawater on the uptake and impact of heavy metals in 3 species of marine invertebrates. *Marine Pollution Bulletin*

Widdicombe S, Spicer JI, Kitidis V (2011) Effects of ocean acidification on sediment fauna. In: Gattuso J-P & Hansson L (Eds.), *Ocean Acidification*, Oxford University Press. pp. 176-191.

Widdicombe S, Dashfield SL, McNeill CL, Needham HR, Beesley A, McEvoy A, Øxnevad S, Clarke KR, Berge J (2009) Effects of CO_2 induced seawater acidification on infaunal diversity and sediment nutrient fluxes. *Marine Ecology Progress Series* 379: 59-75.

Receptor Class	Potential Impact Mechanisms
Plants associated with agricultural ecosystems Crops and grasses **Plants associated with natural systems** Plants associated with forest, moorland, heath, wetland, and alpine ecosystems	Stress / death as a result of the effects of CO_2 concentrations on roots. Stress / death as a result of CO_2 ponding and impacts on the canopy. Stress / death as a result of degradation of soil quality (acidification, toxicity etc).
Animals that inhabit agricultural or natural ecosystems Invertebrates (e.g. insects) Vertebrates (including mammals, amphibians, birds) Microbiota	Death (of animals unable to move away from a localised surface ponding event). Potential for chronic low-concentration exposure effects e.g. on skeletal structure or other effects (some burrowing animals may have reduced sensitivity). Impacts due to a reduction in feed quality and availability. Habitat damage / loss (see impacts on plant receptor classes).
Terrestrial freshwater bodies / resources (lakes, rivers, springs) Surface water resources as receptors in their own right Aquatic plants e.g. algae Vertebrates (e.g. fish) Invertebrates (e.g. mosquito larvae)	Surface water body acidification / toxicity. Stress / death on aquatic plants as a result of CO_2 concentrations. Impacts on animals due to a reduction in feed quality and availability. Habitat damage / loss (see impacts on plant receptor classes above). It is necessary to distinguish between stratified and more homogeneous lakes.
Aquifers that may be exploited as drinking or irrigation water resources Aquifer water resources as receptors in their own right Microbes that might inhabit the aquifer	Degradation of water quality as a result of biogeochemical processes leading to acidification / toxicity etc. (it is not possible to be more specific without site-specific geochemical information). Microbial populations could be regarded as receptors in their own right, in addition to contributing to biogeochemical processes.
Humans Non-operators who might be exposed to impacts as a result of CO_2 leak/migration to and through the environment	Death as a result of sudden releases to and accumulation within basements/subsurface features. Impact on urban environment (gardens, other structures and resources). It is extremely unlikely that a storage system would be built sufficiently close to a large urban population, that releases could then occur to a basement, and that the release would be acute enough to lead to death. Similarly it is unlikely that any leak would happen to interact with basements associated with a less laterally extensive settlement. Related scenarios must therefore be, by definition, high impact (in that death could occur) but very low likelihood.

Table 1: Receptor Classes for European Terrestrial Systems.

Service type	Specific ecosystem services
Provisioning	Food; fibre; timber and fuel; genetic resources; biochemicals, natural medicines and pharmaceuticals; ornamental resources and freshwater
Regulating services	Air quality maintenance; climate regulation, water regulation, erosion control, water purification and waste treatment; regulation of human diseases; storm protection
Cultural services	Cultural diversity; spiritual and religious values; knowledge systems; educational values; inspiration; aesthetic values; social relations; sense of place; cultural heritage values; recreation and tourism
Supporting services	Production of oxygen, primary production, nutrient cycling, water cycling; provision of habitat

Table 2. The Millennium ecosystem Assessment's typology of ecosystem services

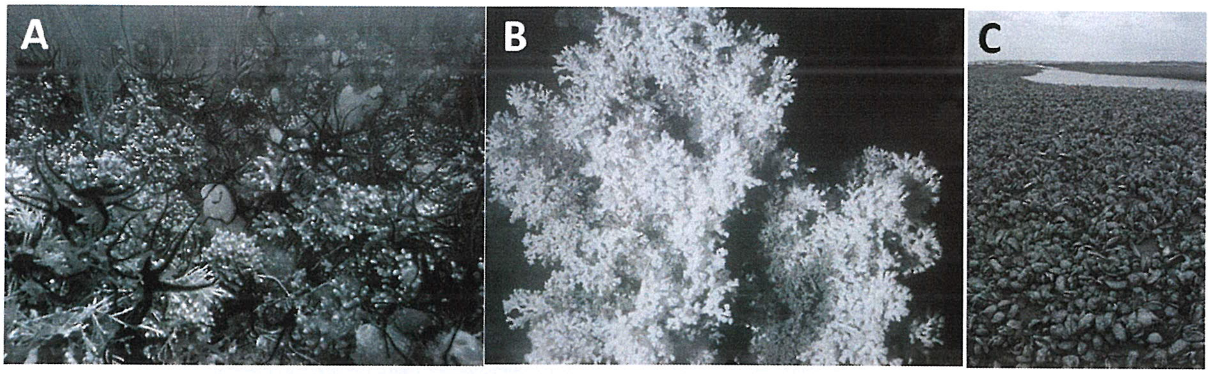

Figure 1: Examples of biogenic habitats that are created by calcifying organisms; a) Mearl[1], b) cold water coral *Lophelia*[2], c) mussels[3]. (picture credits: [1]N Kamenos, [2]JM Roberts, [3]R Ellis)

Database: Generic CO2 FEP Database, Version 1.1.0

167/179 Full list / Impacts / Impacts on the physical environment / Modified surface topography

Edit This Record
Create a link to this FEP
Suggest FEP improvement

FEP

Name

7.2.8.1 Sinkhole formation

Description

Addition of CO2 in a limestone or carbonate-rich aquifer could result in dissolution of the rock matrix and the enlargement of voids. If this process takes place at relatively shallow depth collapse may result in subsidence at the surface and sinkhole formation.

For example, CO2 leakage around a borehole drilled to extract natural CO2 from a reservoir in Florina, Greece, resulted in subsidence around the borehole that filled up with water (see image below).

Florina sinkhole produced as a result of CO2 leakage, image reproduced with permission from George Hatziyannis, Institute of Geology and Mineral Exploration (IGME), Greece

Relevance to performance and safety

Large scale collapse structures may cause significant change to surface topography and possible CO2 migration paths. Sinkholes can provide locations where leaking CO2 can accumulate.

References

There are no references.

Links

There are no links.

167/179 NO FEP influences are stored for this database (Generic CO2 FEP Database, Version 1.1.0)

This record last modified: 2004-03-04.

Quintessa

Figure 2 Example of an 'impacts' category FEP

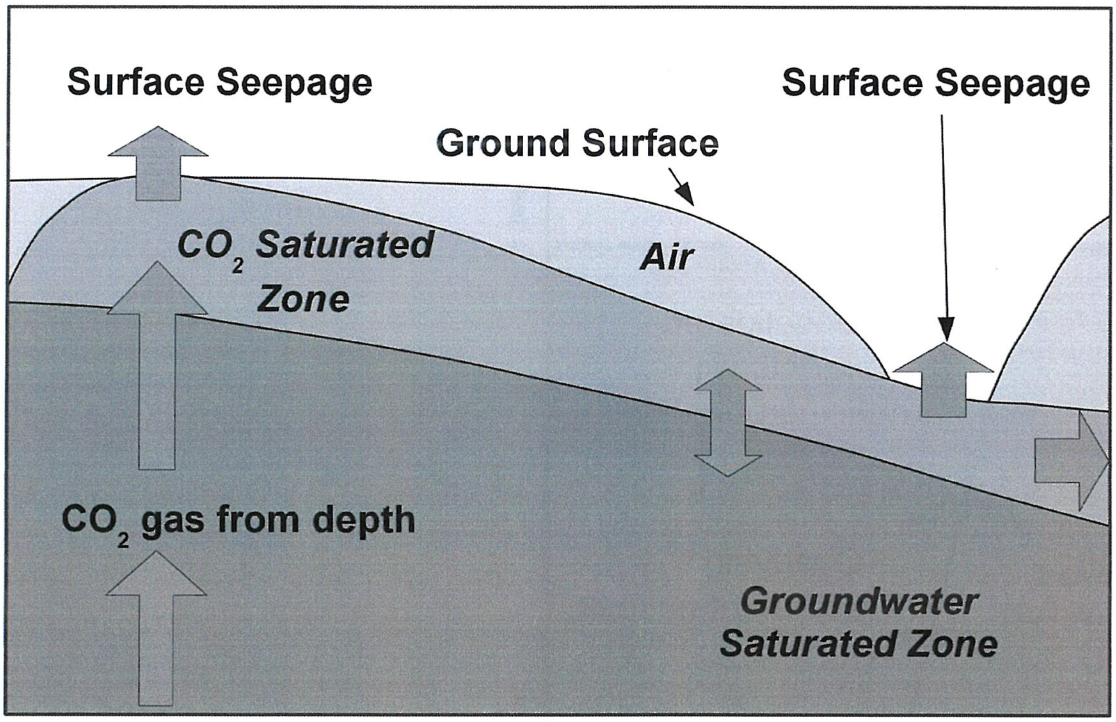

Figure 3. CO_2 Transport in the Near-Surface Environment

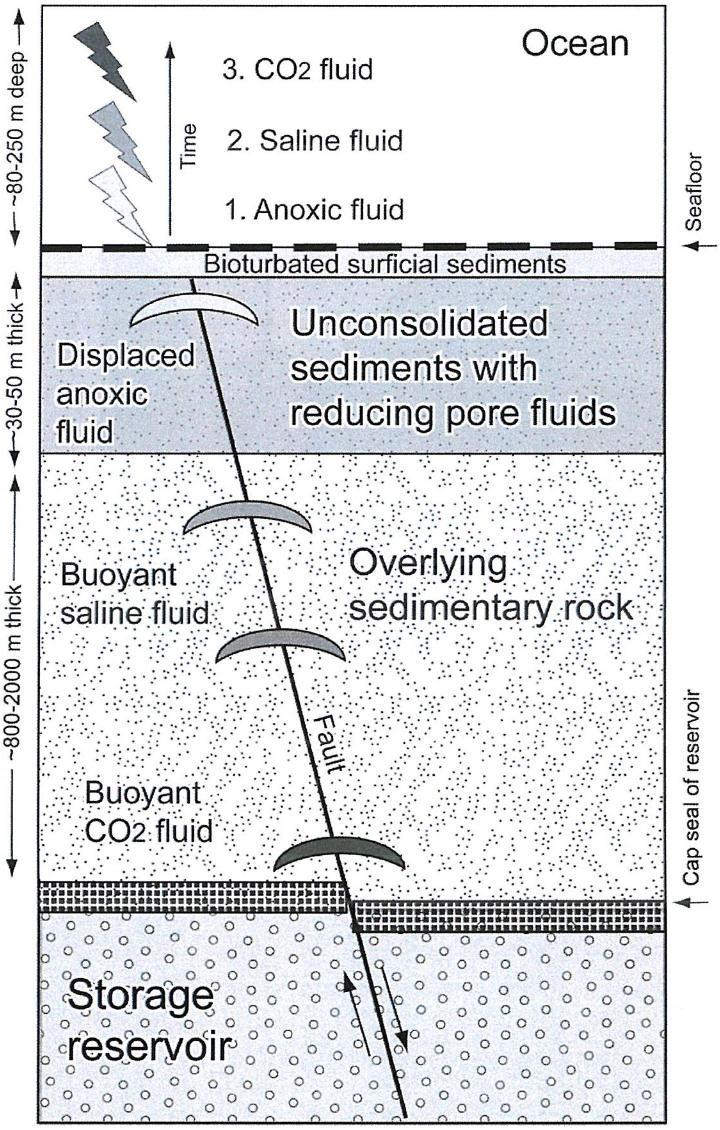

Figure 4. Schematic diagram of potential CO_2 leakage from an offshore sub-seafloor reservoir along a fault with buoyant CO_2 plume (dark-tinted crescent) driving buoyant expulsion of formation brines (medium-tinted crescent) that in turn drives the expulsion of reducing pore fluids (pale-tinted crescent) at the seafloor. The base of the reservoir capping seal, and seafloor are the two most important boundaries at which to undertake monitoring.

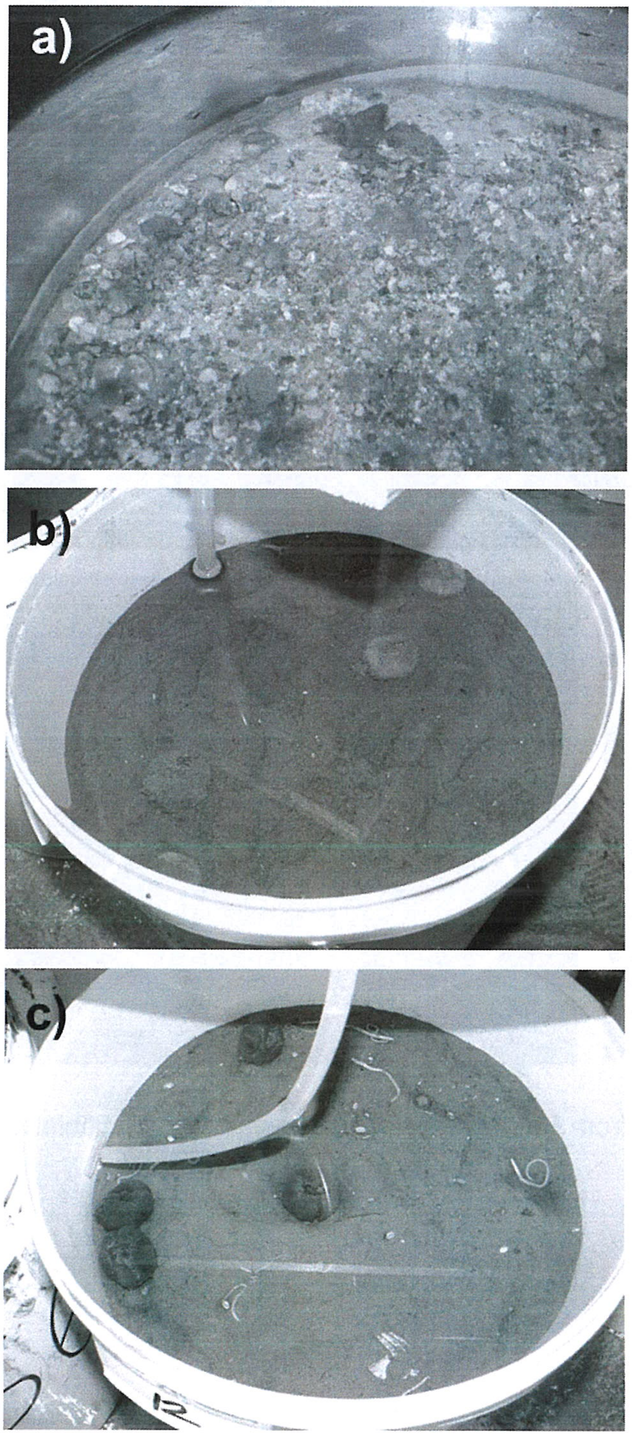

Figure 5: Visual biological responses to elevated levels of CO2: a) A pink cyanobacteria bloom which appeared on the sediment surface after exposure to CO2 acidified seawater (pH7.5) for 2 weeks. b) The appearance of burrowing heart urchins (*Echinocardium cordatum*) at the sediment surface after exposure to CO2 acidified seawater (pH6.5) for 2 weeks. c) Observed mortality of infaunal animals (including *E. cordatum*) after exposure to CO2 acidified seawater (pH5.6) for 2 weeks

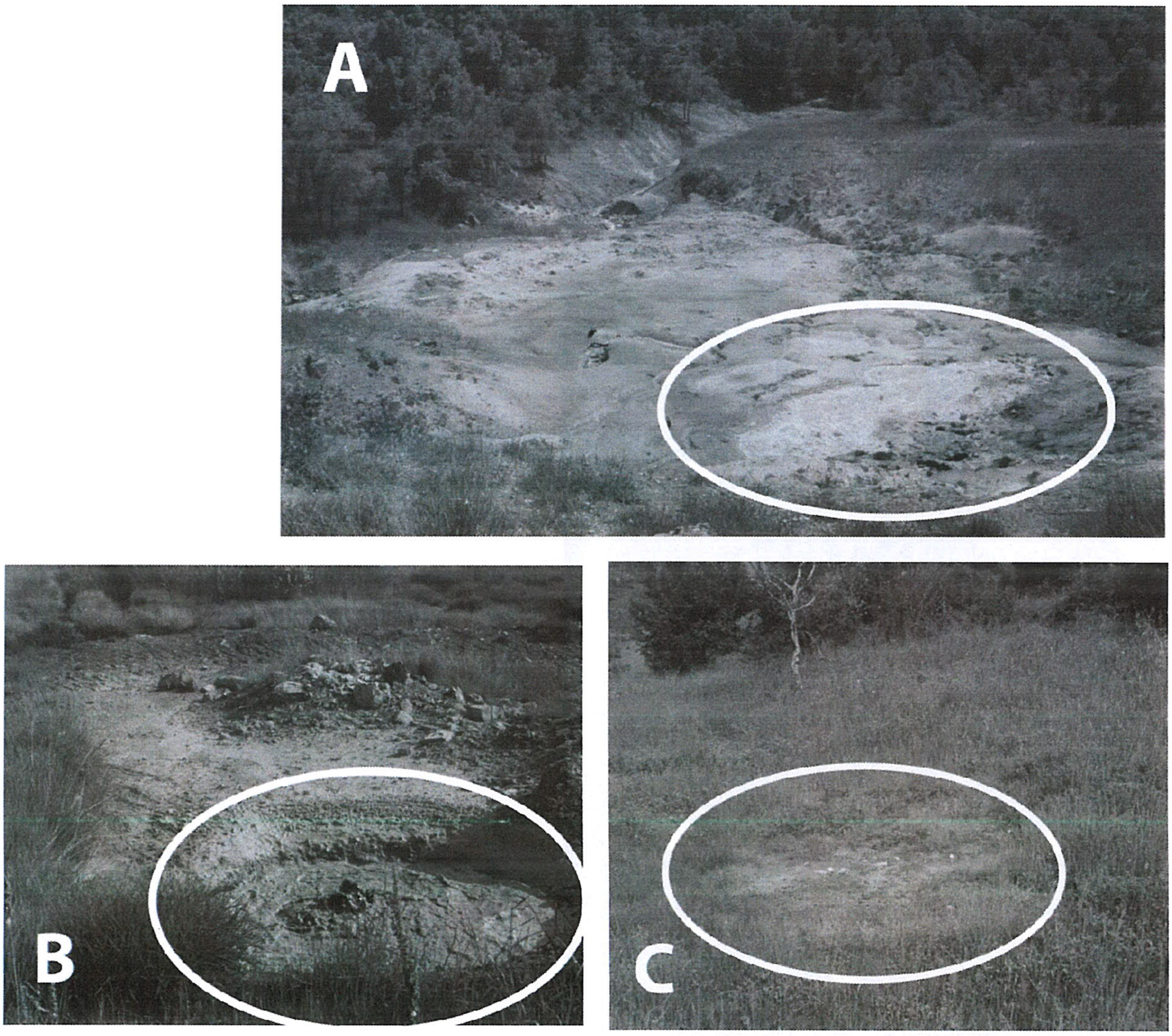

Figure 6. Photos of Italian CO_2 seeps inland from Naples a) Mefite D'Ansanto, b) Mefitiniella Polla and c) a diffuse seep at Casale.

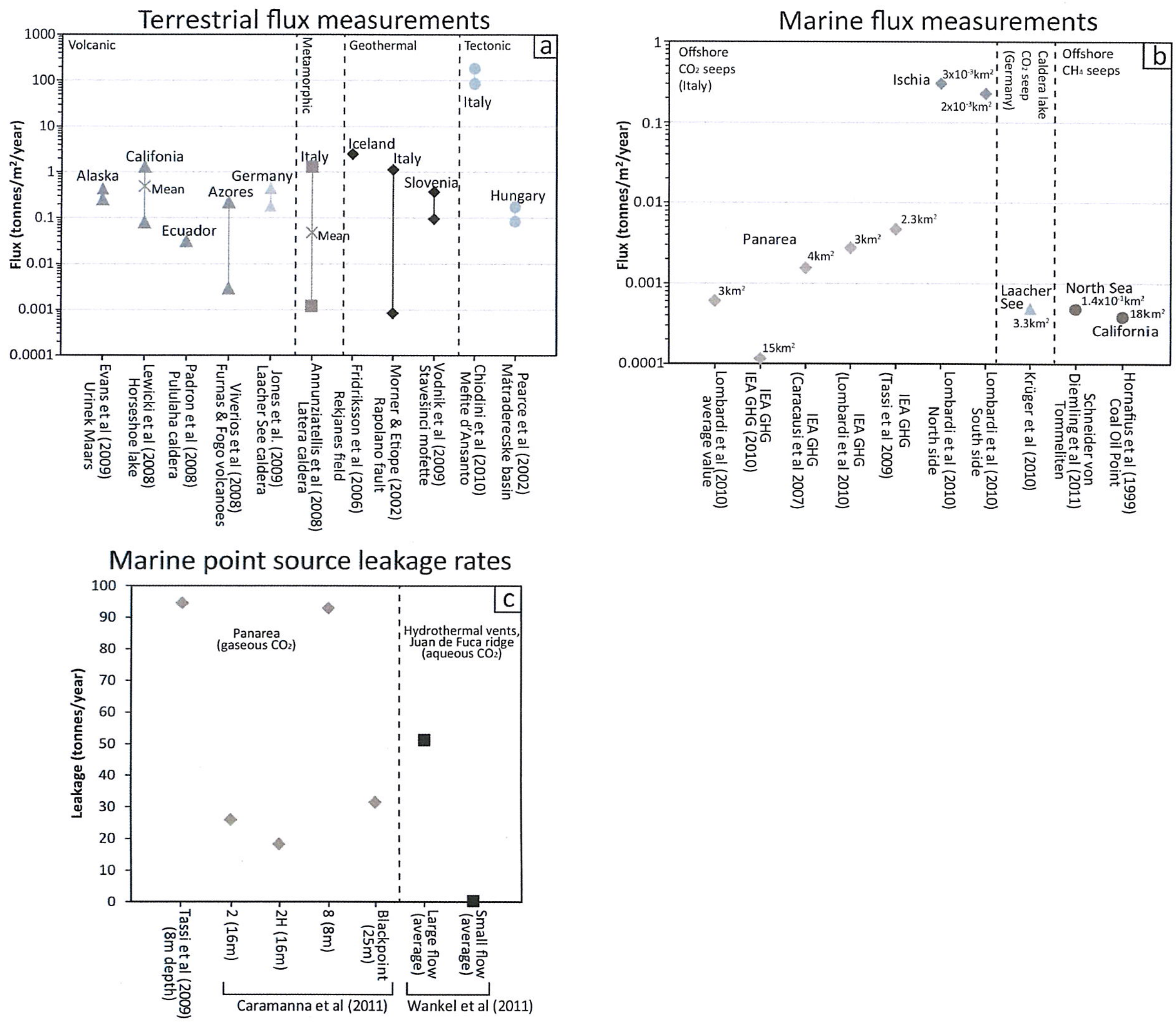

Figure 7. Published leakage rates from (a) onshore seeps (b) offshore seeps and (c) point source measurements of individual seeps at Panarea. Where the seep is smaller than the measuring equipment a leakage rate can be measured; where the seeps is spatially extensive, a flux rate must be determined and a representative area estimated in order to estimate the leakage rate. In (a) flux values are grouped by the source of the the CO_2 described by the authors of the respected publication. In (c) the value from Tassi et al (2009) is for the same seep as vent 8 from Caramanna et al (2011).