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Review of current available knowledge and thinking regarding realistic rates of loss of CO_2 from sub-sea geological formations

Report IRIS - 2012/037

Project number:	7911894
Project title:	Can seepage of CO_2 stored in sub-sea geological formations disrupt important behavioural traits of benthic invertebrates?
Client(s):	Norges Forskningråd CLIMIT
Research program:	
ISBN:	978-82-490-0767-7
Distribution restriction:	Open

Bergen, 15.03.2012

16/03/2012

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Preface

This is the report for the WP 1 Review of current available knowledge and thinking regarding realistic rates of loss of CO_2 from sub-sea geological formations, from the project "Can seepage of CO_2 stored in sub-sea geological formations disrupt important behavioural traits of benthic invertebrates?"

Stavanger, 19. March 2012

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Contents

Summary

This report presents a review of current available knowledge and thinking regarding realistic rates of loss of carbon dioxide from sub-sea geological formations.

Leakage rates obtained from natural environments are the most common source of data to be used as analogues to industrial CO_2 sequestration. Most data are available from the terrestrial environment, however, actual rates and total amounts of released carbon dioxide are often uncertain. The same is the case for the marine environment but a recent discovery of a carbon dioxide seep at Salt Dome Juist in the southern North Sea has revealed interesting data from observations and modelling. The highest leakage rate scenario can probably be expected from pipelines or well head failures.

Physical processes causing vertical and horizontal mixing at a leakage site will be controlling factors determining the impact carbon dioxide inputs will have on pH and the marine biological life.

A regional scale model suggest that leakage of CO_2 input be less than 1 pH unit for a worst case scenario with leakage from a ruptured pipeline. Observation of reduction of 1.5 units at Salt Dome Juist offshore the Frisian Islands documents that locally more extreme values are possible even if these are only short-term leakage events. Simulation and modelling based on actual leakage rates found in the literature will be key in estimating realistic ranges of pH variation in the marine environment.

1 Introduction

The aim of work package 1 is to give an overview based on scientific literature of realistic leakage rates in the unlikely event that large amounts of CO_2 leak from a man-made CO_2-storage system and into the marine bottom-water environment.

The hypothesis tested by the project is that low pH conditions resulting from a potential leakage of CO_2 from sub-sea storage have a detrimental impact on important behavioral processes in key marine benthic organisms that could affect their individual fitness, result in their migration away from the area and/or disrupt chemical sensory reception in crustaceans. The first of two exposure system designs to be employed will use a continuous flow system with seawater bubbled through with varying levels of CO_2 gas and delivered to a header tank before being pumped into the exposure arenas containing the test animals and their associated monitoring equipment. The aim of this approach will be to generate stable pH conditions that can be readily adjusted to provide stepwise changes in seawater pH.

It is only reasonable to expect there exists a pH so low that benthic animals one way or another will change their behavior according to the above hypothesis, however, it is not clear whether leakage from a sub-sea CO_2-storage can lead to such a change in bottom-water pH.

In the experiments to be conducted pH will be adjusted by CO_2 gas bubbled through water before it enters exposure arenas containing the test animals. This means that leakage rates in the natural environment may be difficult to compare directly with the rates in the laboratory experiments. Many factors can moderate the impact of leakage rates, among others, mixing and exchange of bottom-waters, local topography, CO_2 from a single point source or a diffuse source etc. This report will therefore include a section outlining likely leakage scenarios and processes that are of importance.

The remainder of the report is structured as follows.

- Section 2 provides an overview of CO_2 leakage scenarios and processes of importance to evaluate realistic pH ranges (caused by CO_2 leakage system)
- Section 3 presents examples of CO_2 leakage in the geological environment from the literature
- Section 4 discusses realistic pH ranges expected to be found from modelling of natural environments
- Section 5 lists conclusions and recommendations

2 Leakage scenarios

2.1 Mechanisms and patterns of CO_2 leakage

2.1.1 Localised or diffuse sources

The most plausible mechanisms of leakage from man-made CO_2 storage systems to the ocean bottom are likely to occur through point-source or localised releases, e.g. through a well or through a fault or fracture system that exists in CO_2-bearing geological stratum. Lewicki et al. (2007) compiled a list of 8 industrial leaking storage sites for CH_4 and CO_2 finding that all were caused related to a point-source.

An alternative scenario is leakage occurring from a diffuse source over a large area. In this case CO_2 dissolves in the porewater at depth and spreads laterally within the sediments before its release at the seafloor. Leakage rates are probably not as high as for the localised sources, but the total amounts of leaked CO_2 may be significant and possible impacts on sediments and bottom water environment cannot be disregarded.

In the event that CO_2 leaks from deep storage formations to the surface it will most likely follow a pathway that is related to a channelized system of unsealed fault and fracture zones (Dockrill and Shipton, 2010; Holloway et al., 2007; Lewicki et al., 2007; Shipton et al., 2005). Gas chimneys observed on seismic and associated pockmarks on the seafloor represent another possible pathway for CO_2 gas (Cathles et al., 2010; Judd and Hovland, 2007; Schroot and Schüttenhelm, 2003). The presence of pockmarks is however normally associated with leaking CH_4 and not CO_2. This all points in the direction that a leakage at the surface is likely to be confined within a limited area defined by the extent and orientation of the underlying pathway system (Lewicki et al., 2007, and references therein).

2.1.2 Free CO_2 or CO_2-charged waters

The form in which CO_2 reaches the bottom-water environment can be either as free gaseous CO_2 (bubbles) or as CO_2-charged pore water. The free CO_2 readily dissolves in water with the effect of lowering the pH and increasing the water density (Leifer et al., 2006; McGinnis et al., 2011). If a sufficient amount of CO_2 enters the sea-floor in a gaseous state, the induced buoyancy can initially create an upwelling plume of water and gas. The result may be a loss of CO_2 to the atmosphere if the plume reaches the sea-air interface before the CO_2 has dissolved in water but with the dissolution of CO_2 water density increases and the CO_2-enriched water may eventually sink to sea-floor forming a more or less stable bottom water layer with lower pH.

Leakage of CO_2-charged fluids will also form a carpet-like layer at the seafloor but this could be more stable as there may be less turbulence compared with the plume situation described above.

2.1.3 Other moderating factors

When CO_2 flows into the bottom water environment, either as a diffuse seepage through the porous sediments or from any point source, the impact it will have will be moderated by physical processes such as tidal currents, wind induced basin currents, river inflow, annual variation in mixing and stratification of the water column etc. Depressions in seafloor topography can be a focus for denser CO_2-charged waters.

3 Results

This section presents examples from the literature of known CO_2 leakages. Most of the presented data are from the terrestrial environment but estimates of leakage rates can be of relevance for a marine environment. Examples from the marine environment are scarcer. One recent discovery of a natural CO_2 seep at Salt Dome Juist will be addressed more extensively as it contains measurements of pH reductions caused by CO_2 release (Linke and AL374-Cruise-participants, 2011; McGinnis et al., 2011). The third subsection describes the results of regional scale simulations of CO_2 leakage at two sites in the North Sea area (Blackford et al., 2008).

3.1 Known terrestrial CO_2 leakages

An overview of known leakages of CO_2 (and CH_4) from storage sites was compiled by Lewicki et al. (2007). Results are presented below in Tables 1 through 3. The reference numbers (A# or B#) in this section refer to items in the tables. The storage sites have been divided into natural accumulations and industrial storage sites. Some of the industrial storages are natural accumulations of CO_2 (and CH_4), but they were considered as industrial in the sense that holes had been drilled for the purpose of water, oil, or gas exploration, such as the Paradox Basin, USA (B2); production of CO_2 for EOR projects in the Sheep Mountain field (B1), USA (Stevens et al., 2001); or the production of geothermal energy from the Italian Torre Alfina (B4) and Travale (B5) fields.

Tables 1 and 2 summarise the Features, Events and Processes (FEPs) of natural and industrial leakage, respectively. Table 3 contains additional aspects of CO_2 and CH_4 leakage, most interestingly leakage rates or magnitude of CO_2 released. For references to the data source of this compilation please cf. Lewicki et al (2007) and the supplemental material contained in the appendixes of the paper (available as separate download from the publisher www.springerlink.com/content/05636256580q4613/)

In most of the cases displayed in Tables 1 and 2, CO_2 originates from degassing of cooling magma as the magma rises in the crust and releases its CO_2 as a result of decreasing pressure. Other notable sources are metamorphism of carbonate rocks from contact with hot magmas or within subduction zones, thermal alteration of organic-rich shales and coal-beds, biodegradation of oil and gas, and dissolution of carbonates. Most of these sources are of a regional scale and by far larger than any likely man-made CO_2 sequestration site. Lewicki et al. (2007) assigns 7 out of 13 examples of natural leakage to be from a diffuse source, however for most of the 13 cases the leakage pathway is along faults and fractures. In 2 cases the pathway is not explained by the authors as leakage is generated by lake turnover (Aeschbach-Hertig et al., 1996; Freeth and Kay,

1987) the CO_2 source is ultimately an underlying magma body and could therefore likely be related to a fault and fracture system as well.

Lewicki et al. (2007) found that most of the industrial cases were caused by well blowouts resulting in a free-flowing CO_2 gas leakage, sometimes associated with geysering where CO_2-charged waters release CO_2 to the atmosphere when reaching the surface. In 2 cases the leakage of natural gas (methane) took place at depth due to a cracked well casing or failure in cement sealing between the well and formation. The gas migrated along the well or in fracture systems towards the surface where it spread out in groundwater aquifers and erupted as natural gas geysers (Watney et al., 2003, *in* Lewicki et al., 2003 online supplement).

Though the compilation is not complete, and several of the examples mentioned do not report a leakage rate, the authors claim it to be representative for the known variation of natural and industrial CO_2 (and CH_4) leakage examples (Lewicki et al., 2007). In relation to the Latera caldera case (A5) a more recent published estimate of 220 kg CO_2/day from a single vent was found (Beaubien et al., 2008). From Table 3 magnitudes of surface CO_2 or CH_4 released are reported as 1 500 tonnesday at Solfatara over a 0.5 km^2, 74 tonnesday at Albani Hills over 0.06 km^2 and 506 tonnesday dissolved in shallow ground water, and 33tonnesday at Crystal Geyser in Paradox Basin. The 25 000 tonnes CO_2 released from the Torre Alfina geothermal field happened over an unreported period.

The EOR sequestration site at Rangely (Colorado, USA) is estimated to leak at a rate less than 3800 tonnes CO_2 per year over an area of 78 km^2, which is equivalent of 0.14-3.0 $mmol/m^2/d$ (Klusman, 2003a, b). Since the beginning of 1986 the Rangely field has accepted $23x10^6$ tonnes CO_2.

3.2 Marine CO_2 leakages

In the following examples marine CO_2 leakage will be described with most of them occurring from natural accumulations. Judd and Hovland (2007) compiled a list of seabed fluid flow from around the world. Most of these are dominated by methane leakages with a few references to CO_2 dominated cases, all of which being natural accumulations and seeps. One such example is the large volumes of gas emitted from hydrothermal vents in the Hellenic Islands where gas bubbles are observed to depth of 110 m. From a 34 km^2 area around the island of Milos an estimated $1.7x10^{10}$ to $8.5x10^{10}$ moles per year or 2050 to 10250 tonnes CO_2 per year are emitted (Dando et al., 1995a). It was also found that the release of gas and nutrients from the hydrothermal vents increased after seismic events (Dando et al., 1995b).

Within the project “ECO2 - Sub-seabed CO2 Storage: Impact on Marine Ecosystems” marine sites have been selected as natural analogues for CO_2 leakage (http://www.eco2-project.eu/home.html):

- The Mediterranean Panarea gas seeps located in shallow waters off Panarea Island in Italy with a reported emission of ca. 52.7 tonnes CO_2 per day (Steinbrückner, 2009),

- the Jan Mayen gas vents located at ~700 m water depth in the North Atlantic, and
- the CO_2 droplet seeps in the Okinawa Trough at ~2000 m water depth.

There are no reported amounts or rates of leaked CO_2 for the Jan Mayen and Okinawa Trough.

Estimates of carbon dioxide emissions from the nearby Vulcano are ca. 180 tonnesday (Baubron et al., 1990) and 2 900 to 5 800 tonnesday from Stromboli (Allard et al., 1994). The latter two also include emissions directly to the atmosphere on land.

Salt Dome Juist

McGinnis et al (2011) recently discovered a natural carbon dioxide seep in the southern North Sea, ca. 30 km north of the East-Frisian Island Juist. From water samples collected in the area, the authors recorded CO_2 levels ca. 10-20 times above normal and in one sample (CTD 13) the level was 53 times higher with a corresponding pH of 6.8. This is well below a normal seawater pH of 8.2-8.4 and also outside the range of CO_2-induced annual variation in pH of 7.8-8.4 for the North Sea at Salt Dome Juist (Blackford and Gilbert, 2007). According to measured data and box modelling Blackford and Gilbert (2007) attributed riverine inflow, respiration and benthic pelagic processes to be the cause of this natural pH variation.

An external source of CO_2 is needed to explain the observed CO_2-induced low pH of 6.8. The source and type of CO_2 as it reaches the seafloor offshore Juist are unknown. The use of an acoustic Doppler current profiler (ADCP) over the CTD 13 site showed persistent high signals indicative of gas bubbles or suspended/entrained sediments in the first ca. 2-4 metres over the sea-bottom located at 25m water depth. Results from a bubble model for pure CO_2 and pure CH_4 introduced at the same water depth showed that CO_2 bubbles mostly dissolved within the same range of 2-4 metres from the bottom, while CH_4 bubbles did not change in size due the low solubility of methane in water. If CO_2 seeps at the seafloor as bubbles of gas it will impact the buoyancy of the bottom-water, and if bubbles are sufficient a plume of upwelling water will be created. By modelling such a plume using the highest measured value of CO_2 of ca. 300 µmol/l at CTD 13 and taking it to be the resulting concentration of the plume this would correspond to a CO_2 input of 1 mol/s (ca. 4 tonnesday) and a final plume diameter of 14 m with an area of $150 m^2$ (McGinnis et al., 2011). This will be a conservative estimate of the input rate as the water sample probably already experienced dilution at sampling time.

For CO_2 to form bubbles at site CTD 13 the concentration in the fluid should be about 100 mmol/l (temperature=20°C, salinity=35‰, depth=20m). This would imply a pH of 4.3 for the fluid and this value is much lower than any recorded value for high respiratory shelf sediments (Zhu et al., 2006 *in* McGinnis et al., 2011).

The CO_2 was analysed for its stable carbon isotope ratios and results (δ13C=–24‰ vs. PDB) indicate a possible biogenic origin from breakdown of organic matter (terrestrial C3-plants) or methane oxidation. The subsurface is characterised by salt dome and pillow structures, tectonic faulting and gas chimneys (Lokhorst, 1997; Schroot and

Schüttenhelm, 2003). These structures are a likely pathway for CO_2 to the seafloor and support the idea that the enriched CO_2 levels are related to a point-source (McGinnis et al., 2011).

Though McGinnis et al. (2011) reported that they were unable to locate the CO_2 seep on a return cruise in August 2009, Linke and AL374-Cruise-participants (2011) found it during a cruise with RV ALCOR in May and June 2011.

3.3 Modelling example of pH changes from CO_2 leakage

Modelling of different leakage scenarios in the marine environment can be a viable means to estimate impacts on pH when no hard data is available. Blackford et al. (2008) used a marine system model for North West European shelf seas to simulate impact from CO_2 on pH for three different leakage scenarios. The model uses a horizontal gridding of 7x7km and a vertical gridding of 16 layers of variable thickness depending on water column thickness. The scenarios used are

1) Long-term (365 days) diffuse seepage. Analogous to constant seepage of CO_2 spread homogeneously across the area 7x7km area of the model box representing a movement of CO_2 through permeable seafloor sediments. Simulations were carried out for two levels of CO_2 input, low level of 3.85mmol/m^2/d similar to the upper end of the Rangely fields (Klusman, 2003a, b), and a 100 times increased treatment of 385mmol/m^2/d to indicate the worst case scenario. This gives a total input of 3.02×10^3 tonnes and 3.02×10^5 tonnes CO_2 respectively.
2) Short-term (1 day) point source leakage. Analogous to a fracture in a pipeline persisting for a single day. Model using two inputs, 6.93×10^3 and 6.93×10^4 mmol/m^2/d giving total inputs of 1.49×10^4 tonnes and 1.49×10^5 tonnes CO_2, respectively, about 5 and 50 times a typical pipeline capacity.
3) Long-term (365 days) point source leakage. Analogous to an immitigable fault in the well casing, we assume a catastrophic out-gassing of 6.93×10^3 mmol/m^2/ or 5.43×10^6 tonnes CO_2 over one year, five times the input rate at Sleipner, or 5 years' worth of sequestered CO_2.

The above scenarios were tested and compared in two sites, one located in the southern North Sea (54°N 1°E) at a water depth of 28.5m and well-mixed water column throughout the year, and the second one in the northern North Sea (57.75°N 1°E) at 138m water depth and a strong summer stratification.

The result of simulation for the first scenario showed a maximum reduction in pH of 0.12 for the highest seepage rate and an insignificant change for the lower. This variation is lower than natural range of variability for pH at the two sites.

The result of the short-term leak showed a pH reduction of 0.1 for the north site and 0.2 for the shallower and well mixed water column to the south. Effects tail off within a 3-9 day period. For the high leakage rate (i.e. 50 times higher than pipeline capacity) a reduction of pH by more than 0.5 units for 1 day was observed for the north site and up to 1 unit for the south site. The duration of disturbance in pH lasted for 10 and 20 days respectively.

Results of the long-term leakage showed a pH reduction of less than 0.5 units for north site, and was maximum during summer water column stratification. Simulations in the south site showed a reduction of 1 pH unit. For both sites only a small area with the strongest perturbations are seen centred over the leakage site. Hydrodynamic processes including strong tidal currents are the primary driver for CO_2 dispersion.

3.4 Leakage rates from transport system

Koornneef et al. (2010) estimated release rates from failing pipelines to range between 0.001 and 22 tonnessecond depending on the rupture diameter and size. Other studies report rates of 8.5 tonnessecond and 15 tonness (Kruse et al., 1996, & Turner et al, 2006, in Koornneef et al., 2012). Well head failure was reported to be ca. 500 tonnes per second (Koornneef et al., 2012). These figures are by far the highest leakage rates found and are generally several orders of magnitude higher than what has been reported from natural and industrial CO_2 storage sites.

4 Discussion

As pointed out by Blackford et al. (2008), and by the Norwegian Research Council when requesting this literature study, it is important that any conclusion drawn from the experiments of the current project is given with reference to what can be expected in the event of a CO_2 leakage. As mentioned in the introduction chapter, leakage rates *per se* may not be comparable to what is actually reported from laboratory experiments.

Reported data from terrestrial sites in section 3.1 show large variability and some of them are of limited relevance in the context of a carbon sequestration site, e.g. the Lake Nyos event where 240 000 tonnes of CO_2 were released due to lake turnover. The accumulation of CO_2 in hypolimnion of a permanently stratified lake basin is probably only comparable to silled basins of fjords or possibly some parts of the Baltic Sea.

In the rest of the terrestrial cases the magnitude of CO_2 released at the surface are reported to be in the range of a few tonnes per day up to 1500 tonnes per day.

The magnitude of hydrothermal vent emissions is difficult to interpret in relation to a leakage situation from a man-made CO_2 sequestration site. This is in part due to the special geological setting around volcanoes with high temperatures and pressures close to the surface (Allard et al., 1994; Beaubien et al., 2008; Dando et al., 1995a; Dando et al., 1995b; Gerlach, 1991; Steinbrückner, 2009). Such events are also located in areas of high seismic activity and therefore not an ideal location for storage of CO_2. It doesn’t mean that the sites can be of no interest as analogues if one uses observed data for simulating pH response to CO_2 input, hydrodynamics, etc.

According to the recently published CO2 storage atlas for the Norwegian North Sea (NPD, 2011) there is a large potential for CO_2 storage in subsea reservoirs. This makes the Salt Dome Juist example very interesting as it is reporting reduction of ca. 1.5 pH units. Despite the source and the leakage rates being unknown, it has been documented that the CO_2 input from seepage caused the pH reduction. The reduction can also be considered a conservative estimate as dilution in the water column likely had taken place when sampling occurred. Using the observed concentrations of 300 µmol/l and assuming a plume-generated source McGinnis et al. (2011) estimated a leakage rate of ca. 4 tonnesday and a plume diameter of 14 m.

Seepage at Salt Dome Juist is intermittent and probably associated with methane as has been shown for pockmark seeps in the North Sea (Judd and Hovland, 2007; Linke and AL374-Cruise-participants, 2011). A question in this context is whether methane being less soluble compared to carbon dioxide is required for developing gas chimneys for quick passage from a reservoir to the surface (Cathles et al., 2010).

The modelling done by Blackford et al. (2008) for the North Sea is most relevant for illustration of worst case events in the North Sea on a larger scale. The modelling appears very robust and underlines the importance of hydrodynamics as the most important dispersing factor and thereby moderating impacts of a CO_2 leakage. The model results show that pH perturbations will be limited and in most situations less than 1 pH unit even for the catastrophic out-gassing of 5.43×10^6 tonnes CO_2 over one year, five times the input rate at Sleipner.

One of the issues of the Blackford et al. (2008) model is that the grid blocks are quite large, 7x7 km, implying that any input will be distributed over a 49 km^2 and within a very large volume of water. This can cause severe underestimations of local maxima in a natural environment. Another issue is that for the point source leaks all input CO_2 is dispersed within the grid block instantaneously and not like in realistic situations where this could take several days by tidally driven horizontal mixing (Holt et al., 2001 *in* Blackford et al., 2008). Salt Dome Juist is a possible example of the problems related to modelling on a too large scale. It is therefore recommended that simulations are done on a smaller scale in areas around a leakage site and then fitted to a more regional scale model to capture basin circulation patterns.

The magnitude of potential CO_2 leakage rates estimated from pipeline failures are larger than any other rates found in the examples presented in this report from natural environments. Leakage from a pipeline is however limited by the amount in pipes and the time it takes to close the input valve. It should therefore be compared to the short-term event modelled by Blackford et al. (2008) which used a total of 14 900 tonnes CO_2 over a single day. This is equivalent of 0.173 tonnessecond and two orders of magnitude less than the rate presented by (Koornneef et al., 2012, and references therin; Koornneef et al., 2010). Blackford et al. (2008) report rates as 50 times higher than a "typical capacity of the pipelines used to deliver CO_2 to well systems, whereas Koornneef et al. (2012) use maximum flow rates for the pipeline. If the maximum flow rates are realistic then this of course would result in a stronger modelled impact on CO_2.

From the literature presented in this report it is difficult to set a definite range for pH to be expected from a worst case scenario. What can be said is that modelling will be a key instrument in the years to come to assess impact of CO_2 leakage on pH. In general a higher leakage rate will result in lower pH for given boundary conditions of physical dispersion processes.

5 Conclusions

Regional scale modelling of two sites in the North Sea showed that impacts on pH would be limited to a reduction of 1 pH unit.

CO_2 leakage has been documented to cause local scale reduction of pH in the North Sea of at least 1.5 pH units at Salt Dome Juist. With the estimated low input of ca. 4 tonnes per day it is reasonable to expect that the pH can be reduced by at least 2 pH units or more on a local scale.

Models for simulation of possible leakage events are badly needed to improve general understanding of CO_2 dispersion in a marine environment and how this influences pH. In particularly it is of interest to know more about the range of pH on a smaller scale close to leakage points.

To obtain a better understanding about whether or not CO_2 escaping from sub-sea geological storage sites poses any threat to local marine biological life, it is essential to include relevant biological data generated in laboratory studies within model designs. A major goal of this project is to contribute towards meeting the need for such data.

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Table 1 Summary of FEPs of natural leakage of CO_2. Source: Lewicki et al. (2007).

Site	CO_2 source	Geologic model for accumulation	Event triggering leakage	Pathway for leakage	Type of surface leakage
A1. Mammoth Mountain, CA USA	Magmatic + thermal decomposition of carbonates	Accumulation at ~2 km depth in porous/ fractured rock under caprock	Seismic activity and reservoir pressurization	Faults and fractures	Fast, diffuse, vent, spring
A2. Solfatara, Italy	Magmatic + thermal decomposition of carbonates	Relatively shallow zone of fractured rock contains gas phase and overlies aquifers, then magma body at several km depth	No specific leakage event captured	Faults and fractures	Diffuse and vent
A3. Albani Hills, Italy	Magmatic + thermal decomposition of carbonates	Deep pressurized reservoirs in structural highs of sedimentary bedrock	Slow releases with several sudden large releases also occurring, possibly triggered by seismic activity	Faults and fractures	Diffuse, vent, spring/ well, 1995 and 1999 events fast
A4. Clear Lake, CA, USA	Thermal decomposition of metasedimentary rocks, minor magmatic component	CO_2 derived from liquid-dominated geothermal reservoir hosted in marine metasedimentary rocks	No specific leakage event captured	Faults and fractures	Gas vents, springs
A5. Latera caldera, Italy	Thermal decomposition of carbonates, magmatic component	CO_2 accumulates in liquid-dominated, carbonate geothermal reservoir capped by hydrothermally altered volcanics	No specific leakage event captured	Faults and fractures	Diffuse, vent, spring
A6. Mátraderecske, Hungary	Geothermal/copper-zinc mineralization	CO_2 accumulates in karst water reservoir (~1 km depth)	No specific leakage event captured	Faults and fractures	Diffuse, vent, spring
A7. Dieng, Indonesia	Magmatic	Unknown	Volcanic, possibly ‘‘pneumatic’’, eruptions	Fissure	Eruptive, gas vents, springs
A8. Southern Negros, Philippines	Geothermal	Unknown	Unknown	Faults	Gas vents, springs, diffuse (kaipohans)
A9. Rabaul, Papua New Guinea	Magmatic	Unknown	Unknown	Fractures	Fast, vent
A10. Lakes Monoun and Nyos, Camaroon	Magmatic	Accumulation in deep lake and stable stratification	Rapid lake turnover triggered at Monoun by landslide; Nyos trigger unknown	NA	Eruptive (limnic)
A11. Laacher See, Germany	Magmatic	NA	Seasonal lake overturn and mixing	NA	Diffusive and bubbling from lake surface, diffuse from lake shore
A12. Paradox Basin, UT, USA	Thermal decomposition of carbonates	Reservoirs are vertically stacked, sandstone units, in fault-bounded anticlinal folds, capped by shale/siltstone units	No specific leakage event captured	Faults and fractures	Diffuse, gas seeps, springs
A13. Florina Basin, Greece	Thermal decomposition of carbonates	Reservoirs are vertically stacked, limestone and sandstone units (upper unit at 300 m depth), capped by silts and clays.	No specific leakage event captured	Slow leakage along rock discontinuities	Springs, gas seeps

NA not applicable

Table 2 Summary of FEPs of industrial leakage of CO_2 or CH_4. Source: Lewicki et al. (2007).

Site	CO_2 or CH_4 source	Geologic model for accumulation	Event triggering leakage	Pathway for leakage	Type of surface leakage
B1. Sheep Mountain, CO, USA	Thermal decomposition of carbonates	Reservoir is anticlinal fold, bounded on one side by thrust fault, sandstone, ave. depth 1500 m, capped by marine sediments and a laccolith	Well blowout	Well	Free flowing CO_2 gas from well, CO_2 leakage from fractures above drill site
B2. Paradox Basin, UT, USA	Thermal decomposition of carbonates	Reservoirs are vertically stacked, sandstone units, in fault-bounded anticlinal folds, capped by shale/siltstone units	Well blowouts	Wells	Cold geysers
B3. Florina Basin, Greece	Thermal decomposition of carbonates	Reservoirs are vertically stacked, limestone and sandstone units (upper unit at 300 m depth), capped by silts and clays	Well blowout	Well	CO_2 gas leakage from soils, water-filled pool formation around well
B4. Torre Alfina geothermal field, Italy	Geothermal	Geothermal reservoir with a gas CO_2 cap at ~660 m depth, capped by sequences of shales, marls, and limestones	Well blowout	Well	Free flowing CO_2 gas from well, diffuse emissions from ground around well
B5. Travale geothermal field, Italy	Geothermal	Shallow (<1,000 m) sedimentary reservoirs overlying deep (3,000–4,000 m) metamorphic and intrusive igneous reservoir, capped by low-permeability sedimentary rocks	Well blowout	Well	Free flowing steam and gas from well
B6. Yaggy gas storage facility, KA, USA	Injected natural gas	Gas injected into salt caverns at 150–200 m depth	Cracked well casing	Wells and fractures	Free flowing/geysering gas and water from abandoned wells
B7. Leroy gas storage facility, WY, USA	Injected natural gas	Gas injected into confined sandstone and dolomite aquifer at 1,000 m depth	Corrosion of well casing	Wells	Bubbling gas through surface water bodies near wells
B8. Kingfisher, OK, USA	Natural gas accumulation	Sedimentary reservoir at ~2,900 m capped by shales	Well blowout	Well and fractures	Geysering gas and water through surface water bodies

Table 3 Additional aspects of CO_2 or CH_4 leakage associated with natural (N) and industrial (I) processes Source: Lewicki et al. (2007).

Site	Geographic setting/land use	Magnitude of surface CO_2 or CH_4 leakage	Consequences of release	Monitoring and remedial measures
A1. Mammoth Mountain, CA USA (N)	Recreational area (US national forest, ski resort)	~250 t day^{-1} from 480,000 m^2 area	Formation of tree kill areas, one person with symptoms of asphyxiation, four people killed	Temporal and spatial monitoring of CO_2 concentrations and fluxes in tree kill areas; measurements of groundwater chemistry; public education
A2. Solfatara, Italy (N)	Recreational area (private park/ campground) surrounded by urban area	1,500 t day^{-1} from 0.5 km^2 area	No vegetation in degassing area	Temporal and spatial monitoring of soil CO_2 fluxes, monitoring of heat release; monitoring of fumarole gas chemistry; seismic and deformation monitoring; public education
A3. Albani Hills, Italy (N)	Urban area	74 t day^{-1} as surface gas emissions (61,000 m^2 area) and 506 t day^{-1} as dissolved CO_2 in shallow ground water	High CO_2 concentrations in homes; deaths of livestock (1999 event); past human deaths	Measurements of soil CO_2 fluxes and concentrations; monitoring groundwater chemistry; identification of residential areas at risk, development of zoning bylaws, and development of public education programs
A4. Clear Lake, CA, USA (N)	Rural	~1 t day^{-1}	Four people killed	Measurements of soil and vent CO_2 fluxes and concentrations, mineral pool closed to public
A5. Latera caldera, Italy (N)	Rural, small towns	Unknown	Vegetation stress or kill	Soil gas concentration surveys, hazard mapping
A6. Mátraderecske, Hungary (N)	Rural area, village	Average CO_2 flux ~200–400 g m^{-2} day^{-1} (total degassing area unknown)	High CO_2 concentrations in homes, death of several people	CO_2 detection and control devices installed in homes, demolition of homes with hazardous CO_2 levels, public education
A7. Dieng, Indonesia (N)	Rural	Unknown	~145 people killed, vegetation stress or kill	Vent gas chemical analysis
A8. Southern Negros, Philippines	Rural	Unknown	Vegetation stress or kill, animals killed	Vent and diffuse gas chemical analysis
A9. Rabaul, Papua New Guinea	Rural	Unknown	Three people killed, birds killed	NA
A10. Lakes Monoun and Nyos, Camaroon (N)	Rural, villages	Nyos: 240,000 t CO_2 in eruptive event	Loss of human (~1800 combined) and animal life (e.g., thousands of cattle), vegetation damage	Controlled lake degassing using pipes, monitoring of lake chemistry, public education
A11. Laacher See, Germany (N)	Rural	~14 t day^{-1}	NA	Monitoring CO_2 fluxes and concentrations from lake surface and shore
A12. Paradox Basin, UT, USA (N)	Rural	Soil CO_2 fluxes up to 100 g $m^{-2}day^{-1}$; total emission rate unknown	NA	Measurements of soil CO_2 fluxes; monitoring groundwater chemistry
A13. Florina Basin, Greece (N)	Rural, small towns	Unknown	NA	Measurements of groundwater chemistry
B1. Sheep Mountain, CO, USA (I)	Rural	Unknown	NA	Dynamic injection of drag-reduced brine followed by mud
B2. Paradox Basin, UT, USA (I)	Rural	Crystal Geyser: ~33 t day^{-1}	NA	Measurements of atmospheric CO_2 concentrations
B3. Florina Basin, Greece (I)	Rural, small towns	Unknown	Death of one person	Leakage area closed off to people

Table 3 Continued

Site	Geographic setting/land use	Magnitude of surface CO_2 or CH_4 leakage	Consequences of release	Monitoring and remedial measures
B4. Torre Alfina geothermal field, Italy (I)	Rural	~25,000 t	NA	Cementation of exploration well; borehole installation to focus subsurface gas flow and vent CO_2 at height in atmosphere; atmospheric CO_2 concentration monitoring
B5. Travale geothermal field, Italy (I)	Rural	Unknown	NA	Well allowed to discharge fluid, monitoring of fluid temperature, pressure, and chemistry
B6. Yaggy gas storage facility, KA, USA	Small town	Unknown	Gas explosions, two people killed, buildings damaged	Geophysical monitoring, wells plugged
B7. Leroy gas storage facility, WY, USA	Rural	$\sim 1.8 \times 10^7$ m^3	NA	Tracer tests, decreased injection pressures
B8. Kingfisher, OK, USA	Rural	Unknown	NA	Geophysical, geochemical monitoring. Well plugged.

NA not analysed