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Natural CO₂ sites in Italy show importance of overburden geopressure, fractures and faults for CO₂ storage performance and risk management.

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Abbreviated title: Comparison of CO₂ reservoirs in Italy
Abstract

The study of natural analogues can inform the long-term performance security of engineered CO$_2$ storage. There are natural CO$_2$ reservoirs and CO$_2$ seeps in Italy. Here, we study nine reservoirs and establish which are sealed or are leaking CO$_2$ to surface. Their characteristics are compared to elucidate which conditions control CO$_2$ leakage. All of the case studies would fail current CO$_2$ storage site selection criteria, though only two leak CO$_2$ to surface. The factors found to systematically affect seal performance are overburden geopressure and proximity to modern extensional faults. Amongst our case studies, the sealing reservoirs show elevated overburden geopressure whereas the leaking reservoirs don’t. Since the leaking reservoirs are located within <10 km of modern extensional faults, pressure equilibration within the overburden may be facilitated by enhanced crustal permeability related to faulting. Modelling of the properties that could enable the observed CO$_2$ leakage rates finds high permeability pathways (such as transmissive faults or fractures) become increasingly necessary to sustain leak rates as CO$_2$ density decreases during ascent to surface, regardless of the leakage mechanism into the overburden. This work illustrates the value of characterising the overburden geology during CO$_2$ storage site selection to inform screening criterion, risk assessment and monitoring strategy.

Key words: CO$_2$ storage, geopressure, site selection, natural analogue, CO$_2$ leak, Italy.
Carbon Capture and Storage (CCS) could significantly reduce anthropogenic CO₂ emissions from large industrial sources of CO₂. However to be an effective climate change mitigation strategy the injected CO₂ must remain in the subsurface for timescales of multiple thousands of years (Shaffer, 2010). Leakage of CO₂ out of a reservoir could compromise the long-term emission reductions achieved by a CCS project (Zwaan and Gerlagh, 2009; EU CSS Directive, 2009), and if leaked CO₂ then migrates to the surface or into aquifers there may be local environmental and human health impacts (Jones et al., 2015). Unintended leakage to surface in the early phase of technology roll-out could compromise the public acceptability of future CCS, as well as the economic feasibility due to remediation expenditure and liability pay-out (Zwaan and Gerlagh, 2009, Heptonstall et al., 2012) and, in the EU, possible fines for CO₂ emissions (Dixon et al., 2015). Thus any incidence of leakage from engineered stores may have ramifications for the CCS industry on a global scale.

For these reasons, it is important that the storage site characterisation and selection process maximises the likelihood that injected CO₂ will be securely retained in the subsurface for the timescales intended (thousands of years). Characterisation and selection criteria must be applicable in a range of geologic settings, and without imposing excessive financial costs. In addition to geologic, technical and economic considerations, siting is also constrained by the proximity of the CO₂ source, permitting procedures and public perception. Sites selected for storage do not therefore have to be the most geologically favourable (Hannon Jr and Esposito, 2015) but must comply with selection criteria. To ensure that CO₂ leakage is avoided, these criteria must be guided by a thorough understanding of the geologic characteristics that are most relevant to site integrity. Table 1 summarises the site selection criteria from guidelines published to-date (Miocic et al., 2016), which are intended to maximize the likelihood of long term CO₂ containment. The site selection process must characterize the risks of geological storage, and understanding how CO₂ could move out of a reservoir and potentially through the overburden and to the surface is critical for constraining and managing risk.

Natural CO₂ reservoirs cannot serve as direct analogues to engineered CO₂ storage sites. The latter are specifically selected for characteristics that minimize leakage, and are charged from a point source at rates and for timescales that are unlikely to mimic any natural process. However instances of CO₂ migration to the surface from naturally occurring reservoirs provide an opportunity to assess the conditions required for leakage from the reservoirs and to understand the crustal fluid pathways for migration from depth (Dockrill and Shipton, 2010, Kampman et al., 2010, Wilkinson et al., 2009, Annunziatellis et al., 2008). Similarly, instances where CO₂ has been successfully retained for geologically long time periods offer opportunities to assess the conditions that will enable effective storage and CO₂-water-rock interactions (Allis et al., 2001, Gilfillan et al., 2009). The most important controls on the security of CO₂ retention can be established by comparing the characteristics of reservoirs that leak with reservoirs that seal (Miocic et al., 2016).

Resource exploration drilling in Italy has revealed the presence of CO₂ accumulations at a range of depths below surface (Casero, 2004, Chiodini et al., 2010, Trippetta et al., 2013,
Collettini et al., 2008). Italy is also a region of widespread surface CO$_2$ degassing; over 308 CO$_2$ seeps have been catalogued at 270 locations in mainland Italy and Sicily (Chiodini and Valenza, 2008). Here, we explore the geological conditions that govern whether reservoirs leak or retain CO$_2$ and establish the mechanisms of leakage. To do this, we identify CO$_2$-bearing reservoirs from borehole data and establish which boreholes are located geographically close to CO$_2$ seeps that may represent leakage from that reservoir to surface. We then examine and compare the structure and conditions of the CO$_2$ boreholes to investigate the controls on whether a reservoir leaks or retains CO$_2$. Finally, to inform the potential mechanisms of leakage, we assess the properties of possible pathways through the overburden that could enable CO$_2$ seepage at the rates and styles observed at the Earth surface. Understanding these natural processes over geological timescales is important for informing the long-term performance security of engineered CO$_2$ storage, since engineered storage sites will be selected and managed to minimise the risks of CO$_2$ migration. This work can therefore guide effective site assessment, injection strategy, and remediation strategies in the case of leakage.

A summary of the geology and CO$_2$ fluids in Italy is presented in the next section. For completeness, the section that follows outlines CO$_2$ flow in rocks and the potential mechanisms of migration from a containing reservoir into the overburden (CO$_2$ leakage) and to the Earth surface (CO$_2$ seepage).

**An overview of CO$_2$ geofluids in Italy**

Hydrocarbon exploration drilling in Italy has encountered subsurface CO$_2$ accumulations, either as a component within hydrocarbon reservoirs (Casero, 2005) or as the dominant gas (Collettini and Barchi, 2002, Bicocchi et al., 2013). Such accumulations are mostly found in Central Italy, which is also where CO$_2$ degassing is most intense (Chiodini et al., 2004). In this region, there is a strong regional NW-SE structural trend (Fig 1) resulting from the westward subduction of the Adria plate beneath the European margin. Crustal shortening stacked several tectonic-stratigraphic units originally located on the Apulian Paleozoic crystalline carbonate basement, with flysch and synorogenic foredeep sediments (Scrocca, 2005; Figure 1A). To the west, coeval extension opened marine and continental basins and the Tyrrhenian Sea (Ghisetti and Vezzani, 2002), leading to high heat flow and volcanism. Seismogenic normal faulting is currently active in the Apennines where exposed fault scarps date from 12-18 Ka (Roberts, 2008). Here, CO$_2$ fluids trapped at depths > 5 km play a critical role in the nucleation and evolution of seismogenesis, and therefore in the deformation style and geodynamics of the region (Miller et al., 2004, Malagnini et al., 2012).

CO$_2$ degassing is most active towards the Tyrrhenian, west of the region of active extension (Chiodini et al., 2004). CO$_2$ seeps are mostly low temperature emissions that are manifested as vents (pressurised CO$_2$ release, some are referred to as CO$_2$-driven mud volcanoes e.g. (Bonini, 2009b), diffuse soil degassing, springs, and pools of bubbling water (Chiodini et al., 2008, Minissale, 2004, Roberts et al., 2011). Geochemical studies find the CO$_2$ has a number
of sources, including shallow biogenic processes, carbonate hydrolysis, mechanical breakdown and thermo-metamorphism of carbonates, and mantle degassing (Frezzotti, 2009, Italiano et al., 2008). There are few studies of the origins of CO$_2$ trapped in the subsurface in Italy.

Previous work at CO$_2$ seeps in Italy has explored the factors affecting the human health risk they pose, and the geological and geomorphological controls on their distribution and characteristics, to inform risk assessment and monitoring design above storage sites (Roberts et al., 2014, Roberts et al., 2011). This article extends this work to examine the subsurface geological attributes that control CO$_2$ leakage to surface. This is the first study to summarize the properties of CO$_2$ traps in Italy and learn from these analogues to minimise risk of leakage at engineered CO$_2$ stores.

**CO$_2$ flow in geological formations**

CO$_2$ fluids are retained in geological formations either as a free phase or dissolved in formation water. Depending on the subsurface conditions, free phase CO$_2$ may be present in a dense or light form, where we define ‘dense’ as CO$_2$ with densities greater than the critical density ($\rho_c = 464$ Kg m$^{-3}$) and ‘light’ as CO$_2$ with densities below the critical density. CO$_2$ phase behaviour is primarily controlled by subsurface temperature and pressure conditions, but is also affected by the presence of other fluids. Free phase CO$_2$ will dissolve when it is in contact with undersaturated formation waters, which results in an increase in the water density (Spycher et al., 2003).

How free phase or dissolved CO$_2$ flows through a rock formation is dependent on the properties of the fluid itself and of the rock. A rock volume will commonly exhibit a distribution of fluid pathway geometries due to heterogeneity intrinsic to geological units and the presence (and orientation) of fractures (Krevor et al., 2015). The permeability of the rock will vary according to the properties of the fluid flowing through it. This ‘effective permeability’ ($K_E$) is determined by the bulk permeability of the rock ($K_{rock}$) and the fraction of the total permeability accessible to each fluid phase (the relative permeability, $K_{rcoh}$).

\[
K_E = K_{rock} \times K_{rcoh}
\]

In single-phase flow all pores are saturated with a single fluid. For CO$_2$-saturated water flowing through a water-wet rock, $K_E$ is equal to $K_{rock}$. However, for two-phase flow, such as free-phase CO$_2$ flowing through a water-wet rock, $K_{rcoh}$ is influenced by the saturation of formation water in the pores or fractures through which the CO$_2$ is flowing.

Rate of fluid flow per unit area, otherwise known as fluid flux, through a rock volume increases with effective permeability and fluid pressure gradients, and lower fluid viscosity. This is commonly approximated by capillary (or ‘Darcy’) flow:
where \( Q \) (flux) is CO\(_2\) flow rate (m\(^3\) s\(^{-1}\)) over the seepage area, \( A \) (m\(^2\)), \( K_E \) is the effective permeability of the fluid (m\(^2\)), \( \delta P \) is the pressure gradient, (Pa m\(^{-1}\)) where \( P \) is pressure and \( z \) is depth (m), and \( \mu \) is CO\(_2\) viscosity (Pa s\(^{-1}\)).

Light phase CO\(_2\) is less viscous and more buoyant than dense phase, and experiments find the effective permeability for light phase CO\(_2\) is higher than dense phase (Bachu and Bennion, 2008). According to equations 1 and 2, light phase CO\(_2\) will flow more readily than its dense phase. Once flow is established in a rock, the relative permeability to CO\(_2\) may increase due to drying effects, whereby formation fluids dissolve into the flowing CO\(_2\) phase, decreasing the water saturation (Pruess, 2008b).

Darcy’s law does not characterise fluid flow in fractures, where permeability pathways are spatially focussed rather than distributed throughout the rock volume. If the fracture spacing, orientation, and aperture is known then fracture flow can be modelled discretely. However, where this information isn’t available, then fractured rocks can be approximated as porous media, where fracture permeability is upscaled to bulk permeability values that represent the flow properties of the rock volume (see Kuhlman et al., 2015, and references therein).

Mechanisms of CO\(_2\) migration from its containing reservoir to surface

Some naturally occurring CO\(_2\) reservoirs have been found to successfully retain CO\(_2\) for millennia (Gilfillan et al., 2008) and in a range of geological environments (Lewicki et al., 2007). Other sites leak CO\(_2\) to surface (Miocic et al., 2016) which can occur through a range of mechanisms. Free phase CO\(_2\) is less dense than surrounding pore waters and will rise buoyantly, becoming structurally trapped beneath a sealing unit if both a low-permeability rock and a containing structure are present. Dissolved and free phase CO\(_2\) can leak from the reservoir formation by diffusion, but this is an extremely slow process (Lu et al., 2009). However, high leak rates (e.g. tonnes CO\(_2\) per day) through the overburden of natural reservoirs will most likely arise from a buoyant free phase of CO\(_2\) which may leak by capillary transport through pores or microfractures in the overburden, or along unsealed faults and associated damage zones (Zweigel et al., 2004, Bachu, 2008). Otherwise, in natural CO\(_2\) systems, a low-permeability seal may be bypassed if free-phase CO\(_2\) ‘spills’ from a trapping structure. In this case, the overburden directly above the CO\(_2\) reservoir has not been compromised, but the space for CO\(_2\) in the reservoir-trap structure has simply been exceeded, though CO\(_2\) storage reservoirs will be engineered such that the capacity will not be exceeded. Advective flow of CO\(_2\)-bearing waters could transport CO\(_2\) from the reservoir more rapidly than diffusion. Such flow could occur through high permeability pathways through the overburden, or by hydrodynamic flow within the aquifer.
The capillary entry pressure of free-phase CO\textsubscript{2} within a given caprock determines the maximum column height of the free-phase CO\textsubscript{2} in the reservoir before it invades the seal by capillary transport. The capillary entry pressure is a function of the fluid properties (e.g. interfacial tension, contact angle) and rock properties (e.g. rock pore and pore throat geometry), or fracture aperture and roughness (Bachu and Bennion, 2008, Naylor et al., 2011). An extremely high gas pressure will be necessary to overcome the capillary threshold pressure of a shale caprock, however following capillary breakthrough, CO\textsubscript{2} can then flow through the seal and overlying overburden at capillary pressures below the initial entry pressure, facilitating further leakage. Subsidiary fluid components can affect the fluid properties of the CO\textsubscript{2} phase, and so can enhance or retard capillary breakthrough.

Confining pressure, defined by overburden thickness and density, improves seal quality by increasing the mean stress, and therefore rock strength, until the yield stress of the rock is approached. Hence, at higher confining pressures, greater fluid pressures are required for the seal to mechanically fail (Osborne and Swarbrick, 1997). Confining pressure also reduces rock permeability by closing pores. Additionally, as rocks are buried, diagenesis may occlude pore-throats and fracture apertures by cementation (Nara et al., 2011). Elevated fluid pressures can lead to hydraulic opening of fractures or shear on existing fractures due to reduction in effective stress resulting in enhanced permeability (Gudmundsson et al., 2001, Yang and Manga, 2009). The effect of pore fluid pressure (\(P_f\)) on rock strength can be represented by the pore fluid factor, \(\lambda v\), which is the ratio of pore fluid pressure (i.e. reservoir pressure, \(P_{res}\)) to lithostatic stress (Streit and Cox, 2001) after (Hubbert and Rubey, 1959).

\[
\lambda v = \frac{P_{res}}{\rho_{rock} \times g \times z}
\]

where \(\rho_{rock}\) is rock density (typically assumed to be 2500 Kg m\textsuperscript{-3}), \(g\) is acceleration due to gravity (ms\textsuperscript{-1}), and \(z\) is depth. For hydrostatic pressure, \(\lambda v = 0.4\), and for lithostatic pressure, \(\lambda v = 1\). The pore fluid factor indicates how close a coherent rock body is to failure, and will therefore be underestimated when applied to a fractured rock unit. Rock bulk permeability could therefore be increased by CO\textsubscript{2} buoyancy or fluid pressure, which in extreme cases can encourage rock failure (Collettini et al., 2008).

Should CO\textsubscript{2} leak from its primary reservoir, it may continue to migrate via available pathways through the overburden. During ascent, it is likely to encounter multiple reservoir and caprock units, and so CO\textsubscript{2} may accumulate in any overlying secondary reservoirs (Pruess, 2008a) until these reservoirs, too, are breached or bypassed. Several mechanisms may attenuate the mass of migrating CO\textsubscript{2} during its ascent, including residual trapping, or dissolution into unsaturated pore waters. Therefore the mass of CO\textsubscript{2} that reaches the near surface it likely to be only a proportion of the mass that migrated from the deep rock formations, or none may reach the surface at all. Depending on the lithostatic pressure and geothermal gradient profile, CO\textsubscript{2} will typically become subcritical at depths shallower than 1
km. Subcritical CO₂ will pass through two hydrologic zones; the phreatic (ground-water saturated) zone and the vadose (unsaturated) zone. In its light phase, CO₂ will be significantly more buoyant than groundwater in the phreatic zone. However CO₂ at ambient temperatures will be denser than soil gas in the vadose zone, and so may disperse laterally in the shallow subsurface, perhaps above the water table (Annunziatellis et al., 2008, Kirk, 2011). Depending on the soil properties, this could make the area of elevated soil CO₂ degassing substantially larger than the leak pathway from depth.

Observations at CO₂ and CH₄ seeps around the world find that gas release typically occurs over a discrete area (<0.01 km²) though in some cases the region of CO₂ phenomena where seeps occur may be much larger (several km² or more) (Elío et al., 2015, Talukder, 2012, McGinnis et al., 2011, Heinicke et al., 2006, Nickschick et al., 2015, Chiodini et al., 2004, Chiodini et al., 2010, Burnside et al., 2013).
**Methods**

CO₂ seep data was taken from Googas (Chiodini and Valenza, 2008), a web-based catalogue of degassing sites in Italy and Sicily, which documents seep location and seep type, and, where available, rate of CO₂ degassing, gas composition and temperature. In the catalogue, the rate of CO₂ degassing is classified into low (<1 t CO₂ /day), medium (1-10 t/d), high (10-100 t/d) and very high (>100 t/d).

*Step 1: Selecting case studies*

First, we identified CO₂ reservoirs, and established which are geographically close to CO₂ seeps, and therefore may be leaking.

Well logs and accompanying drilling notes for non-commercial boreholes in Italy are publicly available (www.videpi.com). By examining the VIDEPI dataset and in consultation with ENI and Independent Resources PLC, we selected non-commercial boreholes where test results document that the reservoir fluids are predominantly composed of CO₂. These boreholes, and boreholes nearby, were studied to constrain the subsurface structure and conditions.

A geographical information system (GIS) was populated with seep and well bore data. We included data on: ‘active’ faults as defined by seismogenic fault scarps mapped (Roberts, 2008); seismically capable faults (ISPRA, 2007), the present day stress field (Barba et al., 2009), elevation (SRTM 90 m; (Jarvis, 2008); subsurface carbonate structure (Nicolai and Gambini, 2007), and isotherms at 1 and 2 km depth (Geothopica, 2010). The distance from the well bore to the nearest CO₂ seeps was calculated from this GIS.

*Step 2: Case study geology*

To explore the geological conditions that affect whether a CO₂ reservoir is sealed or is leaking, we determined the geology for each reservoir, the overburden thickness and properties, regional structure and subsurface conditions, using the publically available well logs, and other published data.

Many of the selected boreholes were drilled in the 1960s and 1970s and therefore lack downhole information available from more modern boreholes, including many well tests. Downhole rock formations and their properties were determined from the well log (from well cuttings and core) and accompanying lithological descriptions, and any data from formation tests. We define the CO₂ reservoir as the shallowest rock formation that has high CO₂ gas saturation, and ‘seal thickness’ was defined by the maximum and minimum thickness of impermeable rock units overlying the CO₂ reservoir. Deviated drilling was corrected to the true vertical depth (TVD) and assumed a standard depth error of approximately ± 10 m and normally distributed to 1 standard deviation.

To reconstruct downhole conditions a number of assumptions had to be made. Formation pressure information was estimated from formation tests where available or from the density of drilling fluids (mud weight). Pore fluid pressures from mud weights usually exceed the actual formation pressure. To account for this, we adjust the formation pressures by
10%, following the methodology of Wilkinson et al., (2013). Formation pressure measurements were not sufficiently regularly spaced, nor were mud weight data sufficiently detailed, to distinguish the CO₂ and water legs from the pressure profiles. However, where formation tests documented a transition from CO₂ to the water leg, minimum CO₂ column heights were estimated.

A number of boreholes provided the information to calculate corrected geothermal gradient from downhole temperature measurements. Unusually low downhole temperatures are the expected result of circulation of cold drilling mud within the borehole. In these cases, and cases where downhole temperatures are unavailable, the geothermal gradient was interpolated from the geospatial dataset. Loss of drilling fluid circulation or significant mud absorption, which are sometimes recorded on the borehole logs, can be useful indicators of geological horizons with enhanced permeability, or where the rock fracture gradient has been exceeded. Overpressure was defined as measured pressure exceeding calculated hydrostatic pressure by 3 MPa, which allows for uncertainty in both measured depth and the mud weights.

**Step 3: Modeling CO₂ properties**

Downhole pressure \( P \) and temperature \( T \) conditions constructed from the well logs were used to model CO₂ properties, including density, viscosity, buoyancy and solubility at depth. The sensitivity of these fluid properties to the calculated \( PT \) conditions were tested at 10 m intervals, for which we assumed a standard error of ± 0.1 MPa and ± 5 °C, to 2 standard deviations. Surface temperature and pressure of 15 °C and 1 atm were assumed.

CO₂ density and viscosity was modelled using the (Huang et al., 1985, Span and Wagner, 1996) equation of state. CO₂ solubility was calculated using the equation of (Spycher et al., 2003) using values for fresh water rather than brines because formation tests in most of the wells show low salinities in the reservoir units. The viscosity of fresh water was calculated using the polynomial equation for variable temperature and pressure from (Likhachev, 2003). We neglect the effect of dissolved CO₂ on the viscosity of water, which is small at these temperatures (Islam and Carlson 2012), and also the effect of subsidiary gases such as CH₄ and H₂S which can affect CO₂ behaviour (Savary et al., 2012).

For column heights that could be estimated from the well log, the buoyancy pressure \( B \) of the CO₂ at the crest of the reservoir structure intersected by the well was calculated by:

\[
B = (\rho_{H₂O} - \rho_{CO₂}) \times g \times h_{CO₂}
\]

where \( \rho_{H₂O} \) is the density of water (Kg m⁻³), \( \rho_{CO₂} \) is the density of the CO₂ (Kg m⁻³), \( h_{CO₂} \) is the CO₂ column height (m), and \( g \) is gravitational acceleration (ms⁻²).

**Step 4: Classifying the reservoirs**

Each CO₂-bearing borehole was classified according to whether the corresponding reservoir is interpreted to be leaking CO₂ to surface or not, depending on its proximity to CO₂ seeps.
and the nature of the seep itself. Whether the distance between a borehole and a seep is
considered to be ‘near’ or ‘far’, was determined by spatial analysis of the distance
distribution between the boreholes, the CO₂ reservoir structure, CO₂ seeps and faults. If
there are no CO₂ seeps located at the surface close to the CO₂-bearing borehole, the CO₂
reservoir is determined to be sealing. If there are high-flux or dry CO₂ seeps located at the
surface near to the CO₂-bearing borehole, then the reservoir is inferred to be leaking. It is
not uncommon for springs emerging from carbonate rocks to contain small quantities of CO₂
from the dissolution of carbonates, which is not related to CO₂ leakage from depth, and so if
the seeps are CO₂ springs with small CO₂ content, or are located relatively far away from the
borehole then the leakage is classified as inconclusive.

**Step 5: CO₂ leakage pathways**

To evaluate the geological conditions that could enable the observed fluid leak rates from
case studies inferred to be leaking CO₂ to surface, we examined the Darcy flow equation for
CO₂ fluids at reservoir conditions. Reservoir fluid leakage into the overburden could occur by
distributed migration through the overburden over a broad area (small $K_E$, large $A$) or
focused migration via fault-related fracturing in the overburden (large $K_E$, small $A$). So, we
calculate the combinations of overburden effective permeability ($K_E$) and area ($A$) necessary
to sustain leakage from the reservoir at the observed rate of surface seepage.

Conservative mass transport is assumed, i.e. no CO₂ attenuation/loss during ascent to
surface. For leakage of free-phase CO₂, the minimum leak rate from the reservoir (m³s⁻¹) to
deliver CO₂ to the surface at the measured rates (often reported in tonnes per day) was
 calculated from CO₂ densities ($ρ_{CO₂}$) modelled at $PT$ conditions in the reservoir. The
minimum leak rate of CO₂-saturated formation water needed to supply CO₂ to the near-
surface at the measured CO₂ degassing rate was also calculated from the change in solubility
of CO₂ in fresh water at reservoir conditions to surface conditions. These calculations
assume water emergence temperatures of 15°C, and thus CO₂ solubility in freshwater is
~0.042 molal at 10 m depth.

The results could then be informed by any permeability measurements from rocks that
comprise the overburden, and area of CO₂ seepage at the surface. This area can be
considered on two scales; the area of a single seep, or the total area of a seep cluster (if
relevant). It is important to note that the area of leakage in the subsurface could be much
larger or smaller. The area of the CO₂ ‘cap’ in the reservoir, and of high-permeability
pathways offered by fault-related deformation was also estimated to inform our results.
**Results**

Figure 1 shows the location of the thirteen studied CO₂-bearing boreholes, neighbouring dry wells and all documented CO₂ seeps. Four additional boreholes on Figure 1 are known to contain CO₂ (Castelpagano 001, Vallauria, San Donato and Perugia 2), but their well logs are not publicly available and so are not studied here. Where two or more wells intercept what may be the same CO₂ reservoir we refer to a CO₂ field. We classify the case studies into those with overburdens that successfully seal CO₂ (BS1, SAT1, Ben1/2, Mu1), that leak CO₂ to surface (MF1, PPS1), or are inconclusive, i.e. it is not clear whether or not CO₂ is securely retained in the subsurface (Tr1, MT1).

This section presents an overview of the broad structure and rock formations in the boreholes and their relationships before detailing each case study (including observations from the boreholes, subsurface structure, any nearby geological structures and seeps, and whether the case study is interpreted to be leaking or sealed). Fig. 2 shows the lines of cross sections that describe the subsurface structure in Figures 3-6, and Table 2 summarises the reservoir and overburden geology, pressure conditions and proximity to the nearest surface CO₂ seeps for each CO₂-bearing borehole studied.

All but one of the CO₂-bearing boreholes are located in the Central Apennines, and record CO₂ in anticline or horst structures in the Apulian Carbonate Platform units (Figure 1C). Many of the well logs note that the Apulian Carbonate Platform units were associated with significant mud losses or loss of circulation, which can indicate a lower than anticipated pressure and / or increased rock permeability e.g. presence of fracture system. A series of thrust sheet deposits cap the CO₂ reservoirs. These nappes can be Middle-Triassic to Miocene basinal flysch units of the Allochthonous Complex (including the basinal carbonates of the Lagonegro formation or pelagic deposits of the Sannio formation), or Miocene to Pleistocene age sediments (turbidites, muds, sandstones and conglomerates). The thrustened contact between the reservoir and overburden is marked by a tectonic breccia or by a Messinian evaporite unit in some boreholes (indicated on the well logs in Figures 3-6). The thrust pile is now dissected by extensional structures relating to back-arc extension, including NW-SE and E-W trending high angle faults, which tend to control seismogenesis in Central Italy (Patacca et al., 2008). In Pieve Santo Stefano 1 (PSS1), CO₂ is hosted in the Burano Formation, a thick sequence of Upper-Triassic evaporitic carbonates which the Apulian Carbonate Platform overlies.

**Benevento CO₂ Field**

Three boreholes, Benevento Sud 1 (BS1), San Arcangelo di Trimonte (SAT1), and Tranfaglia (Tr1) penetrate the large Benevento CO₂ field in the Campania region of Italy, as shown in Figure 3.

In BS1 CO₂ is continuously recorded in Apulian Carbonate Platform units from ~2707 m to 4139 m (1432 m gross CO₂ column), and measurements show up to 98.5% CO₂ by volume, with small quantities of CH₄ (maximum 5.1%). Directly overlying the reservoir are 9 meters of Cretaceous anhydrite & gypsum, overlain by 25 meters of Messinian mudstone, and then...
1km of Miocene muds and marls. In SAT1 well tests record CO₂ in the Apulian Carbonate Platform unit (at ~1660 m depth) and also in a shallower ~50 m thick carbonate breccia, separated from the platform carbonate by ~80 m of muddy limestone breccia. It is not clear whether this represents continuous CO₂ from ~1520 m depth, or two distinct CO₂ shows.

The TR1 borehole intercepts a reservoir in the Apulian Carbonate Platform units at 2773 m depth containing 98% CO₂. Directly above lies 17m of massive anhydrite, but there are shows of 2-17% CO₂ above the anhydrite for a further ~ 200 m and wet gas shows in the overburden all the way to surface. Without detailed geochemical data we cannot determine if the CO₂ documented above the reservoir in Tr1 represents CO₂ migration from the Apulian Carbonate Platform units through the anhydrite overburden, or in situ generation associated with the wet gas.

There are no formations in the TR1 borehole that qualify as a good seal; most of the overburden is comprised of siltstone/calcareous units of the Allochthonous Complex. This is in contrast to the SAT1 and BS1 boreholes, where the Allochthonous Complex overlying the CO₂ reservoir is comprised primarily of mudstones. The overburden is overpressured exceeding 10 MPa in all three boreholes however, which suggests that the units are low permeability.

The wells that intersect the Benevento field record different fluid pressure in the reservoir; BS1 and Tr1 show hydrostatic reservoir pressure whereas in SAT1 the CO₂ is overpressured. As a result, the modelled CO₂ at reservoir conditions are different, finding that CO₂ is retained in dense (BS1) and light (Tr1) phase, and or close to the phase transition (SAT1). These differences in pressure and CO₂ properties may indicate compartmentalisation of the reservoir.

The Buonalbergo CO₂ seep is located 3.5 km from TR1, 5.3 km from SAT1, and 10.3 km from BS1. No further information, such as quantities of degassed CO₂, is available about this seep other that it is a CO₂ spring (Chiodini and Valenza, 2008). Its visual appearance is unremarkable, suggesting that gas flux is not particularly high. The CO₂ dissolved in the spring could source from the Benevento CO₂ field or CO₂ in shallower formations (like those in Tr1 which show small quantities of CO₂ and hydrocarbons that could break down to CO₂). Otherwise it could source from carbonate rock dissolution (karstification) which is common where carbonate rocks form the shallow subsurface. Given the absence of a convincing seal in the Tr1 overburden and the presence of the Buonalbergo spring nearby, it is inconclusive whether the CO₂ documented in the Tr1 borehole is leaking to surface. The CO₂ reservoirs intercepted by BS1 and SAT1 are considered sealed.

To the North of these wells, the Benevento boreholes (Ben1 and 2) also encountered CO₂ at ~ 3 km depth. These boreholes drilled a broad structural high (see Fig. 1C), and were also found to contain some short-chain hydrocarbons (max 6.2% CH₄ by volume) at ~3300 m (Ben2). These wells show significant overpressure in the overburden which is comprised of several muddy units, but the reservoirs are hydrostatically pressured. There are no CO₂ seeps in the vicinity of these boreholes so the reservoir is considered to be sealing.
There are two recently active SW-dipping normal fault systems near to these boreholes (BS1, SAT1, TR1 and Ben1/2). The Southern Matese Fault (less than 10 km from the boreholes) is a NW-SE trending complex of faults that has been historically seismogenic (ISPRA, 2007, Di Bucci et al., 2006). The Telese Fault scarp, a N-dipping topographic break-in-slope, is between 16 – 22 km away from the boreholes (Roberts, 2008). Previous earthquake sequences to the east show that extension is largely NW-SE (Milano et al., 2006).

**Monte Taburno CO₂ Reservoir**

To the East of the Benevento CO₂ field, the Monte Taburno 1 (MT1) borehole cuts a separate structure containing >90% CO₂ at 2 km depth (Figure 4). CO₂ is mostly found in the Apulian Carbonate Platform but also in the overlying thin layer of muddy Mio-Pliocene thrust top deposits. This is capped by 511 m of dolomitic limestone, the bottom-most 2 m of which (i.e. capping the reservoir) is anhydrite-bearing, and then by over a kilometre of low-permeability muds and sands of the Lagonegro and Sannio formations of the Allochthonous Complex. Overburden pressures are hydrostatic, but the CO₂ reservoir shows ~9 MPa overpressure and under these conditions the CO₂ will be contained in its supercritical state. MT1 is 10 km from the Telese fault and 7 km from the SW-dipping Montesarchio and Ioannis seismogenic normal faults (Roberts, 2008). The Motta thermal spring is 1.6 km away and has a small CO₂ emission (Chiodini and Valenza, 2008), but no further information is available. Similar to the Buonalbergo spring near the Benevento field, there are several possible sources of CO₂ in a small spring that do not necessitate a subsurface CO₂ reservoir. Given the proximity of MT1 to the Motta thermal CO₂ spring, it is inconclusive whether the Monte Taburno reservoir is leaking to surface.

**Muscillo CO₂-CH₄ Reservoir**

The Muscillo 1 (Mu1) borehole, located in the Basilicata region, penetrated a shallow accumulation of CO₂-CH₄ in the Apulian Platform Carbonate (Figure 3). A CH₄ leg overlies a gas phase CO₂ leg at 694 m below the surface, and both are low saturation. The reservoir top is marked by a thin breccia. The overburden is comprised of claystone and siltstone terrigenous deposits. In the outer thrust domain where the borehole is located, these sediments tend to represent rapid filling of structural depressions related to the development of extensional tectonics. Down-well pressures are hydrostatic and there are no CO₂ seeps in the vicinity of this well. No other subsurface information is available and so its structure is poorly constrained. The nearest faults are over 40 km from the well. We classify the Muscillo reservoir as sealing, though we note that low CO₂ saturation could indicate residual trapping of leaked CO₂.

**Frigento CO₂ Reservoir**

Three boreholes penetrate the Frigento Antiform, located in region of Campania: Monte Forcuso 001 (MF1), Monte Forcuso 002 (MF2) and Ciccone (Cic1) (Fig. 4). This structure in the Apulian Carbonate Platform correlates with a gravity and thermal anomaly (Improtta et al., 2003a; Fig. 1C). The geothermal gradient here reaches over 90°C/km at the crest of the anticline (Chiodini et al., 2010). The MF1 borehole is the only one to encounter CO₂. It
intercepts a c. 472 m gross CO₂ column in the Apulian Carbonate Platform at just over 1 km depth, above a fresh water leg. The absence of CO₂ in neighbouring boreholes constrains the extent of the CO₂ cap (< 2 km radius). The overburden is mostly comprised of muds and marls of the Allochthonous Complex’s Lagonegro formation, and also brecciated and cemented sandstone. The overburden and the reservoir are at, or close to, hydrostatic pressure. The MF2 and Cic1 boreholes, located on the flanks of the anticline, do not contain free phase CO₂, only fresh water and saline water respectively. The differences in formation salinity and pressure in these boreholes may indicate compartmentalisation of the reservoir.

The regional stress field (Barba et al., 2009) shows NW-SE extensional faulting which is currently active; the 1980 Irpinia earthquake (M 6.9) nucleated on the NE-dipping Irpinia fault 32 – 35 km to the south of the reservoir. The SW-dipping Ufito normal fault scarp is located less than a kilometer to the NE of the MF2 borehole, and 4.3 km from MF1 (Fig 2; Improta et al., 2003b; Roberts, 2008). This is thought to be a splay from the Irpinia fault (Brozzetti, 2011), and thus the Frigento Antiform is located in the hanging wall of both faults.

Mefite D’Ansanto and Mefitiniella Polla CO₂ vents (seep no. 4 & 5 in Fig. 1C) are located above the structural high point of the NW-SE trending Frigento Antiform (see Fig. 4). Mefite D’Ansanto emits more CO₂ than any other seep in Italy, releasing ~ 2000 t(CO₂)day⁻¹ by venting and diffuse degassing over an area of 4,000 m² (Chiodini et al., 2010). Mefitiniella Polla is a smaller CO₂ vent located 3.6 km NW from Mefite D’Ansanto, and though the seep rate has not been measured, field observations find it vents CO₂ vigorously. On the flanks of the Frigento antiform, less than 3 km ENE from Mefite, are the San Teodoro thermal springs. These springs do not release CO₂, but their emergence temperatures (~15-27°C, similar to the Mefite seeps) and geochemistry (Minissale, 2004) indicate rapid fluid ascent of waters that have circulated in deep carbonate rocks, probably via fault related flow paths (Duchi et al., 1995). Travertine deposits have been mapped within 5 km of the seeps (Roberts, 2013) but these are no longer active, and there have been no geochemical investigations regarding their age or source.

Although there is currently insufficient geochemical information to irrefutably link the subsurface reservoir with the Mefite CO₂ seeps, or nearby thermal springs, it is reasonable to consider that the CO₂ released at the Mefite seeps could originate from the CO₂ reservoir located in the underlying anticline (Chiodini et al., 2010, Pischiutta et al., 2013). We therefore classify the Frigento CO₂ reservoir as leaking.

Acerno CO₂ Reservoir

The Acerno 1 borehole (Ac1) penetrates the deepest studied CO₂ reservoir, located in a horst structure in the Apulian Carbonate Platform, 4363 m beneath Mount Picentini (Fig 5), Campania region. The reservoir is overlain by a 305 m thick evaporite and mud seal, then interlayered nappes of the Allochthonous Complex, basement carbonates, and muds of the thrust top deposits. Both the overburden and the reservoir are overpressured, with a pore fluid factor of 0.6 in the reservoir. Multiple mud losses were experienced when the well penetrated the Apulian Carbonate Platform, which suggests the mud densities were too high
for the reservoir properties (e.g. pressure or presence of pervasive fracture system),
however the mud densities were not adjusted. The borehole was plugged after drilling 300
m into the Apulian Carbonate Platform. The single drill stem test in this borehole yielded
over 90% CO₂, which we model to be in dense phase at reservoir conditions. The borehole is
in the footwall of the east-dipping Sabato normal fault which is considered to be
seismogenic (ITHACA), and 11.5 km from the Volturara Fault scarp (Roberts, 2008). There are
no CO₂ seeps located above the Acerno structure, but 11 km to the ENE is the San Benedetto
CO₂ spring, which releases 10-100 t(CO₂)d⁻¹ (Chiodini and Valenza, 2008), and 15 km to the
NW is the Contursi seep cluster (Fig. 1C; no. 6). The Acerno reservoir is classified as
inconclusive.

Caprese CO₂ Reservoir

The Pieve Santo Stefano 1 (PSS1) borehole, located in Tuscany, commercially exploits a
multi-layered CO₂ reservoir at ~3.6 km depth in the Caprese Antiform (Bicocchi et al., 2013)
(Fig. 6). The main CO₂ reservoir is hosted within dolomites and evaporites of the Triassic
Burano group (Bonini, 2009b) where thin reservoirs of fractured dolostone (porosity 2-6%) with high porefluid pressures are sandwiched between sealing anhydrite layers (Trippetta et
al., 2013). The CO₂ cap in the Caprese Antiform is likely to be elliptical in shape, with a
maximum radius as great as 5 km (Bicocchi et al., 2013).

The reservoir brines are highly saline due to the interaction of meteoric waters with the
evaporites (Bicocchi et al., 2013). Logging notes record significant mud losses while drilling
through the overburden which is multi-layered and approximately hydrostatically pressured.
Beside the anhydrites of the Burano group, there are few low-permeability units in the
caprock that would offer a convincing very low permeability seal, though in general the
Ligurian Units that comprise the overburden are considered to be low permeability (Bicocchi
et al., 2013).

The region around the Caprese Antiform is associated with CO₂ reservoirs and seeps. For
example, approximately 40 km to the SE of PSS1, the San Donato and Perugia 2 boreholes
penetrate the Monte Malbe structure (an anticline bounded by two active normal faults) and find pressurised CO₂ fluids in the Burano group (Trippetta et al., 2013). Indeed, North
East trending, steep dipping faults in the region form part of a regional transverse lineament
known as Arbia-Val Marecchia Line (AVML) which has been associated with CO₂ seepage
(Bicocchi et al., 2013). More locally, the seismogenic Alto-Tiberina Fault is ~8 km south east
of the PSS1 borehole and bounds the west side of the quaternary Upper Tiber Basin
(Collettini and Barchi, 2004, Heinicke et al., 2006, ISPRA, 2007).

The Caprese Michelangelo seeps and the Fungaia seeps are within 4 km of the PSS1 well.
Caprese Michelangelo is cluster of at least 4 seeps in an area 400 m². The style of seeping is
varied; there are CO₂ vents, bubbling water and diffuse degassing (seep no. 1 in Fig. 1C). The
gas emission rate of two seeps has been measured; one seep in the Caprese cluster classifies
as medium (1- 10 t d⁻¹) and a seep in the Fungaia cluster classifies as high (10-100 t d⁻¹).
(Chiodini and Valenza, 2008). Here, we refer to the Caprese Michelangelo and Fungaia seeps
collectively as the Caprese seeps. The rate and characteristics of these seeps (such as water content and area) are observed to vary with rainfall and following seismic events on the Alto-Tiberina Fault (Heinicke et al., 2006, Bonini, 2009b).

CO₂ fluids from the PSS1 wellhead, the Caprese seeps, and fluid inclusions from the PSS1 cores have a common origin (Bonini, 2009b, Bicocchi et al., 2013, Trippetta et al., 2013). The seeps are aligned along NE-SW trending faults that may connect to the deep CO₂ reservoir (Bonini, 2009b, Bicocchi et al., 2013). On the basis of this information, we interpret that the Caprese CO₂ seeps source from the deep reservoir in the Caprese Antiform, and so this is classified as leaking.
Analysis: Comparing the characteristics of leaking and sealing reservoirs

Four of the studied CO₂-bearing boreholes (PSS1, MF1 and Tr1, MT1) are located within 3 km laterally of documented surface CO₂ seeps. We interpret that two reservoirs are leaking; the Caprese (intercepted by the PSS1 borehole) and the Frigento (intercepted by MF1 borehole).

Both reservoirs are hosted in antiform structures, and a number of CO₂ gas seeps with high rates of degassing are located within 3.5 km of the boreholes. In contrast, for Tr1 and MT1, very little is known about the small CO₂ springs located within 3.5 km of the boreholes, and so it is inconclusive whether the CO₂ in these reservoirs is leaking to surface. There are no seeps located within at least 10 km of the remaining boreholes (BS1, SAT1, Ben1/2, Mu1) and so these are sealed.

Properties of the CO₂

Pressure, CO₂ density, and where possible, calculated CO₂ buoyancy pressure at the reservoir tops is shown in Figure 7. Most of the studied reservoirs contain CO₂ in dense phase; MF1 and TR1 contain light phase CO₂, and Mu1 is the only well to contain gaseous CO₂. No reservoirs contain liquid phase CO₂. The physical properties of the CO₂ (phase or buoyancy) do not appear to be a first-order control on whether a CO₂ reservoir is leaking or sealed.

The sealed Benevento Sud reservoir has a higher estimated CO₂ buoyancy pressure at the reservoir-caprock interface (5.0 MPa) than the seeping Monte Forcuso reservoir (3.5 MPa). The CO₂ column heights for SAT1 and Tr1 are unknown. If we assume the same CO₂-water contact in all three wells, the CO₂ buoyancy in SAT1 and Tr1 will be even higher than in BS1 because CO₂ is less dense. Despite this, unlike the Frigento formation, the Benevento reservoirs are not obviously leaking. The Muscillo reservoir is the opposite; the net buoyancy pressure on the seal is effectively zero at the present day because gas saturation is so low. In this reservoir CO₂ will also have extremely low relative permeability which will restrict its mobility.

CO₂ solubility in fresh water at reservoir conditions is typically between 1-1.5 molar (~40 - 60 kg(CO₂) m⁻³(H₂O)) for all case studies. The formation waters in these reservoirs therefore have potential to dissolve significant quantities of CO₂, and have a greater solubility capacity than surface waters.

In most of the case studies a CO₂ leg overlies a water leg in the reservoir, and CO₂ saturation in the cap is high. The exceptions are PSS1, where the reservoir is complex and CO₂ (in high saturation) is trapped within more permeable layers between evaporite layers, and Mu1, where CO₂ saturation in the reservoir is low. Further, a unit overlying the primary CO₂ reservoir in Tr1 also has low CO₂ saturation. Low CO₂ saturation could result from several mechanisms. If the reservoir’s seal has been breached, low CO₂ saturation confirms that the reservoir is leaking or has leaked in the past. If the caprock is acting as a good seal, but CO₂ saturation is low this could indicate that there was insufficient CO₂ charge to fill the reservoir. In situ generation of CO₂ may result in low saturation if the quantities of CO₂ generated are small. Similarly CO₂ coming out of solution from formation waters as they
depressurize during ascent may result in low CO₂ saturation. In the absence of further geochemical information on the CO₂ and formation waters, it is not possible to distinguish these scenarios.

Other gases which may affect the properties of the CO₂ mixture are present in small quantities in many of the CO₂ reservoirs, including short-chain hydrocarbons such as CH₄, and H₂S. Small proportions of H₂S decreases interfacial tension of CO₂ (Bennion and Bachu, 2008, Savary et al., 2012), whereas CH₄ increases interfacial tension and decreases the fluid density (Naylor et al., 2011). Since only trace amounts (0.1% C%v.v) of H₂S are recorded in some boreholes its effects on CO₂ properties will likely be negligible. In contrast, sealing reservoirs Ben2, BS1 and Mu1 contain over 5% CH₄ (C%v.v) and so the buoyancy of the CO₂-CH₄ mixture in these reservoirs will be greater than for pure CO₂. However, the effect of CH₄ on the interfacial tension will be more significant than the effect on the buoyancy (Naylor et al., 2011). As a result, relatively small quantities of CH₄ may be enhancing reservoir sealing at the Benevento reservoirs.

**Properties of the CO₂ Reservoir**

The geological structures of all the reservoirs are broadly similar: CO₂ has accumulated in platform carbonate units, and the overburden is comprised of thick, heterogenous nappes. This is similar to hydrocarbon discoveries in central-southern Italy, may of which are hosted in fractured Apulian Carbonate Platform (Casero, 2005). Whether the reservoir is hosted in an anticline or horst does not affect whether it leaks or seals.

The leaking Caprese and Frigento reservoirs are both hosted in thrust-related anticlines located in Quaternary graben structures. However the depth of the reservoirs is very different (see Table 2), and so confining pressure is not a primary control on the seal quality. The Caprese reservoir is deep and pressured beyond hydrostatic; in this reservoir CO₂ is in its dense phase. The Frigento reservoir is much shallower, hydrostatically pressured, and so CO₂ is in its light phase. The two reservoirs have similar temperatures since the shallower Frigento formation is located in a region with an anomalously high geothermal gradient.

In three boreholes (Ben1/2, BS1, Tr1) the reservoir carbonate units are close to hydrostatically pressured, in contrast with the significantly overpressured overburden. These reservoirs must be hydrologically connected to the surface; either by permeable faults or through surface outcrop. Examples of hydrocarbon reservoirs at hydrostatic fluid pressures overlain with high-pressure caprock are common in overpressured basins (O’Connor et al., 2008). Isolated reservoir units will be in pressure equilibrium with the encasing low permeability units (such as shales). However, if reservoirs are connected to surface via lateral outcrop or fracture/fault networks, fluids can escape and drain the overpressure in the reservoir, bypassing any buoyant fluids trapped in the overlying formation. The overburden can remain overpressured even though fluids may slowly bleed into adjacent lower pressure reservoirs. In contrast, the Caprese and Monte Taburno structures contain overpressured reservoir fluids with a close to hydrostatically pressured overburden. This is
often indicative of reservoir compartmentalisation, which (Trippetta et al., 2013) interpreted for the complex and multi-layered Caprese structure.

The CO₂ contained in PSS1, MT1, Ac1, and SAT1 is overpressured. High fluid pressures can enhance or retard seal integrity, depending on the mechanism of seal failure. CO₂ density increases with reservoir pressure, which in turn decreases CO₂ buoyancy. CO₂ overpressure therefore reduces the likelihood of capillary seal failure. Indeed, reservoir overpressure in the leaking Caprese structure decreases CO₂ buoyancy by ~0.3 MPa compared to hydrostatic conditions. However, significant fluid overpressure can lead to seal failure by fluid-driven fracture propagation. For example, in the case of PSS1, Ac1, and SAT1 the reservoir pore fluid pressures are over 60% of lithostatic. These fluid pressures could jeopardise the integrity of the seal, particularly if the seal contains pre-existing fractures that are critically stressed. However, since only the Caprese reservoir leaks CO₂, reservoir fluid pressure alone cannot control reservoir leakage. Regardless of the degree of overpressure in the reservoir, overpressure in the seal and in the overburden above the seal can act as a significant barrier as it increases the pressure required to drive CO₂ upwards and through the seal and overburden.

Properties of the Overburden

Although the geological structure of all the cases studied is broadly similar, the overburden is variable in both rock type and thickness. Figure 8 shows the seal thickness, defined as the total thickness of units documented from drill cuttings that would likely be impermeable to CO₂.

There is no correlation between reservoir depth (overburden thickness) or seal quality/thickness and the presence of surface CO₂ seeps. Some well logs record thick low-permeability sequences in the overburden; for example in SAT1 there are 1520 m of muds overlying the reservoir all the way to surface, and overlying the BS1 reservoir there are muds which, although becoming a little siltier towards the surface, remain low permeability. In contrast, TR1 records 17 m massive anhydrite directly overlying the reservoir but no definable seal above this; the overlying (calcareous) siltstone records low saturation CO₂ (for ~200 m above the anhydrite) and wet natural gas all the way to surface. Similarly, PSS1 records 70 m of gypsum above the CO₂ reservoir overlain by sandy-marls (~160 m), but no other low-permeability formations above this.

In some wells, the thrusted contact between reservoir and overburden is marked by a tectonic breccia (see Table 2), and several boreholes (BS1, Tr1, Ac, MT1) Messinian anhydrite-bearing units (massive, or associated with muds) directly overlie the CO₂ reservoir. Such low-permeability units may contribute to the sealing capability of the overburden at the sites. However, the Burano Triassic Evaporite formation forms the reservoir/seal complex of the leaking Caprese reservoir. Thus, while evaporites often make a very effective seal, their presence or absence is not the only factor in determining overburden integrity.

The relationship between CO₂ seepage and overburden overpressure is summarised in Figure 9. CO₂ reservoirs that lack strong overpressure in overburden units (max. pressure /
hydrostatic pressure < 1.3) are associated with surface seeps (boreholes MF1, PSS1). In contrast, where the overburden shows significant overpressure (max. pressure: hydrostatic pressure > 1.3) there are no surface seeps within 10 km of the borehole (Ben2, BS1, SAT1). The remaining boreholes are inconclusive (Ac1, Mu, Tr1, MT1). The pressure conditions in the overburden seem to be a primary control on successful CO2 retention.

Figure 10 shows the relationship between the fluid pressures in the overburden and the lateral distance from the wellbore to active normal faults (faults with exposed scarps that are considered to pose a seismic hazard). The boreholes that penetrate the two leaking CO2 reservoirs are located within 5 -7 km of the surface trace of seismogenic normal faults. These boreholes record no overpressure in the overburden. Reservoirs located further from these faults show overpressure in the overburden rock units.

The exception to this trend is borehole Mu1 which is over 40 km from any known recent faults, and yet shows only minor deviation from hydrostatic pressure. However this reservoir is at a relatively shallow burial depth compared to the other study sites (c. 700 m) and the overburden consists of sands, silts, clays and conglomerates which may be permeable even if not breached by faulting.

**Analysis: Characteristics of leakage and implications for risk management**

As described in the sections above, the Frigento and Caprese antiforms are considered to be leaking. Both structures have a cluster of CO2 seeps at the surface above the reservoir, and both have hydrostatically pressured overburden. However, in many respect they are end-member case studies; the Frigento antiform is one of the shallowest CO2 reservoirs and has an anomalously high geothermal gradient, whereas the Caprese formation is the deepest CO2-bearing structure in a region with relatively low geothermal gradient. The downhole conditions in the wells that penetrate these structures are therefore very different (as can be seen in Table 2). This has implications for the area-permeability criteria to leak a given mass of free-phase CO2 from the reservoir. For example, for the same mass of CO2 to leak from the reservoir, the volume of free phase CO2 that must leave the Caprese reservoir ($\rho_{CO2} = 830$ Kg m$^{-3}$) is a quarter of the volume that must leave from the Frigento reservoir ($\rho_{CO2} = 200$ Kg m$^{-3}$). As such, small volumes of free-phase CO2 escaping from the Caprese structure would mean relatively high rates of CO2 leakage. For both structures, much greater volumes of CO2 saturated water must leak from the reservoir than free-phase CO2; six times the volume of free phase CO2 for the Frigento formation, and up to ten times for the Caprese formation. Thus, larger permeabilities are needed for CO2 saturated waters to transport the same rate of CO2, unless the relative permeability to water is at least an order of magnitude higher for free phase CO2.

**Pathways of CO2 leakage**

CO2 leakage from a reservoir could, in theory, occur over a large area (distributed flow through a large rock volume), or over a smaller area (focussed by enhanced permeability pathways such as those offered by faults, whether the fracture network is localised or more distributed). We use the Darcy flow equation (equation 1) to approximate flow through the
rock volume and fracture networks, in order to examine the area and permeability requirements to permit CO2 leakage from the Caprese and Frigento reservoirs into the overburden (not through the overburden to surface). Figure 11 shows the combinations of overburden effective permeability ($K_E$) and area ($A$) for leaking free phase or dissolved CO2 at 100 and 2000 t(CO2)d⁻¹ from the Caprese and Frigento antiform, respectively. These leak rates correspond to the maximum estimated CO2 release rate at Fungaia and Mefite D’Ansanto seeps, since there are no published estimates for CO2 release from all the seeps in the Caprese and Mefite seep clusters. The permeability of formations measured from the PSS1 and MF1 well logs, and elsewhere, guide the possible caprock permeability. Further, reasonable possible leakage areas are indicated on Figure 11 for discrete and clustered seepage, the possible extent of a free-phase CO2 caps in the antiforms, and the geometry of rock deformation related to faulting. Similar calculations are not performed for the case studies that are inconclusive (Tr1 and MT1) because we do not have information about seep rates, or seep area.

Figure 11 and the table inset shows that high leak rates of free phase CO2 can occur over smaller areas and lower permeability than for CO2 saturated water. Enhanced permeability pathways (i.e. faults) may not be necessary for free phase CO2 fluids to leak from the Caprese reservoir at 100 t d⁻¹. CO2 could leak at this rate over an area smaller than that of the Caprese Michelangelo seep cluster if the permeabilities of the overlying rock formations are similar to measurements of the overburden recorded in the PSS1 well log. For the same CO2 leak rate and permeability, CO2 dissolved in water would need areas similar to the Caprese seep cluster, or faults. In contrast, to leak 2000 t d⁻¹ from the Frigento reservoir, Darcy flow of free phase CO2 through mudstones (maximum permeability ~ 0.8 mD) would require leakage over an area much larger than that estimated for the CO2 reservoir top. For CO2 leakage over smaller areas, such as those of faults, overburden permeabilities approaching $10^2$ mD are necessary. At the ~1.1 km depth, such permeability could only be provided by a network of open fractures, which could localised or distributed, and could be related to faulting. Fluid flow rates of 480 l s⁻¹ of CO2 saturated waters would transport 2000 t d⁻¹ of CO2 from the Frigento reservoir. Such flow rates are not impossible, since spring flow rates in Italy can exceed 800 l s⁻¹ (Minissale, 2004). However, rock permeabilities greater than $10^7$ mD would be needed to enable these flow rates over a discrete area, which is difficult to achieve unless the rocks are karstified. Although karst environments are common in Central and Southern Italy (Santo et al., 2011), it is unlikely that karst in the overburden is responsible for CO2 leakage from the reservoir, since karst environments are typically found in the region of the water table (current or historic). However, it is possible that karst could aid the rapid seepage of CO2 from the near surface.

Driving mechanism for CO2 leakage

The results discussed above consider possible rock properties and geometries required to permit a given rate of fluid flow into the caprock, not the mechanism driving the fluid flow. For free phase or dissolved CO2 to migrate from the reservoir and into the overburden, there must be a driving force. This could be buoyancy pressure of free-phase CO2, which is less
dense than formation waters. Modelling of CO$_2$ properties at downhole conditions finds that
CO$_2$ in the Frigento formation is much more buoyant than CO$_2$ in the Caprese reservoir.
Indeed, in PSS1 finds CO$_2$ will be in its dense phase (with low buoyancy) for several
kilometres above the reservoir. Instead, fluid pressure in the Caprese reservoir could be
driving CO$_2$ leakage, since the reservoir pore fluid pressure is much greater than hydrostatic.

Whether fluid pressure or buoyancy is driving fluid leakage, these forces will change during
fluid ascent. For example, as shown in Figure 12a, CO$_2$ leaking from the Caprese reservoir
will remain in its dense phase for a few kilometers and pass very close to the liquidus, where
buoyancy will be lowest, during its ascent from 1 km depth, if the fluids are in thermal
equilibrium with the geotherm. This means that CO$_2$ experiences a rapid increase in
buoyancy as its density decreases approaching 800 m depth, and CO$_2$ solubility will
concurrently decrease rapidly. These are depicted in Figure 12b and c, which also shows
that, though CO$_2$ buoyancy is high in the Frigento reservoir, the buoyancy increases gradually
and to a lesser degree during ascent to surface. For example, during the 500 m ascent
between 1250 - 750 m, $\rho_{CO_2}$ decreases by $\sim$325 Kg m$^{-3}$ in PSS1, and $\sim$75 Kg m$^{-3}$ in MF1. This
could have pronounced effect on the way that CO$_2$ leaks to surface. For PSS1 the area-
permeability of flow paths would need to rapidly increase to sustain the mass flux of leaking
CO$_2$ since there will be a corresponding volume increase of the leaking fluids over this depth
interval.

**Effective permeability**

Our calculations do not account for effective permeability of CO$_2$ compared to water. The
relative permeability of CO$_2$ can be very low when flow first establishes in water-wet rocks.
However the Caprese and Mefite seeps are long established degassing sites. Due to drying
out effects, single-phase flow could now be established along the leak paths, and so
effective permeability may approximate to rock permeability.

For CO$_2$ saturated waters migrating through water-wet rocks, the waters will initially behave
as a single phase. However two-phase flow may initiate towards the phase transition depth,
where solubility rapidly decreases (see Figure 12C) causing CO$_2$ to exsolve. The resulting
decrease in the effective permeability will impede flow of both phases, although though the
buoyancy of the water may increase as a result of ‘gas lift’ (the buoyant CO$_2$ bubbles). The
exsolved CO$_2$ will re-dissolve if it comes into contact with unsaturated water, and so will only
remain as a separate phase if its flow path is isolated from the ascending fluids (e.g.
channelized flow in faults) or if the rocks through which it is flowing are not water-saturated.
This is more common at shallower depths (vadose zone). If CO$_2$ remains as a separate phase,
then its buoyancy and high interfacial tension could allow free phase CO$_2$ to follow a
different flow path to its parent waters.

It is also important to note that fracture flow is not accurately represented by Darcy’s law.
However in the absence of further information about the fracture properties of the
overburden, the simplified approach allows us to explore the constraints on the geological
conditions that could enable leakage at the observed rates.
Our calculations assume conservative mass transport of leaked CO₂, i.e. that there is minimal CO₂ loss during ascent, and so CO₂ leaks from the reservoir at the same rate that it reaches the Earth’s surface regardless of its subsurface interactions. When CO₂ leaks first establish, or if leakage occurs through a large rock volume rather than a focussed flow path, it is more reasonable to assume that CO₂ will disperse and attenuate as CO₂ becomes residually trapped or accumulates in secondary formations. Similarly, for many geological situations, the migrating CO₂ will encounter multiple barriers and caprocks that will inhibit escape to surface. However for long-established degassing sites, such as those studied here, the rocks and fluids that the CO₂ comes into contact with during ascent are probably saturated with CO₂. The quantity of CO₂ loss during ascent from the Caprese and Frigento reservoirs may therefore be limited. However it is unlikely that the mass transport is truly conservative, and in fact, geochemical studies at the Caprese reservoir and seeps find evidence of CO₂ mixing with shallow waters during ascent (Bicocchi et al., 2013).
Synthesis and discussion

Our study of CO₂ reservoirs in Italy identify that reservoirs that are successfully sealed have low-permeability units and overpressured units in the overburden, and are located over 10 km from seismogenic normal faults.

The thrustsediments that comprise the overburden of the studied reservoirs have experienced compressional tectonics, which is one mechanism of elevating pore fluid pressures beyond hydrostatic (Osborne and Swarbrick, 1997). Overpressure is only preserved in low-permeability rocks, since the pressure will dissipate where there is sufficient permeability (whether due to the presence of slightly more permeable rock types in the overburden, or a connected fracture and/or fault network, whether it is localised or distributed). While we find that there is no simple relationship between overpressure, and the type of rock comprising the overburden, we do note that for many of the sealing reservoirs an evaporite-bearing formation caps the CO₂ reservoir. The presence of evaporites will contribute to the sealing capability of the overburden due to their low inherent permeability and the possibility that when mobilised they can cement pores or fractures (Trippetta et al., 2013). This may be the case for the Caprese reservoir where the CO₂-bearing horizons are overpressured and are confined by evaporites (Bicocchi et al., 2013), but there are no other evaporite layers in the overburden, and the Caprese reservoir is leaking. However, observing the borehole pressure profiles for leaking and sealing reservoirs finds that the most overpressured formations in a caprock are rarely those that are evaporite-bearing (see figures 3-6), and the boreholes that show greatest overpressure are not necessarily those that contain evaporite. Thus, the presence of evaporites does not systematically affect the overburden integrity or overpressure.

Several factors affect fracture connectivity in rocks, including confining pressure (corresponding to depth) and regional stress regime. We find that confining pressure does not affect the maximum overpressure, but that proximity to active normal faults (as defined by Roberts (2008)) does. Away from these faults, overpressure from the contractional tectonic regime could be preserved in the heterogeneous and compartmentalised thrust top deposits. The primary control on overburden overpressure may hence be the hydraulic conductivity of localised or distributed fractures within the overburden; high connectivity resulting from either the presence of recent ‘open’ extensional faults, or from high overpressures resulting in a reduction of overburden stress. For example, CO₂ leakage from the Frigento reservoir may be facilitated by the low confining pressures (from being relatively shallow) opening fractures in the overburden, and by permeability offered by extension and fault damage zones related to the nearby Ufìto normal fault. In contrast, the leaking Caprese reservoir is overpressured although its overburden is not. Faults in the region could have relieved any overpressure that once existed in the overburden units, however the reservoir horizons are not in pressure communication with their overburden because they are interlayered with the low-permeability evaporites of the Burano formation. This reservoir is deeply buried and the resultant high confining pressure will have closed mesoscale fractures in the reservoir and much of the overburden, unless the high fluid
pressures in the reservoir opens them locally or faults are critically stressed. Both scenarios are feasible. PSS1 is located <8 km from a seismically active fault, and also the pore fluid pressure in the Caprese reservoir could be sufficient to open fractures in the caprock, locally enhancing rock fracture permeability and enabling CO$_2$ escape from the reservoir. Indeed pressure pulses associated with seismicity have increased CO$_2$ degassing at the Caprese Michelangelo seeps (Bonini, 2009a, Heinicke et al., 2006). These observations stress the need to understand the crustal stresses around potential storage sites.

Although we do not consider this here, the burial history might have affected the geomechanical properties, and as such the fluid flow properties of the overburden, and therefore whether a reservoir leaks or seals. Further work could aim to resolve how the geomechanical context influences reservoir leakage.

The recorded overpressure in low permeability units could be an artefact of deriving formation pressure from drilling mud weights. When drilling through low permeability rocks, the borehole will not be in pressure communication with the rock and so high mud weights will be tolerated without affecting the well integrity. However, we assume that this is not since for two reasons: firstly, significant health and safety risk is associated with drilling with the incorrect mud weight, and it is considered poor practice to drill using mud weights that are not carefully calibrated to the subsurface conditions. Secondly, for many of the well logs it is clear that the mud weights have been adjusted many times during drilling to reflect the complexity of the overburden formations.

**Implications for storage site selection**

Pressure seals are commonly observed in the overburden of hydrocarbon provinces. They are a highly effective seal for two reasons; first they indicate the presence of very low permeability formations, like those proposed for caprocks in sequestration operations. Secondly, where the overburden fluid pressure exceeds that of the reservoir, the net fluid pressure gradient over the interval between the reservoir and overpressured formation is directed downwards. Fluids would therefore flow into the reservoir rather than up from the reservoir into the overburden. Despite this, to date, little attention has been paid to the role of pressure seals in ensuring secure CO$_2$ storage. For the case studies in Italy that are presented here, it is not possible to determine which of these two retention mechanisms offered by the pressure seal is important for CO$_2$ security – if any.

Current industrial screening practices and the regulatory framework for site selection typically focus on possible mechanisms of CO$_2$ leakage from the reservoir into the overlying caprock (capillary breakthrough, tensile fracturing of the caprock or fault slip, and brine displacement), or necessary reservoir conditions, rather than the barriers to fluid flow offered in the overburden overlying the reservoir (Hannon Jr and Esposito, 2015). Multilayered reservoir-caprock systems are identified as an effective barrier for leakage for storage site selection criteria (IEA-GHG, 2009), but the only site selection guidance document to mention caprock fluid pressure gradients are those prepared by the World
Resources Institute (2008) which note that the presence of a pressure differential between the reservoir and caprock is one characteristic that may demonstrate the ability of the caprock to prevent vertical migration of injected CO₂.

Table 3 summarises the published criteria for storage site selection that will minimize the risks associated with geological storage of CO₂ and how our case studies would perform against these criteria. All the reservoirs studied here, whether leaking or sealing, would not be deemed suitable for CO₂ storage. This suggests that site selection criteria are robust, and perhaps err on the side of caution. Table 3 shows how many of the reservoirs fulfill the most prescriptive criteria such as caprock thickness and reservoir pressure and temperature conditions. Only one reservoir, Muscillo, would be deemed too shallow for storage, since it is less than 800 m deep. Most of the other case studies would be deemed too deep according to Chadwick (2008) and CASSEM (2011), but not according to IEA-GHG (2009), who provide no depth cut-off. Avoiding deep reservoirs does not minimize the risks of leakage, but rather, the cost and ease of injection and monitoring, which at depths below 2500 m may become too difficult or expensive. In any case, the Aquistore CCS project in Canada is injecting at 3400 m (Rostron et al., 2014) and so clearly only the minimum depth criterion is prescriptive.

There is some uncertainty regarding the selection criteria for reservoir structures, and caprock continuity. The leaking Frigento reservoir would fail several selection criteria (it is shallow, CO₂ in the reservoir is in is light phase, see Table 3), however the only criterion that the Caprese reservoir might fail regards proximity to faults. Site selection guidelines for CCS recommend that reservoirs selected for CO₂ storage should have no faults, or should at least have small or low density of faults. However these are descriptive criteria; the constraints that define ‘low fault frequency’ or ‘small faults’, and whether this refers to fault length or fault throw, or only open faults, are not clear. Nor is it clear how their potential for storage integrity should be characterized; there are many examples from the hydrocarbon sector of sealing normal faults, and so the regional crustal stresses should also be considered. Further, the criteria refer mostly refer to faults in the reservoir (which our results indicate are not necessary for rapid CO₂ leakage from PSS1), rather than buried or surface faults in the overburden or nearby. Our results suggest that, for dense phase CO₂ to leak from a reservoir at a considerable rate (>100 t/d) faults do not need to connect from reservoir to surface, however to seep CO₂ to surface, permeable faults are needed to provide flow paths for less dense CO₂. We would therefore argue that any faults in the overburden, as well as those that intersect the reservoir should be characterised during site screening. Though the site selection criteria in Table 1 do not make it explicit, it is unlikely that sites located close to seismogenic faults would be considered for CO₂ storage.

The caprocks of most case studies are suitably thick, however it is difficult to determine if they would be considered ‘uniform’ or ‘extensive’ as required by (IEA-GHG, 2009, Chadwick, 2008). This is because the well logs provide the only information about the case study overburden. Since most are comprised of thin interlayered nappes, the caprocks may not be considered uniform on that basis. It is clear though several case studies have interlayered...
caprock-reservoir units comprising the overburden. This structure could be desirable above prospective CO₂ stores because interlayered reservoir units could, in the case of leakage, act as secondary or tertiary reservoirs and inhibit surface seepage. Our study suggests that CO₂ is securely retained in reservoirs with caprocks that would be deemed unsuitable for storage according to current criteria. It might be reassuring to policy makers and the public to learn that imperfect geosystems are capable of trapping large quantities of CO₂ in the reservoirs.

This work has identified two key controls on CO₂ retention: fluid pressure in the overburden and lateral distance of the reservoir from an active fault. The criteria for desirable properties of the caprock and overburden above prospect CO₂ stores should therefore be improved. The regional stress regime and the overburden should be characterised during site assessment, to identify the geological structure, pressure conditions, and possible fracture and fault properties (orientation, connectivity, stress state) in the overburden units. We recommend that the pressure seal becomes one of the first-order screening criteria for storage site selection. Furthermore, we support previous work proposing the artificial pressurisation of overburden units as an effective remediation option should leakage from an engineered CO₂ storage reservoir occur, since this would decrease or reverse the normal fluid pressure gradient (Reveillere and Rohmer, 2011, Benson et al., 2003).

The ascent of leaked CO₂

The Caprese Michelangelo and Mefite seeps are low temperature CO₂ emissions, mostly characterised by CO₂ venting, where CO₂ is released above ambient pressure (Chiodini and Valenza, 2008, Roberts et al., 2011). CO₂ is denser than air at surface temperature and pressure, and therefore subsurface pressure must be driving the escape of these fluids rather than buoyancy alone, otherwise gas would spread below surface in permeable soils. Pressurised CO₂ escape implies that flow is restricted below the surface. Previous work by Roberts et al (2014) found that CO₂ vents in Italy tend to occur along faults in low permeability rocks, and suggest that these rocks could be restricting CO₂ release from a more permeable (and CO₂-saturated) lithology beneath. Thus CO₂ release through low permeability rocks is limited to permeable pathways offered by open faults, and with minimal lateral CO₂ spread. As such, CO₂ flow could be restricted in the shallow subsurface.

Changes to fluid and rock properties encountered during ascent may restrict CO₂ flow at depth, too. Our calculations find that as CO₂ density decreases during ascent, the seepage area or rock permeability must increase for mass transport to be conserved, unless fluids are not in pressure equilibrium with the rocks that they flow through. Baffles to flow are intrinsic to matrix and fracture complexities in geological units and may encourage the channelling of ascending fluids. Fracture connectivity and rock permeability will not be continuous during fluid ascent from the reservoir. For example, there are several rock units in the Caprese overburden that have much lower permeability than that of the carbonate units directly overlying the reservoir, and so fracture permeabilities would be necessary for CO₂ transport through these units. What this amounts to is that, while free phase CO₂ may not initially
need fault related rock permeability to leak from the Caprese reservoir, such pathways will become necessary for CO₂ transport to the surface. The location of CO₂ seeps in Italy is largely fault controlled (Roberts et al., 2014, Ascione et al., 2014) and indeed the Caprese Michelangelo seeps emerge along fault traces (Bonini, 2009b). As such, natural CO₂ seeps illustrate the importance of considering the implications of fracture permeability for carbon capture and storage integrity (Bond et al., 2017).

Similarly, if CO₂ is migrating in its dissolved form, baffles to flow will arise from changes in the effective permeability when two phase flow establishes towards the phase transition depth, where CO₂ will start to exsolve from saturated waters. Flow rates will be inhibited as the effective permeability decreases, though gas lift may oppose this effect and as discussed in our analysis, the CO₂ and water phases have different properties and so may follow different flow paths. If both phases subsequently reach the surface, several seep types will emerge in the seep cluster. Otherwise, if the hydraulic head driving the ascending waters is not great enough to enable the fluids to reach the surface, only dry CO₂ seeps will manifest. In this way, CO₂ can be transported from the reservoir in its dissolved phase and seep as a free phase at the surface. Conversely, CO₂ can leak from the reservoir as a free phase and dissolve into overlying aquifer units during ascent, and seep as a dissolved constituent in springs. Detailed geochemical studies could elucidate possible transport paths.

This is important for site selection. The likely style of CO₂ seep that might establish at the surface near a leaking store has implications for the design of subsurface and surface monitoring systems for both verification and for early warning systems. Additionally, if a leak or seep is detected, then the remediation strategies adopted would be dependent on the style of seep (Hepple and Benson, 2003). Our work suggests that the characteristics of the overburden would allow some degree of forecasting of the risk and the potential risk mitigation strategies.

Conclusions

We have studied nine boreholes in Italy that penetrate CO₂ reservoirs. Two reservoirs have high-flux surface CO₂ gas seeps within 2.5 km of the wellbore and are inferred to be leaking, whereas five have no surface seep expression and are inferred to be effectively sealed. The remaining two have small CO₂ springs located within 5 km of the borehole. These reservoirs are deemed to be inconclusively sealing, since the springs could originate from water circulation through carbonate rocks rather than from reservoir leakage.

The CO₂ reservoirs exhibit a range of subsurface structures and conditions. Reservoirs successfully retain CO₂ in light or dense phase, and in some cases this CO₂ can be close to the critical point or exert high buoyancy pressures on the caprock. The presence of surface CO₂ seeps is also unaffected by the structure or burial depth of the CO₂ reservoir, though the presence of evaporites may enhance its sealing capabilities. There are no seeps above reservoirs with fluid overpressure in the overburden; high fluid pressures may indicate the presence of an effective seal. The pressure seal could indicate the presence of a very low permeability formation, or where the net fluid pressure gradient between the reservoir and
overpressured formation is directed downwards. Where there is a pressure seal, CO₂
buoyancy must be extraordinarily high to penetrate – or hydrofracture - the overpressured
formation. CO₂ seeps are located at the surface above reservoirs with hydrostatically
pressured overburden. These case studies are located near seismogenic extensional faults,
which may be responsible for subsurface pressure connectivity at these sites, which,
together with the higher permeability potentially offered by fault-related damage zones,
may enable CO₂ to leak to surface.

We assess the geological conditions that could enable CO₂ leakage from the reservoir at the
rates observed at the surface seeps. This finds that CO₂ is most likely to leak from the
reservoir in a free phase. While formation waters have the potential to dissolve large
quantities of CO₂, high leak rates of free phase CO₂ can occur over smaller areas and lower
permeability than those needed for transport of CO₂-saturated water at the same rate.
Significant (> 100 t d⁻¹) leakage of dense phase CO₂ from the reservoir can occur by flow
through the overburden without the need for faults or enhanced permeability pathways. In
contrast, for the same mass flux of CO₂ leaking in its light phase, fault permeabilities are
necessary since seepage through the overburden would otherwise have to occur over areas
too large to be geological feasible. Changes in CO₂ properties during ascent from the leaking
reservoir may therefore lead to the fluid channelling along high permeability pathways such
as faults. This leads to CO₂ venting and seep clustering observed at these sites in Italy.

This work informs the site selection of potential CO₂ stores, and the monitoring and leakage
remediation strategies at selected sites. We find that all cases studied, leaking or sealing,
would fail current storage site selection criteria. Although caprock thickness and reservoir
conditions would be deemed suitable for most case studies, the proximity to faults would
like be considered detrimental to storage security. However there is little guidance on the
acceptable properties (density, scale, aperture) of fractures or faults, which is significant
because our work suggests that, where the primary seal is breached, permeable fractures
could permit significant leak rates from reservoirs containing dense phase CO₂. We
recommend that the overburden should be well characterised to inform the site selection
process and monitoring design, and that more work is needed to detail the selection criteria
for suitable overburden properties. The presence of a pressure seal could be used as a first
order screening criteria for potential stores, where this information is available. Monitoring
should focus on high permeability pathways, such faults. It must be borne in mind that faults
do not need to connect the reservoir to the surface; even if they do not connect to the
reservoir at depth, they could provide efficient fluid pathways to surface; or they could
provide pathways through a caprock into the overburden. Artificial pressurisation of
overburden units overlying a breached engineered CO₂ store could be an effective
remediation option.
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Figure Captions

Figure 1A: Cross section of Italy modified from (Improta et al., 2000). Most CO$_2$ reservoirs are hosted by the Apulian Carbonate Platform (ACP) in the Inner Thrust Belt, and the Allochthonous Complex form the overburden. 1B: Map of Italy modified from (Patacca et al., 2008) detailing topography and the location of CO$_2$ seeps (dry and wet) and wells (including CO$_2$ wells not studied here), geological terrane boundaries (Ghisetti and Vezzani, 2002). 1C: Map of the Southern Apennine region, showing the location of CO$_2$-bearing wells, stress field data (Barba et al., 2009); Sh min = minimum horizontal stress), mapped seismogenic normal faults (Roberts, 2008) and deep platform carbonate structure (Nicolai and Gambini, 2007).

Table inset: Detail of seeps shows in (C), including name, seep type (v = vent; bw = bubbling water; s = spring; d = diffuse) and flux information (M = medium, H = high and NQ = not quantified; see text for definitions).

Figure 2: Map of the Southern Apennine region, showing the location of studied CO$_2$-bearing wells, CO$_2$ seeps (shaded according to whether dry (vent, diffuse seeps) or wet (springs, bubbling water), mapped seismogenic normal faults (Roberts, 2008), and lines of cross sections in Figures 3 - 6.

Figure 3: Benevento and Monte Taburno structures (cross section A-A’ in Fig. 2) and pressure-depth profiles for the Tranfaglia (Tr1), S. Arcangelo di Trimonte (SAT1), Benevento Sud (BS1), Monte Taburno (MT1) and Muscillo wells. CO$_2$-bearing formations are shaded in the depth profile of the well logs. It is unclear if the Motta and Buonalbergo CO$_2$ springs are related to the subsurface CO$_2$ fields, though they do exhibit significant deep CO$_2$ contributions. BS1, SAT1 and Tr1 show significant overpressure in the overburden. Data from: borehole logs; (Chiodini et al., 2010, Di Bucci et al., 2006, Improta et al., 2003b, Nicolai and Gambini, 2007).

Figure 4: Subsurface structure (cross section B-B’ in Fig. 2) and boreholes that penetrate the Frigento Formation (Ciccone, Cic1; Monte Forcus 1, MF1; Monte Forcus 2, MF2). MF1 drills a CO$_2$ accumulation in the ACP at hydrostatic pressure (see shaded horizon on the depth profile), but MF2 and Cic1 drill into the water leg. Mefite D’Ansanto (and Mefitiniella polla not shown here) are high flux CO$_2$ vents. San Teodoro, located on the SW flank of the antiform, is a sulphurous thermal spring that does not degass CO$_2$. Data from: borehole logs; (Di Bucci et al., 2006, Improta et al., 2003b).

Figure 5: Subsurface structure of the Acerno and Contursi reservoirs (cross section C-C’ in Fig. 2) showing the location of the Acerno (Ac1) and Contursi (Co1) wells. Acerno (Ac1) contains CO$_2$ at 4263 m below surface (see grey shaded horizon on well log depth profile). The Contursi borehole (Co1) did not intercept any CO$_2$ accumulation at depth and so is not considered in our analysis. There are no known seeps above the Acerno horst structure. Data from: borehole logs, Improta (Improta et al., 2003b, Scrocca, 2005).

Figure 6: Depth and pressure profile of the Pieve Santo Stefano borehole. This borehole is located in Tuscany, in the Northern Apennines (see Fig 1). The multi-layered CO$_2$ reservoir (shaded in grey in the well log) is hosted in thin dolomite layers (sandwiched between
anhydrite layers) of the Burano Formation. The CO₂ is significantly above hydrostatic pressure conditions. The Caprese Michelangeo and Fungaia CO₂ vents are located near to the Pieve Santo Stefano well and are considered to represent surface seepage of the reservoir. \textit{Data from:} borehole logs; (Bonini, 2009a, Heinicke et al., 2006).

**Figure 7:** CO₂ pressure-density phase diagram at reservoir/seal boundary of CO₂ bearing reservoirs. Calculated CO₂ buoyancy is shown next to the data points where information is available. Critical density and critical pressure are shown as thin grey lines (and annotated). Only one reservoir, Mu1, contains CO₂ in gas phase, all other case studies contain supercritical CO₂ in both dense and light phase. Neither CO₂ density nor buoyancy determines if a reservoir is sealing in these case studies.

**Figure 8:** Thickness of impermeable rock formations in the overburden, as interpreted from the well logs of CO₂ reservoirs, and the leaking/sealing classification of the reservoir. The thickness of low permeability formations does not control whether or not the reservoir leaks CO₂ to surface.

**Figure 9:** Fluid overpressure in the overburden of studied CO₂ reservoirs and the interpretation whether or not the reservoir is leaking CO₂ to surface. The degree of overpressure is indicated by the ratio of fluid pressure ($P_f$) to hydrostatic pressure as interpreted from the density of the drilling mud in the well log. The data points are coloured according to whether the reservoir is interpreted to be leaking (red), sealing (green) or is inconclusive (orange). CO₂ reservoirs with fluid overpressure (> 3 MPa) in the overburden do not have CO₂ seeps located within at least 10 km of the borehole and so are considered to be sealing reservoirs (green). In contrast, for deep CO₂ reservoirs that have little or no overpressure in the overburden are located close to CO₂ seeps (red). The shallow Mu1 reservoir shows low CO₂ saturation, hence why it is not considered to be a significant CO₂ reservoir.

**Figure 10:** Fluid overpressure in the overburden of studied CO₂ reservoirs and the lateral distance of the well to the nearest modern extensional fault structure. CO₂ structures that are located within 8 km of a fault leak CO₂ to surface. The degree of overpressure is indicated by the ratio of fluid pressure ($P_f$) to hydrostatic pressure as interpreted from the density of the drilling mud in the well log. Wells are coloured according to whether the reservoir is leaking CO₂ to surface (red) or not (green) or indeterminately so (orange). Overburden overpressure correlates with distance to modern extensional faults mapped by Roberts (2008). CO₂ reservoirs that are classified as leaking (i.e. are located within 5 km of CO₂ seeps) show hydrostatic pressures in overburden formations, and are located within 8 km of a modern extensional fault. Mu1 does not fit this trend, possibly because it is so shallow; it is located over 40 km away from any mapped structures and so cannot fit on these axes.

**Figure 11:** The area and effective permeability at the reservoir top necessary for reservoir fluids (free phase or dissolved CO₂) to seep at 100 t[CO₂]d⁻¹ from PSS1 reservoir conditions and 100 and 2000 t[CO₂]d⁻¹ from MF1 conditions. For light or dissolved phase CO₂ to leak from
the reservoir at these rates, high permeability pathways in the overburden such as those offered by open fractures or faults are needed. In contrast, it is possible for dense phase CO₂ to leak from PSS1 into low permeability overburden formations at 100 t(CO₂)d⁻¹ without the need for fracture permeability. Typical rock permeabilities and seepage area are annotated to the right of the plot. Permeabilities from well logs are annotated: i = Jurassic Umbria-Marche overburden in PSS1; ii = Allochthonous Complex overburden in MF1 well; iii = APC in MF2. Vertical lines A-D show estimates of minimum area of seepage at Caprese and Frigento case studies: (A) main area of degassing at the Caprese Michelangelo (B) area of degassing at Mefite (C) cluster area at the Caprese Michelangelo (0.2 km x 1.52 km) and the Mefite and Mefitiniellapolla vents (3.5 km x 0.1 km), and minimum area of seepage from (D) the Frigento CO₂ reservoir top (2 km radius circle) and (E) the Caprese CO₂ reservoir top (5 x 10 km ellipse). The table inset show calculated seep areas using relevant permeabilities, and permeability calculations using areas A-E. These illustrate that for dense phase CO₂, high seep rates require only very small volumes of CO₂ to leak from the reservoir compared to light phase CO₂. Similarly, for the same leak rates, much larger volumes of CO₂ must leak from the reservoir compared to free-phase CO₂.

Table 1: Table summarising published CO₂ storage site selection criteria that are recommended to minimize the risks of CO₂ leakage. Adapted from (Miocic et al., 2016).

Table 2: Table summarizing the reservoir and overburden characteristics for each CO₂-bearing borehole, including the properties of the CO₂, the presence of nearby seeps or faults, and whether the reservoir is interpreted to be sealed or leaking CO₂ to surface. If reservoir or overburden formation fluid pressures are 3 MPa above hydrostatic it is considered overpressured. For CO₂ density, ‘dense’ refers to CO₂ with densities greater than the critical
density ($\rho_c = 464$ Kg m$^{-3}$) and ‘light’ refers to CO$_2$ with densities below the critical density, and SC refers to supercritical phase. Where column heights aren’t known, buoyancy pressure, $B$, cannot be calculated. Further detail about the seeps (number, type, flux, temperature) are tabulated in Figure 1B. Modeled conditions in SAT1 are unreliable (see main text for details).

**Table 3:** Table summarizing how the natural CO$_2$ reservoirs in Italy studied in this paper would perform against published criteria for CO$_2$ storage site selection, where (A) Chadwick, 2008 (B) IEA-GHG, 2009 (C) CASSEM, 2011. All the case studies, whether leaking or sealing, would not be deemed suitable for CO$_2$ storage. Two of the features, reservoir structure and caprock continuity are descriptive and therefore difficult to determine whether the case studies would fulfill these criteria or not.
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Pieve Santo Stefano
Pressure (MPa)
Leaking

PSS1

MT1

Inconclusive

Ac1

Tr1 - no definable seal

Sealing

Ben2

Mu1

BS1

SAT1

Seal Thickness (m)

3000 2500 2000 1500 1000 500
Leaking

PSS1, MF1

Inconclusive

MT1

Sealing

Mu1

Ac1, BS1, SAT1, Ben1, Ben2

Significant CO₂ Reservoir

Possible CO₂ reservoir

Maximum estimated fluid / hydrostatic pressure in overburden
Typical Rock Permeabilities

Leakage of CO₂ fluids from the reservoir

Free Phase CO₂
- PSS1 dense phase
- MF1 light phase

Dissolved CO₂
- CO₂ leak rate

Leakage of CO₂ fluids from the reservoir

Free Phase CO₂
- PSS1 dense phase
- MF1 light phase

Dissolved CO₂
- CO₂ leak rate

Discrete Cluster Area Reservoir Top

Monte Forcuso (MF1)
Caprese (PSS1)

Free Phase
- 0.116
- 0.032

Dissolved
- 0.027
- 0.032

Leak Rate (m³s⁻¹)

Top Reservoir Phase Free Phase Dissolved

Discrete
- 2000 t d⁻¹ CO₂ (Mefite D’Ansanto)
- 100 t d⁻¹ CO₂ (Fungaia)

Path
Area (m²) Kₑ (mD) Area (km²) Kₑ (mD)
Discrete A & B B (4000 m²) 6.9e+03 3.6e+05 A (400 m²) 1.6e+03 5.3e+04
Cluster Area C C (0.35 km²) 2.5e+01 1.3e+03 C (0.35 km²) 2 6.9e+01
Reservoir Top D & E D (12.6 km²) 2.2 1.1e+02 E (39.3 km²) - -

Path
Area (m²) K (mD) Area (km²) K (mD)
Fractured APC i & ii 10⁴ 2770 m² 144000 m² 10³ 63.4 m³ 2117 m²
Overburden i & ii ii (0.8) 276 km² 14400 km² i (24) 0.025 km² 0.88 km²
Hydrostatic Reservoir top
Modeled Well Data
Uncertainty
Liquidus
Isotherms
Reservoir top
Modeled
Hydrostatic

A

Pressure (MPa)

CO₂ Density (kg m⁻³)

Top Res. PSS1
Top Res. MF1

B

Well Data
Modeled

Depth Profile
Uncertainty
Liquidus
Isotherms
Reservoir top

Surface

Depth (m)

Top Res. MF1
Top Res. PSS1

C

Well Data

Surface

Depth (m)

Top Res. MF1
Top Res. PSS1

CO₂ Solubility (molal)
Table 1 – *Table summarising published CO₂ storage site selection criteria*. These criteria are recommended to minimize the risks of CO₂ leakage. Adapted from (Miocic et al., 2016).

| Feature       | Criteria/Requirement                                      | Source                                      |
|---------------|-----------------------------------------------------------|---------------------------------------------|
| **CO₂ Properties** |                                            |                                             |
| CO₂ State     | Dense phase                                               | (Chadwick, 2008)                           |
| **Reservoir Properties** |                                            |                                             |
| Structure     | No faults, or small faults. Low faulting frequency.       | (Chadwick, 2008, IEA-GHG, 2009, CASSEM, 2011) |
|               | Multi-layered system                                      | (IEA-GHG, 2009)                           |
| Depth (m)     | Between 800 - 2500                                        | (Chadwick, 2008, IEA-GHG, 2009, CASSEM, 2011) |
|               | Below 800 m                                               | (IEA-GHG, 2009)                           |
| Temperature   | > 35 °C                                                   | (IEA-GHG, 2009)                           |
| Pressure (MPa)| >7.5                                                       | (IEA-GHG, 2009)                           |
| **Caprock Property** |                                            |                                             |
| Thickness (m) | Between 10 – 100 m                                        | (Chadwick, 2008, IEA-GHG, 2009, CASSEM, 2011) |
| Continuity    | Uniform                                                   | (Chadwick, 2008)                           |
|               | (laterally) Extensive                                     | (IEA-GHG, 2009)                           |
Table 2 – *Table summarizing the reservoir and overburden characteristics for each CO₂-bearing borehole*, including the properties of the CO₂, the presence of nearby seeps or faults, and whether the reservoir is interpreted to be sealed or leaking CO₂ to surface. If reservoir or overburden formation fluid pressures are 3 MPa above hydrostatic it is considered overpressured. For CO₂ density, ‘dense’ refers to CO₂ with densities greater than the critical density ($\rho_c = 464$ Kg m$^{-3}$) and ‘light’ refers to CO₂ with densities below the critical density, and SC refers to supercritical phase. Where column heights aren’t known, buoyancy pressure, $B$, cannot be calculated. Further detail about the seeps (number, type, flux, temperature) are tabulated in Figure 1B. Modeled conditions in SAT1 are unreliable (see main text for details).

| Field/Reservoir | Borehole name; abbreviation | Reservoir conditions | CO₂ properties | Overburden conditions | Distance from borehole to: | Interpretation |
|-----------------|----------------------------|----------------------|----------------|----------------------|----------------------------|----------------|
| Benevento Sud   | Benevento Sud 1; BS1       | Depth below surface /m | CO₂ %v.v | Over pressure | Porefluid factor | Density kg/m$^3$ (phase) | Buoyancy / MPa | Evaporite factor | Seal thickness / m (min – maxN) | Overpressure (ratio compared to hydrostatic) | Seep Name (no. in Fig. 1); distance (km) | Fault Distance km$^{-1}$ (name, sense) |
|                 |                            | 2710                 | 98.5        | N            | 0.4          | 624 ± 15 (dense - SC) | 5              | Y (9 m)     | 315 - 2710 | Y (1.56) | None | 5 (S. Matese, N); 15.7 (Telese Fault, N) | Sealing |
|                 | S. Arcangelo di Trimonte; SAT1 | 1520                 | -           | Y            | 0.6          | 503 ± 11 (dense - SC) | -              | N           | 1520 - 1520 | Y (1.62) | None | 4.8 (S. Matese, N); 23.2 (Telese Fault, N) | Sealing |
| Tranfaglia; Tr1 |                            | 2773                 | 98          | N            | 0.4          | 279 ± 6 (light - SC) | -              | Y (17 m)    | None       | Y (1.67) | None | 7 (S. Matese, N); 20 (Ufita Fault, N) | Inconclusive |
|                 | Benevento 002; Ben2        | 3300                 | 94          | N            | 0.6          | 797± 9 (dense - SC) | 1.8            | N           | 30 - 600   | Y (1.68) | None | 12.7 (Boiano, N); 22 (Telese Fault, N) | Sealing |
| Monte Taburno   | Monte Taburno 1; MT1       | 2093                 | >90         | Y            | 0.5          | 569 ± 10 (dense - SC) | 1.1            | Y (2 m)     | 543 - 890  | N (1.08) | Motta (2); 1.6 km | Inconclusive |
|                 | Muscillo; Mu1              | 694                  | 97 (low sat)| N            | 0.4          | 139 ± 19 (light - gas) | 2.2            | N           | 305 - 305  | N (1.09) | None | 8 (Montesarchio, N) | Sealing |
|                 |                            |                      |             |             |             |                     |                |             |            |         |            |       |
| Field/Reservoir | Borehole name; abbreviation | Reservoir conditions | CO₂ properties | Overburden conditions | Distance from borehole to: | Fault | Interpretation |
|-----------------|-----------------------------|---------------------|----------------|-----------------------|---------------------------|-------|---------------|
| Frigento        | Monte Forcuso 1; MF1        | 1128 99.7 N 0.4     | 200 ± 5 (light - SC) 3.5 N 168 - 1128 N (1.21) | Mefiteniella polia (4); 5.4 km Mefite D’Ansanto (5); 1.8 km | 4.3 (Ufita, N) | Leaking |
| Acerno          | Acerno 1; Ac1               | 4263 97 Y 0.6       | 919 ± 8 (dense - SC) - Y (80 m) 70 - 228 Y (1.48) | San Benedetto(6); 11 km Contursi cluster (7); 15.5 km | 2.6 (Sabato Valley; N); 11.5 (Volturata, N) | Sealing |
| Caprese         | Pieve Santo Stefano 1; PSS1 | 3600 92.2 Y 0.7     | 830 ± 8 (dense - SC) 1.1 Y (70 m) 150 - 550 N (1.08) | C. Michelangelo (9); 2.5 Fungaia (10); 3.6 | 7.9 (Upper Tiber Valley, N) | Leaking |
Table 3: Table summarizing how the natural CO$_2$ reservoirs in Italy studied in this paper would perform against published criteria for CO$_2$ storage site selection, where (A) Chadwick, 2008 (B) IEA-GHG, 2009 (C) CASSEM, 2011. All the case studies, whether leaking or sealing, would not be deemed suitable for CO$_2$ storage. Two of the features, reservoir structure and caprock continuity are descriptive and therefore difficult to determine whether the case studies would fulfill these criteria or not.

| Case Studies | Property | CO$_2$ Properties | Reservoir Properties | Caprock Property |
|--------------|----------|--------------------|----------------------|------------------|
|              | Feature  | CO$_2$ State       | Structure            | 800 – 2500 m     | > 800 m          | > 35 °C | > 7.5 | Thickness | Continuity |
|              | Criteria | Dense phase        | (i) Small or no faults | Multi-layered     | > 800 m          | > 35 °C | > 7.5 | 10 – 100 m | (i) Uniform |
|              |          |                    | (ii) Low fault frequency | system            |                  |        |        |           | (ii) Extensive |
| Source       | A        | A, B, C            | B                    | A, B, C           | B                | B      | B      | A, B, C   | (i) A (ii) B  |

**Case Studies**

| Leaks        | MF1      | Y                  | N                  | N                  | N                  | Y      | Y      | Y      | Y      | Y      | ?      |
|--------------|----------|--------------------|--------------------|--------------------|--------------------|--------|--------|--------|--------|--------|--------|
| PSS1         | Y        |                    | N                  | Y                  | N                  | Y      | Y      | Y      | Y      | Y      | ?      |
| Inconc.      | TR1      | N                  | N                  | N                  | N                  | Y      | Y      | Y      | N      | ?      | ?      |
| MT1          | Y        |                    | N                  | N                  | N                  | Y      | Y      | Y      | Y      | ?      | ?      |
| Seals        | BS1      | Y                  | N                  | N                  | N                  | Y      | Y      | Y      | Y      | ?      | ?      |
| SAT1         | N        |                    | Y                  | Y                  | Y                  | Y      | Y      | Y      | Y      | ?      | ?      |
| BEN 2        | Y        | ?                  | N                  | N                  | Y                  | Y      | Y      | ?      | ?      | ?      | ?      |
| Ac           | Y        |                    | N                  | N                  | N                  | Y      | Y      | Y      | ?      | ?      | ?      |
| Mu           | N        |                    | Y                  | N                  | N                  | N      | Y      | N      | Y      | ?      | ?      |