Surface controls on the characteristics of natural CO$_2$ seeps: implications for engineered CO$_2$ stores

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ABSTRACT

Long-term security of performance of engineered CO$_2$ storage is a principle concern because leakage of injected CO$_2$ to the surface is economically and environmentally unfavourable, and could present a human health hazard. In Italy natural CO$_2$ degassing to the surface via seeps is widespread, providing an insight into the various styles of subsurface ‘plumbing’ as well as surface expression of CO$_2$ fluids. Here we investigate surface controls on the distribution of CO$_2$ seep characteristics (type, flux and temperature) using a large geographical and historical data set. When the locations of documented seeps are compared to a statistically random data set, we find that the nature of the CO$_2$ seeps is most strongly governed by the flow properties of the outcropping rocks, and local topography. Where low-permeability rocks outcrop, numerous dry seeps occur and have a range of fluxes. Aqueous fluid flow will be limited in these low-permeability rocks, and so relative permeability effects may enable preferential CO$_2$ flow. CO$_2$ vents typically occur along faults in rocks that are located above the water table or are low permeability. Diffuse dry seeps develop where CO$_2$ (laterally supplied by these faults) emerges from the vadose zone and where CO$_2$ degassing from groundwater follows a different flow path due to flow differences for water and CO$_2$ gas. Wet seeps characterized by water bubbling with CO$_2$ arise where CO$_2$ supply enters the phreatic zone or an aquifer. Springs containing dissolved CO$_2$ often emerge where valleys erode into CO$_2$ aquifers, and these are typically high flux seeps. Seep type is known to influence human health risk at CO$_2$ seeps in Italy, as well as the topography surrounding the seep which affects the speed of gas dispersion by wind. Identifying the physical controls on potential seep locations and seep type above engineered CO$_2$ storage operations is therefore crucial to targeted site monitoring strategy and risk assessment. The surface geology and topography above a CO$_2$ store must be characterized to design the most effective monitoring strategy.

Key words: carbon capture and storage, carbon dioxide, fault, hydrogeology, leakage, monitoring

INTRODUCTION

Industrialized societies that continue to use fossil fuel energy sources are considering adoption of carbon capture and storage technology to meet carbon emission reduction targets (Haszeldine 2009). Naturally occurring CO$_2$ seeps provide opportunity to understand the crustal fluid pathways of CO$_2$ migrating from depth. This not only informs the long-term performance security of engineered CO$_2$ storage, but also enables the development of more accurate seepage risk assessment and surface monitoring strategies.

In central and southern Italy and Sicily, over 308 CO$_2$ seeps at 270 locations have been spatially and historically documented to date (Chioldini et al. 2008). The natural CO$_2$ release is globally significant – discharge from regional aquifers in western central Italy is estimated to account for over 10% of the present-day global CO$_2$ budget from subaerial volcanoes (Chioldini et al. 2004), which is estimated to be 300 Mt per year (Perez et al. 2011).

Groundwater pollution, ecosystem damage and CO$_2$ poisoning of animals and humans are associated with CO$_2$ leakage (Roberts et al. 2011). Italian seeps exhibit a variety of surface expressions (seep types), temperatures and fluxes.

Our previous work examined the health risk from natural seeps (Roberts et al. 2011). The environmental hazard of seeps depends on how CO$_2$ is dispersed rather than the flux alone (Hepple 2005), and historical records of very rare human deaths at Italian gas seeps have found that dry seeps pose the greatest death risk (Roberts et al. 2011). Rock structure influences seep density distribution.
(Chiodini, 1995; Bonini 2009a); however, the local factors governing seep characteristics and distance from deep geological structures are not currently known, so we examine the influence of near-surface geological structures, in particular host lithology and topography, on the distribution of CO2 seep types, temperature and flux.

**Italian CO2 seeps and their origin**

The subaerial CO2 seeps in Italy (Fig 1A) exhibit five types of natural seep: vents, diffuse seeps, springs, bubbling pools of standing water and volcanic fumaroles (Chiodini et al. 2008), and bubbling water and diffuse seeps are the most common (Fig 1B). Several deep boreholes are also known to leak CO2; these seeps are classified as CO2 wells. CO2 is degassed together with lesser amounts of N2, H2S, CH4, H2, Ar, He and CO (Minissale 2004). Gas flux can vary between locations, from <1 t d⁻¹ to >2000 tonnes day⁻¹ (t d⁻¹), but most commonly (37% of seeps with measured fluxes) between 10 and 100 t d⁻¹ (Roberts et al. 2011).

Aside from fumaroles, springs are the warmest seeps (mean temperature ~35°C), bubbling water seeps are cooler (mean temperature ~26°C), and diffuse and vent seep temperatures are coolest (mean temperature ~18–20°C). CO2 degassing is greatest towards the Tyrrhenian sector, where the crust is thinned and there is high heat flow (Fig 1A). Crustal extension is currently active in the Apennine Mountains where CO2 flux is much reduced and trapped CO2 fluids at depths >5 km are known to affect the seismicity and deformation style of the region (Miller et al. 2004).

Nineteen sites exhibit more than one seep type at a single location (dual-system seeps). Diffuse seeps are often paired with either vents or bubbling water seeps (Roberts et al. 2011). While flux, seep types and seep locations are assumed constant here, there is evidence of seasonal seep variation in water content and concomitant migration of edifices by several metres (Heinicke et al. 2006). Additionally, the flux at several seeps has been affected by deep seismic events (Bonini 2009b; Heinicke et al. 2010).

Numerous geochemical studies have examined the sources of CO2 in Italy (Minissale et al. 1997; Chiodini et al. 2004; Minissale 2004; Marzano et al. 2007). Carbon and noble gas isotopes identify several regional contributions to CO2 degassing including shallow biogenic processes; carbonate hydrolysis; deep burial mechanical breakdown or thermo-metamorphism of carbonates; and mantle degassing during volcanism (Chiodini et al. 2004).

Discharges of thermal and cold CO2 fluids are fed by a regional aquifer within Mesoozoic carbonates (Minissale 2004). Travertines are a direct consequence of dissolved CO2, and active and inactive (fossil) travertine systems are widespread. Travertine carbon isotopes show evidence of CO2 contributions from metamorphic and mantle sources (Minissale 2004). Travertines, thermal springs and seeps may be with karst-collapse associated sinkholes which often follow active faults (Santo et al. 2011), showing long-term groundwater flux in these areas.

**CO2 flow in geological formations**

CO2 fluids are retained in deep geological formations (>1 km depth) as either a free dense phase (in either liquid or supercritical phase) or dissolved form. CO2 that remains as a free phase is less dense than surrounding pore waters and so will buoyantly rise, until it meets low-permeability

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**Fig. 1.** (A) Sketch of Italy and Sicily showing the location of the two categories of CO2 seep classes (categories explained in Figure 1B). ‘Wet’ seeps are shown as black circles, ‘dry’ seeps are shown as grey circles. Filled symbols show multiple seeps. (B) Proportion of CO2 seep types (classified according to surface expression, n = 308). Seep classes can be grouped into aqueous (‘wet’) and nonaqueous (‘dry’) categories. Wells are artificial leaking pathways.
geological barriers that restrict or inhibit fluid flow. Such barriers may be low-permeability rocks or sealed faults, which will cause CO₂ accumulation or lateral dispersion, restricting CO₂ ascent until another fluid permeable pathway is encountered or the buoyancy pressures of the fluids exceed the capillary entry pressures of the seal (Naylor et al. 2011).

Any dense-phase CO₂ will dissolve when it is in contact with unsaturated formation waters, which increases the water density (Spycher & Pruess 2005). Significant CO₂ dissolution requires adequate mixing with formation waters, and so CO₂ flow paths that do not encourage significant CO₂ mixing with pore fluids, such as flow through low-permeability rocks or along permeable pathways, will minimize CO₂ dissolution.

High-permeability pathways are required to bring free-phase CO₂ fluids from depth to the surface, and crustal fluid flow is commonly controlled by deformation-induced permeability of fault and fracture networks (Agosta et al. 2010; Faulkner et al. 2010). As CO₂ fluids ascend from depth to the surface, there are several changes to the subsurface environment that will affect fluid flow: (1) Fracture aperture: The damage zone and impermeable core properties of evolved faults behave as a fluid barrier–conduit system (Caine et al. 1996). In the shallow crust, uncremented macro-fractures dominate fluid flow. These macro-fractures might be subsidiary faults and fractures associated with large faults or bedding planes and joints (Agosta & Kirschner 2003; Agosta et al. 2010). The permeability of these fractures rapidly decreases with depth, as they become mechanically sealed. Micro-fractures seal less rapidly so increasingly dominate rock permeability at depths approximately >1.5 km (Nara et al. 2011). At depths below this, fluid flow is governed by matrix and micro-fracture permeability. Here, faults will remain important, as micro-fracture density is greatest in fault damage zones and scales with fault displacement (Mitchell & Faulkner 2012).

(2) Relative permeability effects: A rock volume will commonly exhibit a distribution of fluid pathway geometries due to geological heterogeneity and the presence of fractures. Permeability to fluids such as CO₂ can be provided by matrix or fracture flow, and is a function of the relative permeability – which refers to the fraction of the total permeability that is accessible to each fluid phase. Single-phase flow, such as CO₂-saturated water flowing through a water-wet rock, or CO₂ gas flowing through a gas-wet rock, accesses all rock permeability. However, for two-phase flow, such as free-phase CO₂ flowing through a water-wet rock, the relative permeability is influenced by the formation water saturation in the pores or fractures through which the CO₂ is flowing.

(3) Hydrologic Zones: Fluids migrating from depth will pass through two shallow depth hydrogeological zones on ascent from ~700 m to the surface: the phreatic (water-saturated) zone followed by the vadose (unsaturated) zone. A proportion of gaseous CO₂ will dissolve into phreatic (saturated) pore fluids during this ascent. In the phreatic zone, gaseous CO₂ is less dense than the pore fluids, so CO₂, driven by buoyancy, will migrate via matrix or fracture flow. In the vadose zone, gaseous CO₂ is denser than soil–gas and therefore may collect and laterally disperse above the water table (Annunziatellis et al. 2008). Dispersion in the vadose zone will lead to CO₂ seepage over a larger area than that of the point of emission from the saturated zone.

(4) Pressure (P) and temperature (T): Both pressure and temperature will decrease during the ascent of aqueous fluids, which increases CO₂ buoyancy due to density contrasts. The effects on CO₂ solubility are more complex. As deep circulating CO₂-saturated waters rise towards the surface, CO₂ solubility will first increase (temperature effects), pass a peak and then decrease (pressure effects), whereafter dissolved CO₂ will begin to be released from solution and two-phase flow conditions become established. The transition from dense-phase to gaseous-phase CO₂ is associated with rapid solubility decrease (Spycher & Pruess 2005), increased buoyancy and increased interfacial tension (IFT) with water. Gaseous CO₂ is therefore likely to have different near-surface leakage pathways than aqueous fluids.

Collettini et al. (2008) propose that lithology can affect seep density and flux. The carbonate aquifers of the Apennine Mountains can accommodate great volumes of fluids and allow long residence periods with effective mixing. Models suggest that the carbonate aquifers can hold 10 times more CO₂ than flysch, and 2.5 times more than volcanic rocks before gas leaks at the surface (Collettini et al. 2008). It can therefore be predicted that seeps from volcanic rocks will be more numerous and dry, whereas wet seeps or rarely high flux dry seeps will emerge from aquifers such as carbonates. This is supported by observations that thermal springs, which indicate rapid fluid ascent, tend to discharge in topographic lows along faults at the contact between the Mesozoic limestones and overlying volcanosedimentary formations in Italy (Minissale 2004; Collettini et al. 2008).

Hydrogeological features can influence the dispersion of CO₂ fluids in the vadose zone. Here, we investigate the relationship between seep characteristics (type, flux, temperature) and distribution with respect to host lithology, the landform (as a proxy for groundwater level) and any travertine deposits. Seep type and flux influence the risk to human health, and the most effective methods of CO₂ detection. Therefore, understanding how geological factors influence the nature of near-surface CO₂ dispersion and
surface seepage will inform risk assessment and monitoring strategy above carbon stores.

**METHODS**

Seep data were collected from Googas (Chiodini et al. 2008), a web-based catalogue of degassing sites (where CO₂ flux > background) in Italy constructed as a national project by the Istituto Nazionale di Geofisica e Vulcanologia (INGV). Additional communications have been made with Googas collaborators (G. Chiodini and C. Cardellini and colleagues), alongside personal fieldwork and a review of current published scientific literature. Googas documents 286 seep locations, 323 seeps overall, of which 308 are of dominantly CO₂ rather than CH₄ (Fig 1).

Six CO₂ seep types (bubbling water, diffuse, fumarole, spring, vent and well) are classified by the Googas seep catalogue (Chiodini et al. 2008). Man-made wells are not natural CO₂ leakage pathways, but rather indicate the presence of subsurface CO₂ reservoirs. In the Googas database, seep location, seep type and any accidents are recorded for each seep. Additional information includes any measurements of seep flux, temperature and composition. Flux is measured in tonnes per day (t d⁻¹), and categories are low (<1 t d⁻¹), medium (1–10 t d⁻¹), high (10–100 t d⁻¹) and very high (>100 t d⁻¹). We here refer to low-end (low and medium) and high-end (medium and high) flux seeps. Seep location and characteristics such as flux are assumed to be effectively constant. Case study sites show seasonal seep water content variation and concomitant migration of several metres (Heinicke et al. 2006), and flux variation with local seismic events (Heinicke et al. 2006; Bonini 2009a,b), but these variations are below the accuracy of the data set presented here.

A geospatial information system, ArcGIS, was populated with seep data, SRTM 90 m Digital Elevation Model (DEM; Jarvis et al. 2008), together with fault information, surface lithology and travertine distribution. Where more than one CO₂ seep classification is expressed at a single location, it is treated as several individual seeps and proceeding calculations are corrected to account for this.

Lithological information was extracted from a 1:500 000 scale geological map of Italy. The 128 different lithologies were classified into 18 broad rock types, then further grouped into 6 general rock categories (Igneous, Metamorphic, Basin slope, Terrestrial, Platform margin and Platform interior; see Supporting Information). The number of seeps emerging from each rock type was normalized to the total outcrop area. Travertine is a surface deposit formed from waters with high dissolved CO₂ content. We therefore do not consider it as a host rock lithology.

The elevation above sea level (asl) of each CO₂ seep was extracted from the DEM. We used a GIS function to extract from the digitized geological map the outcropping rock type where the CO₂ seep is located (which we call the host rock lithology).

We determined the range of elevations of rocks types in peri-Tyrrhenian region where seeps outcrop by the following workflow: (i) we used a standard GIS function to generate a synthetic data set of 10 000 randomly (Poisson) distributed points within the areal extent of Italy; (ii) a subset of this synthetic data set was created by selecting points located within 30 km of a known seep; (iii) For each point in this subset, the host rock type and elevation asl were determined by simple GIS functions.

The large number of points in the synthetic data set meant each rock type that outcropped within 30 km of a seep hosted a number of points. As such, the elevations measured by points located in the same rock type should indicate the range of elevations where that rock type outcrops where seeps are located in Italy. This enabled us to examine the elevation range for each seep types and the elevation range of their common rock types.

To examine the effect of local topography rather than overall elevation, we analysed the distance and elevation of seeps from channels. Channel network analysis in ArcGIS identifies where water should flow given topography, and depicts stream networks for basins of given sizes. To define stream networks, the DEM was prepared using standard fill and flow routing algorithms (Tarboton et al. 1991). Critical drainage areas were defined at 8 km² to extract streams of different channel volumes. Strahler stream order (Strahler 1952) was calculated from the resulting valley bottom network. The channel sizes considered are herein referred to as ‘stream’ (order 100) and ‘river’ (order 1000). Here, we are interested in identifying topographic lows in the land surface, so do not verify whether predicted channel networks correspond with real rivers, streams or stream type. Elevation of seeps from the nearest (geodesic) channel (referred herein as Δelev_stream and Δelev_river) was calculated by performing a near-analysis (GIS function) from seeps to stream lines to create points. The elevation of these points in the channel was interpolated from the DEM. Seep elevation from channel base is then calculated by the difference in elevation between the seep and the point we create in the channel nearest the seep.

These analyses allow us to examine the relationship between seep characteristics (including type, flux and temperature) and the host rock type, and also the seep distance and elevation from topographic lows (channel base). Analyses were repeated for a second synthetic data set of randomly distributed points (with the same number of points as the seep database) in the spatial extent of Italy. This tests the deterministic control of shallow geology on CO₂ seep type and distribution, because we can test whether the observations of CO₂ seeps, rock types and elevation are significantly different from random.
RESULTS

Topography

Analysis of the elevation of seeps (asl) shows that seep types show different elevation distributions and all nonvolcanic seeps have lower mean elevations than synthetic data although the difference between vents and the synthetic data is not significant (Fig. 2). Spring and bubbling water seeps show the lowest mean elevations, which is ~100 m less than dry seep types and 160 m below the synthetic random mean elevations. Volcanic fumaroles show the highest mean elevations and lowest range, likely a function of volcano height. However, more generally igneous rocks outcrop at considerably lower elevation than the platform rock categories.

Figure 3A shows that bubbling water and spring type seeps are more common close to the mid-points of river channels than vents and synthetic, randomly distributed, points (66% are located within 500 m of a river). By contrast, CO2 vent and fumarole positions are less commonly located close to the mid-points of river channels. Diffuse seeps show a more complex pattern.

Elevations of seeps within 500 m of the nearest river (Fig. 3B) indicate that wet seeps tend to emerge in topographic lows, whereas diffuse seeps show similar elevation distribution as synthetic random data. Vents while similar to diffuse and synthetic distributions show a peak in their abundance between 200- and 300-m elevation from rivers.

Springs, bubbling water and diffuse seeps are at a similar elevations to the river channels (Fig. 3C). Vents show the greatest elevation from rivers compared to other natural seeps. Despite similar distance distribution from rivers, diffuse seeps show much smaller interquartile range (IQR) and mean elevation from rivers than synthetic data. For streams, not shown here, only bubbling water seeps show any significant difference from the synthetic control data, exhibiting little elevation difference from the nearest stream. For all seep types, we find mean elevation and
elevation from channels has no correlation to CO₂ flux. There is no significant change in seep temperatures with distance from the channel base.

**Travertines**

Eighteen CO₂ seeps are associated with travertine deposition. Most of these seeps are wet seeps, with only 5 dry (all diffuse) seeps associated with travertine. There are only 13 currently active travertines in Italy, and 10 have co-occurring CO₂ seeps, which are all located upslope from the travertine. Inactive travertines are found at a similar elevation to the associated present-day CO₂ seep.

**Host lithology**

Rock type is strongly correlated with elevation asl (Fig 4A). Limestone lithologies form the Apennine Mountains, and therefore carbonate platform rock categories (margin, interior and basin and slope) show much greater elevations asl than terrestrial and igneous rock categories. Seeps emerge from two dominant rock categories that represent four principal rock types. In order of prevalence (when seep frequencies are normalized to the area of outcrop), these are igneous (rhyolites/dacites, and andesites/basalts), and basin slope sediments (mudstone/marls, and turbidites). Limestones (rock type numbers 7–11) commonly host seeps (Fig 4B).

Fumaroles are hosted almost exclusively by igneous rocks which also host numerous high flux dry seeps. Platform carbonates and turbidites host all seep types; however, dry seeps are virtually absent in carbonates and far more common than wet seeps in turbidites (Fig. 4B). Carbonate units host the majority of wet seeps (often high flux – although these also have the greatest quantity of seeps with unknown flux), and no CO₂ vents. Springs are absent from andesites/basalts, metasedimentary rocks, mudstone/marls and conglomeritic sands which host much lower flux seeps.

There is evidence that seep hosting lithology influences seep flux (Fig 5), as proposed by Collettini et al. (2008). The majority of low flux seeps emerge from igneous rock types, although andesites also host a number of high flux seeps. Carbonate units 9–11 (platform, detrital and pelagic carbonates) host only low and medium flux seeps, whereas unit 8 (limestone and sandstone) hosts seeps with high fluxes, where flux is quantified. Mudstones and marls (unit 12) and turbidite (unit 13) host the majority of high-end flux seeps. Quaternary cover (unit 4) hosts few seeps, but these are high flux.

**DISCUSSION**

Nonvolcanic CO₂ seepage in Italy is governed by deep geological structures (Chiodini et al. 2004), and faults are observed to govern seep location (Etiope et al. 2005; Bonini 2009a). The influence of meso-/macro-fractures is greatest at depths above 1.5 km, although fluid pressure can sustain fracture apertures at greater depths. At depths shallower than 1.5 km, competing flow processes may govern fluid flow, influencing the dispersion and expression of
CO₂ fluids, including the seep type, CO₂ flux and temperature. Our analyses find that the shallow hydrogeologic environment (governed by rock type, water table depth and topography) influences these seep characteristics.

**Topographic effects**

The CO₂ seeps that are preferentially located close to the local topographic base level (i.e., close to a channel) may either be (i) emerging from the local low point of the water table, and delivered via degassing CO₂-saturated waters, or (ii) river channels could be preferentially eroding geological features such as faults that act as conduits for deep-derived CO₂. Previous work finds the locations of wet seeps are not strongly governed by distance to fault traces (Roberts 2012), yet these seeps do emerge in channel bottoms. Therefore, the observed control of topographic channels on the location of wet seeps must be through the position of the local water table, rather than through the location of preferentially eroded faults. Early studies on groundwater exploration in fractured bedrock noted strong topographic controls on the productivity of groundwater wells, and that transmissive bedrock was most common in the topographic lowlands (Yin & Brook 1992). Dissolved CO₂ will be controlled by the same processes and will seep to surface in these transmissive zones. CO₂ that seeps at springs could either be transported from depth to the near surface via ascending groundwaters, or CO₂ could ascend via faults or other fluid pathways, disperse towards the vadose zone and dissolve into shallow groundwaters which emerges in these lowlands. The former would likely be springs associated with travertine deposition from degassing of the waters as they emerge and cool.

In contrast to wet seeps, CO₂ vents show a random distribution in the lateral distance from the mid-points of river channels (the same distribution as a randomized synthetic data set, Fig. 3A), yet their elevation distribution...
from rivers is not random (Fig. 3B). This indicates that the location of vents is independent of the water table and perhaps simply governed by fault location. It is unclear why these seeps tend to emerge 200–300 m upslope from local topographic lows (Fig. 3B), but it may be that these vents are preferentially located above subsurface structural highs (Chioldini et al. 2010). Rocks positioned away from the valley bottoms may have greater relative permeability for gaseous flow, as the immediate subsurface is less likely to be water-wet or water-saturated. This would facilitate the focused CO₂ flux that characterizes CO₂ vents.

The distribution of distance of diffuse seeps from river channels is similar to wet seeps until 300 m distance (Fig. 3A), after which the frequency plateaus until 700 m. This is unlikely to be an artefact of a small data set as diffuse seeps are the most common (see Fig 1B). At distances >700 m from a river channel, diffuse seep frequency distribution lies between wet seeps and the randomized data set. In contrast to CO₂ vents, the elevation distribution of diffuse seeps from channels is not different from the random points. Diffuse seeps commonly constitute one of the dual-system seeps, paired with bubbling water or vent seeps (Roberts et al. 2011). We suggest that diffuse and bubbling water seeps represent similar fluid leaking paths with a different surface manifestation: where the water table is at the surface, bubbling water seeps occur, whereas diffuse seeps rise through the unsaturated vadose zone, emerging close to river channels. This is further supported by two observations: firstly, the only dry seeps located with travertines are diffuse, where it is likely that CO₂ degassed from the travertine-precipitating waters emerges from the vadose region above the spring as a diffuse seep; and secondly, while both bubbling water and diffuse seeps emerge from low-permeability rocks, bubbling water seeps are more prevalent in rocks which outcrop at low elevations asl (such as mudstone and marls, or quaternary cover) and are therefore more likely to have a shallower water table. Here, the flow of CO₂ may be restricted by water-wet rocks, leading to more diffuse CO₂ leakage rather than focused CO₂ venting.

**Lithological effects**

We observe that there are proportionally more dry seeps in turbidite rocks than wet seeps, and proportionally more wet seeps in platform carbonates than dry seeps. Differences in relative permeability of aqueous and gaseous fluids in these rocks may account for this. Aqueous fluids will preferentially flow through water-saturated high-permeability rock units such as the carbonate aquifer rocks. Gases in this system will dissolve in these aqueous fluids, leading to CO₂ springs. The low matrix permeability of turbidite rocks may result in preferential flow in fractures, therefore reducing the contact of aqueous fluid flow and reducing the contact of CO₂ gases and water, and hence enabling dry seeps to emerge.

We observe that CO₂ springs commonly emerge from platform carbonates, and these springs are often high flux. This agrees with models of groundwater infiltration rates by Collettini et al. (2008) that also predict that dry seep density will be greatest in more impermeable rocks. We find, however, that igneous extrusive rocks rather than (less permeable) turbidites are the most common seep hosting lithology and, moreover, seeps hosted by igneous rocks are often high-end flux. This may be explained by a variety of factors. Igneous processes supply large quantities of CO₂, and igneous rocks tend to have Na–Cl-type pore waters (Collettini et al., 2008) and higher temperature gradients. High temperature and salinity both reduce CO₂ solubility in water and will therefore reduce the attenuation of free-phase CO₂ fluids by dissolution. Additionally, the negligible matrix permeability and the fractured nature of the igneous rocks, due to fracturing during cooling and later brittle deformation, restrict fluid flow within fractures even more effectively than in turbidites, hence reducing CO₂ solution in the aqueous pore fluids.

A large proportion of high flux seeps (>10 t d⁻¹) are dry types emerging from turbidite mudrocks. As these are generally low-permeability rocks, the flux is not controlled by inherently high rock groundwater infiltration rates. We suggest that these rocks with low vertical permeabilities are acting as a seal to inhibit the seepage of CO₂ fluids from an underlying lithology. Opportunities for these buoyant fluids to escape through the impermeable cover may be few. Therefore, where a pathway exists, such as at a faults or lithological contacts, the resulting seeps are the only regional pathways to release these fluids, resulting in high and localized gas flux and perhaps increased gas pressure, drawn from a wider source region.

**Seep elevations**

Seep elevations vary between seep types and reflect the influence of outcropping rock type on seep development and topographic preferences. For example, the mean elevation of springs is lower than diffuse and vent seeps (Fig. 2) even though springs most commonly emerge from limestone rocks which show greatest elevations (Fig. 4A). This reflects the tendency for springs to emerge in valley bottoms unlike dry seeps. These dry seeps are more likely to emerge away from topographic lows in the lower lying igneous rocks and low-permeability marine sedimentary facies such as mudstone and marls and turbidite rocks. The synthetic random data set shows the greatest spread in elevation, because these points do not concentrate in the peri-Tyrrhenian and are independent of topography.
Temporal variation in seep characteristics

We find seep locations and seep characteristics are influenced by both the thickness of the vadose zone (assumed here to increase with distance from, and elevation above, the local topographic low point) and the flow characteristics of the outcropping rock units. It follows that any changes to the water table (e.g. from seasonal rainfall, climatic change or tectonic evolution) or to the permeability of the rock units (e.g. from sedimentation/burial, tectonic evolution or short-term stress changes due to seismic events), as well as any variation in CO2 delivery from depth (e.g. from increased CO2 generation from the deep source, or depletion of a deep CO2 reservoir), could affect the seep characteristics and locations.

Seasonal variation in the water content of seeps and concomitant migration of the seep location has been observed in Italy (Heinicke et al. 2006). Seasonal increase in the water saturation of outcropping rocks will decrease the relative permeability of rocks in the vadose zone to CO2 gas and so the flow paths may become more dispersed. Lateral dispersion of CO2 in the vadose zone will increase interaction with groundwaters (giving rise to bubbling water seeps) when groundwater depth becomes shallower due to high rainfall. Observation of different seep types over several seasons would be an interesting extension to these studies. Where permeability induced by seismicity allows enhanced fluid flow, the variation in flux is predictable, as observed by Bonini (2009b) and Heinicke et al. (2010). Where the rate of supply of free-phase CO2 to surface is increased, it is feasible that the breadth of CO2 dispersion may also change (larger diffuse seeps) where relative permeability effect prevents venting, or new seeps may be temporarily established due to the increased lateral spread of fluids (more diffuse or bubbling water seeps). If local fault permeability (perhaps to supply CO2 vents) cannot accommodate the greater flux, then the lateral spread of CO2 in the vadose zone will increase. Where relative permeability to CO2 of near-surface rocks does not restrict the increased lateral flow of CO2, diffuse seeps may not restrict the increased lateral flow of CO2, diffuse seeps may...
temporarily exhibit pressurized CO₂ release (CO₂ venting) after seismic events. Long-term studies at a range of different seep types would be an interesting extension to these studies and would inform understanding of seep type development.

Summary of seep type development

Figure 6 is a model of seep type distribution that summarizes the major controls on seep type, location and flux: rock type, water table depth and topography. Although we use CO₂ seeps in Italy as a case study, these factors may govern near-surface CO₂ leakage in any region. Seeps emerging from more permeable rock categories (e.g. fractured carbonates) are typically wet, high flux, and emerge in valley bottoms. Seeps emerging from low-permeability rocks are more numerous and can exhibit a range of fluxes. Seep types in these rocks are determined by elevation, which we suggest controls the depth to the phreatic zone. If these low-permeability rocks are at low elevations asl (e.g. mudstone and marls, quaternary cover), then diffuse and bubbling water seeps are most likely to develop, whereas if these rocks have greater elevations (e.g. evaporitic rocks, turbidites), then diffuse and vent seeps are more likely to develop. This model suggests that where ascending CO₂ fluids meet a permeable horizon in the unsaturated zone, CO₂ will spread laterally, dissolving into pore waters if present, and subsequently emerge at springs. Free-phase CO₂ gas that spreads through this permeable horizon may then emerge as either diffuse seeps or bubbling water seeps, depending on the position of the water table.

Implications for leaking CO₂ stores

The local topography surrounding a seep, together with seep type, influences the health risk posed to humans (Roberts et al. 2011). Sheltered areas enhance density-driven pooling of CO₂ which can rapidly increase CO₂ concentrations to dangerous levels. Although more deaths have occurred at dry seeps than wet seeps (Roberts et al. 2011), we find dry seeps do not preferentially emerge in valley bottoms, and in fact CO₂ vents emerge upslope of a river so decreasing their health risk. It is therefore most important that seep risk assessment identifies where diffuse seeps may emerge at low elevation or where density-driven CO₂ streams may develop. Seep monitoring efforts for gas seepage should therefore target elevated low-permeability rocks near faults. Low-lying permeable rocks at the surface above a CO₂ store will decrease human health risk from CO₂ seeps, as the interaction of CO₂ with groundwaters attenuates dry seepage. Methods of monitoring groundwater for dissolved CO₂ should target outcrops of aquifer rocks in the valley bottoms above a CO₂ store.

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AUTHOR CONTRIBUTIONS

J. J. Roberts designed the research, conducted the data analysis and wrote the paper. M. Wilkinson, R. A. Wood and R. S. Haszeldine contributed to research design and towards the writing of this paper.

COMPETING FINANCIAL INTERESTS

There are no conflict of interests to declare.

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**SUPPORTING INFORMATION**

Additional Supporting Information may be found in the online version of this article:

**Table S1.** Geological units from the 1:500,000 ISPRA geological map which host CO$_2$ seeps.