Natural and industrial analogues for leakage of CO_2 from storage reservoirs: identification of features, events, and processes and lessons learned

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Abstract

Instances of CO_2 leakage from naturally occurring reservoirs serve as analogues for the potential release of CO_2 from geologic storage sites. This paper summarizes, compares, and contrasts the features, events, and processes (FEPs) that can be identified from these analogues which include both naturally occuring releases, and those asociated with industrial processes such as drilling. The following conclusions are drawn: (1) Carbon dioxide can accumulate beneath, and be released from, primary and secondary shallower reservoirs with capping units located at a wide range of depths; (2) Many natural releases of CO_2 are correlated with a specific event that triggered the release; (3) Unsealed fault and fracture zones may act as direct flow paths for CO_2 from depth to the surface; (4) Improperly constructed or abandoned wells can rapidly release large quantities of CO_2; (5) The types of CO_2 release at the surface vary widely between and within different leakage sites; (6) The hazard to human health was small in most cases due to implementation of post-leakage public education and CO_2 monitoring programs; (7) While changes in groundwater chemistry were related to CO_2 leakage, waters often remained potable. Lessons learned for risk assessment associated with geologic carbon sequestration are discussed.

Keywords: CO_2 Storage, Leakage, Natural Analogue, Industrial Analogue, FEP

1. Introduction

The injection and storage of anthropogenic CO_2 in deep geologic formations is a potentially feasible strategy to reduce CO_2 emissions and atmospheric concentrations (e.g., International Energy Agency 1997; Reichle and others 1999). While the purpose of geologic carbon storage is to trap CO_2 underground, CO_2 could migrate away from the storage site into the shallow subsurface and atmosphere if permeable pathways such as well bores or faults are present. While limited CO_2 leakage does not negate the net reduction of CO_2 emissions to the atmosphere, adverse health, safety, and environmental risks associated with elevated CO_2 concentrations must be evaluated, particularly if the release at the surface occurs quickly and/or is spatially focused. Cases of CO_2 leakage from natural reservoirs to the near-surface environment as a result of natural and industrial processes serve as analogues for the potential release of CO_2 from geologic storage sites (e.g., Allis and others 2001; Stevens and others 2001a; Stevens and others 2001b; Benson and others 2002; Beaubien and others 2004; Shipton and others 2004; NASCENT 2005). Analysis of these analogues thus provides important insight into the key characteristics of CO_2 leakage, the resulting impacts of the leakage on human health and safety, ecology, surface water, and groundwater, and the effectiveness of remedial measures applied. Lessons can then be learned from natural and industrial analogues for risk assessment associated with geologic CO_2 injection and storage.

The features, events, and processes (FEPs) relevant to the geologic disposal of radioactive waste have been compiled and used in systems analysis to assess performance and safety (e.g., NEA/OECD 2000). Based on this work, Savage and others (2004) developed a framework for compiling a database of generic FEPs for the evaluation of CO_2 storage sites. However, FEPs associated with geologic sequestration of CO_2, in particular potential CO_2 leakage from storage sites, have not been identified from actual cases of leakage from natural CO_2 reservoirs. The purpose of this paper is to summarize, compare, and contrast the FEPs of examples of CO_2 leakage from natural geologic reservoirs. To this end, a comprehensive (although not exhaustive) set of natural and industrial analogues for CO_2 leakage is summarized (Appendices

A and B). Based on this summary, the causes and consequences of CO_2 leakage resulting from natural and industrial processes are described, with particular emphasis on (a) the geologic model for CO_2 accumulation in the reservoir, (b) events leading to the leakage of the CO_2 from the reservoir, (c) pathways for CO_2 migration to the surface, (d) the magnitude and consequences of the release, and (e) remedial strategies applied. Implications for geologic carbon storage and the related risk assessment work are then discussed.

2. Overview of natural and industrial analogues

Leakage of CO_2 has occurred naturally from geologic reservoirs in numerous volcanic, geothermal, and sedimentary basin settings worldwide. These systems serve as natural analogues for the potential leakage of CO_2 from geologic carbon sequestration sites. While leakage of CO_2 from geologic reservoirs resulting from industrial processes has occurred relatively infrequently, these events serve as analogues for the potential release of CO_2 from sequestration sites due to human-related practices, such as well construction and injection and withdrawal practices. Together, natural and industrial analogues for CO_2 leakage provide important information about the key FEPs that are associated with leakage, as well as the health, safety, and environmental consequences of leakage and mitigation efforts applied.

Appendices A and B describe these aspects of natural and industrial analogues, respectively, for CO_2 leakage. Appendix A begins with a more detailed summary for Mammoth Mountain (USA) due to the large amount of data available for this site, and follows with more limited descriptions of CO_2 leakage in other volcanic, geothermal, and sedimentary basin systems. While the Appendices do not represent an exhaustive list of natural and industrial cases of CO_2 leakage that have occurred worldwide, a suite of well-documented cases in the literature representing a range of geologic settings is included.

To compare and contrast the key characteristics of CO_2 leakage associated with natural and industrial processes detailed in Appendices A and B, CO_2 leakage cases are classified according to the key features of the CO_2 accumulation, the events leading to the leakage of CO_2 from the reservoir, and the processes by which the CO_2 was released at the surface (Tables 1 and 2). In Tables 1 and 2, columns one through three describe these key features, including site location, the source of the CO_2 in the natural accumulation, and the geologic model for CO_2 accumulation, for example, the reservoir, reservoir depth (if known), and capping rocks. Column four in Tables 1 and 2 describes the event triggering the leakage of CO_2 from the reservoir. Columns five and six give the processes by which the CO_2 was emitted at the surface, including the pathway(s) for leakage and the style of surface emission. References for each of the leakage analogues are given in Appendices A and B.

3. Common FEPs

As shown in Tables 1 and 2, there are several key similarities between the FEPs of different natural and industrial cases of CO_2 leakage. First, the sources of CO_2 in natural accumulations are most commonly thermal decomposition of carbonate-rich sedimentary rocks and/or degassing of magma bodies at depth (analogues A1-A5, A7-A12, B1-B4). Second, CO_2 from these sources often accumulates in highly fractured and/or porous rocks (e.g., sandstones, limestones) under low-permeability cap rocks (analogues A1-A6, A11, A12, B1-B4). The cap rocks may be low-permeability rock units (e.g., shale, siltstone) or a zone of hydrothermal alteration.

In the case of natural CO_2 leakage, once the CO_2 leaks from the storage reservoir, fault and/or fracture zones are the primary pathways for CO_2 migration to the surface (analogues A1-A8, A11, A12). These high-permeability zones may be pre-existing, or be created/enhanced due to seismic activity associated with, e.g., fluid migration and pore-fluid pressurization. In the case of CO_2 leakage associated with industrial activity, the event triggering the release is commonly a well blowout, related to injection/withdrawal practices or a defect in a well (analogues B1-B4). Also, the pathway for CO_2 migration to the surface is usually the well bore and/or fractures that have formed around the well bore.

4. Differing FEPs

There are several key differences between the FEPs of the various examples of CO_2 leakage (Tables 1 and 2). The depth of the source of the CO_2 and the reservoir(s) in which the CO_2 accumulates varies widely from < 1 km (e.g., analogues B3, B4) to multiple km (e.g., analogues A1, B1). At an individual site, CO_2 may accumulate in a single reservoir (e.g., analogues A1, A4-A6, B4), or within multiple vertically stacked and/or horizontally compartmentalized reservoirs (analogues A11, A12, B2, B3). Cap rocks and/or low-permeability fault zones can serve to separate multiple CO_2 reservoirs at a given site.

Some examples of natural CO_2 leakage have been correlated with specific triggering events, such as seismic activity or magmatic fluid injection (analogues A1, A3, A7, A9, A10), while other events have not been correlated with such events. However, the lack of correlation in the latter cases may be due to the absence of observations or data collection at the time of the leakage event. Where a trigger event was identified, it was commonly an event that caused geomechanical damage to cap rocks sealing the CO_2 reservoir.

Finally, the style of natural CO_2 leakage at the surface varies widely between different sites, as well as within individual sites. Surface releases occur in the form of diffuse gas emission over large land areas, focused vent emissions, eruptive emissions, degassing through surface water bodies, and/or release with spring discharge (analogues A1-A6, A8, A10-A12). In rare cases, the CO_2 release may have been a self-enhancing or eruptive process (analogues A7, A9). In the case of CO_2 leakage associated with well failures, CO_2 may be emitted at the surface in a focused form as free flowing or geysering CO_2 from the well and/or diffusely through soils, water pools, or fractures around the well site (analogues B1-B4).

5. Additional Considerations

The magnitude and consequences of CO_2 leakage events, as well as the type and success of strategies that were implemented to monitor and/or remediate the leakage, are important additional considerations that should be taken into account in risk assessment associated with geologic carbon sequestration. Table 3 and Appendices A and B detail these aspects for the natural and industrial leakage analogues and show that the magnitude of the surface CO_2 release varies widely between different cases, and does not necessarily depend on the style of the release. For example, the magnitude of diffuse CO_2 emissions from soils varies greatly between different, as well as within, individual sites. At sites where groundwater chemistry was monitored, chemical changes were sometimes observed related to CO_2 leakage (e.g., analogues A1, A3, A11, A12) and resulting groundwater acidification and interaction with host rocks along flow paths. However, groundwaters remained potable in most cases.

In many of the leakage examples, CO_2 was monitored in the near surface environment within and around CO_2 leakage areas, often on a regular basis (analogues A1-A6, A9-A11, B2, B4).

Monitoring strategies include measurements of soil CO_2 flux using accumulation chamber or eddy covariance methods and soil or atmospheric CO_2 concentration using gas analyzer or chromatography techniques. Controlled degassing of CO_2-rich lakes has also been carried out to mitigate CO_2 buildup (analogues A9). In many cases, public education programs were implemented to advise people visiting or living near the CO_2 release areas of potential health, safety, and environmental hazards (e.g., analogues A1-A3, A6, A9). Zoning bylaws have also been established in some cases to control development near high CO_2 emission areas (e.g., analogues A3, A6). The hazard to human health was small in most examples of surface CO_2 releases; this could often be attributed to public education and CO_2 monitoring programs.

6. Conclusions and Lessons Learned

Leakage of CO_2 has occurred naturally from geologic reservoirs in numerous volcanic, geothermal, and sedimentary basin settings. In addition, CO_2 has been released from industrial CO_2 reservoirs due to influences such as well defects and injection/withdrawal processes. These systems serve as natural and industrial analogues for the potential release of CO_2 from geologic storage reservoirs and provide important information about the key features, events, and processes that are associated with releases, as well as the health, safety, and environmental consequences of releases and monitoring and mitigation efforts that can be applied. Based on an analysis of a range of natural and industrial analogues for CO_2 leakage, five key FEPs were identified, from which lessons are learned and should be applied to risk assessment associated with geologic carbon storage:

(1) Carbon dioxide can both accumulate beneath and be released from primary and secondary reservoirs with capping units located at a wide range of depths. Both primary and

secondary reservoir entrapments for CO_2 should therefore be properly characterized at potential geologic carbon sequestration sites.

(2) Many natural releases of CO_2 have been correlated with a specific event that has triggered the release, such as magmatic or seismic activity. The potential for processes that could cause geomechanical damage to sealing cap rocks and trigger the release of CO_2 from a storage reservoir should be evaluated.

(3) Unsealed fault and fracture zones can act as fast and direct flow paths for CO_2 from depth to the surface. Risk assessment should therefore emphasize determining the potential for and nature of CO_2 migration along these structures.

(4) Wells that are improperly constructed or abandoned and become structurally unsound over time have the potential to rapidly release large quantities of CO_2 to the atmosphere. A focus of risk assessment should therefore be an evaluation of the potential for both active and abandoned wells at storage sites to transport CO_2 to the surface, particularly in depleted oil or gas reservoir systems, where wells are abundant.

(5) The style of CO_2 release at the surface varies widely between and within different leakage sites. In rare circumstances, the release of CO_2 can be a self-enhancing and/or eruptive process; this possibility should be assessed in the case of CO_2 leakage from storage reservoirs.

Furthermore, analysis of natural and industrial analogues demonstrated two important points related to human health and safety and groundwater quality. First, the hazard to human health was small in most examples of CO_2 leakage**,** which probably could be attributed to implementation of public education and CO_2 monitoring programs. These “remedial” programs should therefore be employed to minimize potential health, safety, and environmental effects associated with CO_2 leakage. Second, while CO_2 leakage appeared to cause changes in groundwater chemistry due to acidification and interaction with host rocks along flow paths, waters remained potable in many cases. Groundwaters should be monitored for changes in chemistry that could result from leakage from CO_2 leakage from storage sites.

Acknowledgments We are grateful to C.M. Oldenburg for constructive review of this manuscript. We thank the U.S. Environmental Protection Agency, Office of Water and Office of Air and Radiation for funding this study under an Interagency Agreement with the U.S. Department of Energy at the Lawrence Berkeley National Laboratory, contract number DE-AC02-05CH11231.

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Appendix A: Summary Descriptions of Natural Analogues

A1. Mammoth Mountain, California, USA. Mammoth Mountain is a seismically active, dacitic cumulovolcano located on the southwestern rim of Long Valley caldera (LVC), eastern California. The regional geology has been described in detail by Bailey (1989). LVC formed 760,000 years ago by the eruption of 600 km^3 of solid rock equivalent, creating a 32 x 17 km caldera (Bailey and others 1976; Hill and others 1985; Bailey 1989). The Mono-Inyo Craters volcanic chain is the most recently active system associated with LVC and is localized along a north-trending fissure system extending from south of Mammoth Mountain through the western moat of LVC to the north shore of Mono Lake. Mammoth Mountain was formed 200,000 to 50,000 years ago by repeated eruptions of dacite and rhyodacite domes and lava flows from vents on the southwest rim of LVC lying within a field of 160-8 thousand-year-old mafic vents. While contiguous, the magmatic system of Mammoth Mountain is distinct from those of LVC and the Mono craters (Hildreth 2004). Mammoth Mountain is bordered on the west and south by granitic rocks of the Sierran block. Volcanics, meta-volcanics, and meta-sediments also crop out in the area surrounding Mammoth Mountain. The deep reservoir and up-flow zone of the hydrothermal system in the caldera are hosted in meta-sedimentary basement beneath the West Moat (Sorey and others, 1991).

Recent unrest associated with Mammoth Mountain was first identified in 1979 and has been typified since by ground deformation, swarms of small earthquakes ($M \leq 3$), rapid fire bursts of small earthquakes (spasmodic bursts), long-period (LP) and very long-period (VLP) earthquakes, elevated $^3He/^4He$ ratios in fumarolic gases, and diffuse surface CO_2 emissions resulting in large areas of tree kill. Hill and Prejean (2005) described these aspects of recent volcanic unrest at Mammoth Mountain in detail.

A notable eleven-month-long seismic swarm occurred beneath Mammoth Mountain, beginning in May 1989 (Hill and others 1990). The swarm included >3000 earthquakes of M>0, including three M>3 earthquakes. Prejean and others (2003) relocated ~2700 high-frequency brittle-failure (BF) earthquakes (M ≤3.4) that occurred beneath Mammoth Mountain. These earthquakes defined a vertical keel-like structure at depths of 8 to 10 km, overlain by ring-like structures at 5-6 km, and ~3 km depth (see Prejean and others 2003 for spatial-temporal relationships of the 1989 seismic swarm). Earthquake focal mechanisms in the deep seismicity keel were consistent with fluid intrusion into an opening crack (Hill and others 1990; Prejean and others 2003; Hill and Prejean 2005). The 1989 swarm was also characterized by a high *b*-value, spasmodic bursts of high-frequency BF earthquakes, and mid-crustal (10-25 km deep) LP earthquakes (e.g., Hill and others 1990; Pitt and Hill 1994; Hill and Prejean 2005), likely associated with fluid migration beneath Mammoth Mountain. VLP earthquakes were recorded more recently, usually associated with LP earthquakes and spasmodic bursts (Hill and others 2002). These VLP earthquakes were generally constrained to a source volume centered ~3 km beneath the summit of Mammoth Mountain, near the CO_2 reservoir proposed by Sorey and others (1998) (see below). These data may reflect the transport of a slug of fluid (likely CO_2 or a CO_2-rich hydrous phase) through a near-vertical, northwest-striking crack (e.g., Hill and Prejean 2005). Deformation changes were also measured around the time of the 1989 earthquake swarm and were modeled by a crack dislocation centered beneath Mammoth Mountain that was coplanar with the seismicity keel (Langbein and others 1993; 1995).

Mammoth Mountain fumarole (MMF) is a thermal feature located on the upper northern flank of Mammoth Mountain. From 1982 to July 1989, diffuse seepage of gas and steam was observed over a ~50 m^2 area of elevated ground temperatures and no distinct steam vents were observed

(Sorey and others 1993). In September 1989, distinct steam vents were observed and steam velocities from the ground had increased significantly. An increase in $^3He/^4He$ ratios in MMF gases was observed following the onset of the 1989 earthquake swarm beneath Mammoth Mountain (Sorey and others 1993). For example, the $^3He/^4He$ value increased by 58% (i.e., to 5.45 R_A, where R_A is the atmospheric $^3He/^4He$ ratio) from August to September 1989, and then continued to increase to a maximum value of 6.72 in July 1990). For reference, ratios typically range from 6 to 8 R_A for fluids from hydrothermal systems in continental magmatic systems. $^3He/^4He$ values have continued to show an elevated magmatic helium component since the 1989 swarm. $\delta^{13}C$ values of MMF CO_2 increased from –5.3‰ in July 1989 to –4.5‰ in August 1991, probably due to changes at depth (Sorey and others 1993). Overall, the values likely indicate contribution of CO_2 from magmatic degassing and degassing of metasedimentary rocks.

Tree kills formed in six general areas (~360,000 m^2) on Mammoth Mountain in 1990-1991. Also, during the winter of 1990, a park ranger was overcome by CO_2 that had accumulated beneath the snow. A series of soil and aerial gas flux surveys were conducted following these events and it was estimated that at least 250 metric tons of CO_2 per day ($t\ d^{-1}$) were emitted through soils from an approximately 480,000-m^2 area on the volcano (Farrar and others 1999; Gerlach and others 1999). The areas of diffuse degassing appeared to be loosely correlated with the locations of mapped faults. Based on data (1996-1999) for cold springs discharging around Mammoth Mountain, Evans and others (2002) estimated that the total discharge of magmatic carbon in the cold groundwater system was ~20,000 $t\ yr^{-1}$. They also suggested that the long-term discharge prior to the 1989 seismic swarm was ~10,000 $t\ yr^{-1}$. Areas of diffuse CO_2 emissions reflect zones of gas upflow where groundwaters are saturated with respect to CO_2.

Also, while most springs contain high concentrations of dissolved CO_2, they are otherwise dilute, with specific conductance ranging from 100 to 300 $\mu S\ cm^{-1}$ (Evans and others 2002).

The Horseshoe Lake tree-kill area, located adjacent to Horseshoe Lake on the southeast flank of Mammoth Mountain, is the most studied of the areas of diffuse CO_2 degassing on Mammoth Mountain. Here, soil CO_2 concentrations measured using gas analyzers are commonly >30 vol.% and fluxes measured using the accumulation chamber method are commonly >500 $g\ m^{-2}d^{-1}$ (Farrar and others 1995, 1999; Rahn and others 1996; McGee and Gerlach 1998; Sorey and others 1998; Gerlach and others 2001). For reference, background CO_2 concentrations and fluxes outside of the tree-kill area are usually < 1 vol.% and 25 $g\ m^{-2}d^{-1}$, respectively. Based on repeated measurements of soil CO_2 fluxes over grids from 1997 to 2000, total CO_2 emission rates were estimated to be $93 \pm 27\ t\ d^{-1}$ (Rogie and others 2001). Based on measurements of ^{14}C in tree rings around the Horseshoe Lake tree kill area prior to 1997, CO_2 emissions likely began here in 1990, peaked in 1991, and declined by a factor of ~2 through 1998 (Cook and others 2001). Continuous monitoring of soil CO_2 concentrations concurrently with meteorological parameters show annual cycles of CO_2 buildup beneath winter snow pack and decline during the springtime, to remain relatively constant through the summer and fall (McGee and Gerlach 1998; McGee and others 2000). Continuous monitoring of soil CO_2 flux concurrently with meteorological parameters showed that temporal variations in CO_2 flux over this time period were strongly controlled over the measurement period by meteorological parameters (e.g., barometric pressure), rather than changes in processes at depth (Rogie and others 2001).

Based on available geophysical, geochemical, and hydrogeologic data, Hill and Prejean (2005) proposed a model of structure, recent unrest, and gas leakage at Mammoth Mountain, which is summarized here. The deep LP earthquakes observed beneath the southwest flank of Mammoth

Mountain were likely associated with CO_2-rich basaltic magma within dikes and sills located at 10-25 km depth. Activation of the seismicity keel during the 1989 swarm was probably due to elevated strain rates associated with injection of magmatic fluids. Swarms of BF earthquakes at shallower depths defined a series of ring-like structures concentric about the summit of Mammoth Mountain. These structures appeared as pre-existing normal faults dipping away from the summit. Key characteristics of the earthquake swarms were consistent with brittle processes driven by elevated pore pressure and fluid transport. Based on volume and geochemical constraints, Sorey and others (1998) proposed the existence of a $150^{o}C$, high-pressure gas reservoir within the upper three km of the crust beneath Mammoth Mountain. The reservoir's presence is also supported by the source volume for the VLP earthquakes of 2000 and 2001 (Hill and others 2002). The gas reservoir may occupy up to 20 km^3 of porous/fractured rock and is capped by a low-permeability rock unit or hydrothermally altered zone (Sorey and others 1998). CO_2 within the reservoir has likely accumulated over an extended period of time fed by volatiles leaking up from the mid-crustal basaltic magma bodies. Seismicity in the upper 3 km of the crust generally falls along the trends of the surficial structures mapped on Mammoth Mountain.

Overall, recent unrest at Mammoth Mountain has likely been driven by sporadic releases of magmatic fluids from basaltic magma at mid-crustal depths and their migration to shallow crustal depths. As summarized by Hill and Prejean (2005), the deep mobilized fluid likely was a CO_2–rich hydrous phase. As the fluid moved upwards into brittle crust, it diffused vertically and laterally through the pre-existing structures and induced the 1989 earthquake swarm. Upon reaching shallow crustal depths, the fluid ruptured the seal on the pre-existing shallow CO_2 reservoir, likely through some combination of reservoir pressurization and seismic activity. CO_2 gas with a magmatic helium component was then allowed to migrate to the surface, resulting in

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changes in chemistry and gas discharge at MMF and large areas of tree kill and diffuse CO_2 degassing. Mid-crustal LP earthquakes and sustained diffuse CO_2 degassing have continued at Mammoth following the 1989 earthquake swarm. This suggests that CO_2 continues to leak from the shallow reservoir, which could potentially be replenished by volatile influx from depth.

The national forest and ski resort are popular recreation areas on Mammoth Mountain. As a result, high CO_2 levels in areas of diffuse CO_2 degassing pose a potential risk to the health and safety of people using the area for, e.g., skiing, hiking, and fishing. During the wintertime, snow can accumulate to depths greater than 2 m and toxic levels of CO_2 can develop in snow wells (depressions) around trees and buildings, and immediately below the snow surface in areas of high CO_2 emissions (http://lvo.wr.usgs.gov/CO2.html). Apart from the Forest Service employee who was overcome by CO_2, one skier apparently died from CO_2 asphyxiation in a snow well near Horseshoe Lake (Hill 2000), highlighting the potential danger of high CO_2 concentrations in the near-surface environment during winter months. During the summertime, it is hazardous to dig holes in and around areas where the trees have been killed by carbon dioxide gas. The natural collapse pits that have developed on the northwestern shore of Horseshoe Lake as the lake level declines contain high CO_2 concentrations; people (and pets) are warned against entering these pits or digging up loose soil that has been placed in the pits. People are also warned to avoid a crack 1-2 feet wide that extends from the lake onto the west shore and not to lie face down on the ground near Horseshoe Lake or the tree-kill area (http://lvo.wr.usgs.gov/CO2.html). In addition to the public education that is ongoing at Mammoth Mountain, the U.S. Geological Survey continuously monitors the CO_2 concentrations in soils on Mammoth Mountain (see http://volcanoes.usgs.gov/About/What/Monitor/Gas/continuous.html).

A2. Solfatara, Italy. Solfatara volcano is located within Campi Flegrei, a 12-km-wide caldera complex, located to the west of Naples, southern Italy. Campi Flegrei was formed in the eruptions of the Campanian Ignimbrite (37 ka) and the Neopolitan Yellow Tuff (12 ka) (Rosi and Sbrana 1987; Orsi and others 1996). More recent volcanic activity in Campi Flegrei has been dominated by magmatic and hydromagmatic eruptions from 10,500 years ago to the 1538 eruption at the Monte Nuovo cone. Solfatara is a tuff cone consisting of ash and lapilli beds overlying breccia and was formed between 3.8 and 4.1 ka (Rosi and Santacroce 1984). The tuff cone is hydrothermally altered and is cut by two major normal faults striking NW-SE and fractures striking NE-SW and NW-SE.

Two major (1969-1972 and 1982-1984) and two minor (1988-1989 and 1994) periods of resurgent uplift occurred in the Neopolitan Yellow Tuff caldera and define Campi Flegrei's most recent activity. The two major episodes of "bradyseismicity" generated earthquake swarms and net uplift of 3.4 m (Corrado and others 1977; Barberi and others 1984). The 1982-1984 bradyseismic crisis was accompanied by 1.8 m of net uplift and over 16,000 earthquakes between 0 and 4 km depth, most of which were located in the Solfatara and Pozzuoli areas. Extensive subaerial and submarine hot springs and fumaroles characterize current thermal activity in Campi Flegrei caldera (Allard and others 1991). The crater of Solfatara hosts the highest temperature fumaroles (140-160^{o}C) of the caldera (Allard and others 1991). The geochemistry of fumarolic fluids has been used to develop a conceptual model of the hydrothermal system. The main components of the conceptual model include: (1) a heat and fluid source supplied by a magma body at a few kilometers depth, (2) one or more boiling aquifers overlying the magma body, and (3) a fractured zone that is occupied by a gas phase ($T = 215^{o}C$, $P_{H2O} = 3.9$ bar, $P_{CO2} = 0.74$ bar) (Chiodini and others 2001 and references therein). This gas reservoir supplies a total mass emission rate of 4800 t d^{-1} and energy emission rate of 1.2 J d^{-1} to the surface at Solfatara, primarily along major faults (Chiodini and others 2001). Changes in the chemistry of Solfatara fumarolic fluids were recorded prior to the 1982-1984 period of unrest, as well as prior to the minor events of 1988-1989 and 1994 (e.g., Cioni and others 1984; Martini 1986; Tedesco 1994; Tedesco and Scarsi 1999). For example, an increase in the H_2O/CO_2 ratio was observed prior to each of the episodes, indicating an increase in heat flow (e.g., Chiodini and others 2001). Also, increases in He, CH_4, H_2 and $^3He/^4He$ and decreases in ^{20}Ne, ^{40}Ar, and N_2 prior to the 1994 seismic swarm were observed in Solfatara fumarolic gases and interpreted to result from migration of a relatively deep and hot gas phase to the surface and a decrease in the atmospheric gas component (Tedesco and Scarsi 1999).

In addition to vent degassing, the crater of Solfatara hosts intense diffuse degassing of CO_2. Soil CO_2 fluxes have been measured using the accumulation chamber method at multiple locations within the crater; based on these measurements, maps of CO_2 flux have been produced and used to estimate total CO_2 emissions from the area (~1500 t d^{-1} from a 0.5 km^2 area) (Chiodini and others 2001). Areas of elevated CO_2 flux (up to 52,000 g $m^{-2}d^{-1}$) are closely associated with faults and fractures; these permeable structures are interpreted to control gas flow to the surface (Chiodini and others 2001). Soil CO_2 was not monitored during the episodes of seismic swarms and ground deformation. The variations in gas chemistry, ground deformation, and seismic activity have been interpreted to result from overpressurization of the Solfatara hydrothermal system caused by an increase in magma degassing and/or sealing of the system due to argillification (e.g., Bonafede and Mazzanti 1998; Chiodini and others 2001).

Solfatara is a popular tourist destination and is surrounded by an intensely urbanized area. The area of diffuse CO_2 degassing in the crater of Solfatara lacks vegetation, likely due to the high soil CO_2 levels and/or temperatures. While no adverse human health effects or deaths associated with CO_2 degassing at Solfatara have been reported in the literature, the Osservatorio Vesuviano continuously monitors diffuse and vent degassing, including periodic sampling of fumarolic gases, periodic soil CO_2 flux measurements at regular locations within the crater, and continuous monitoring of soil CO_2 fluxes and meteorological parameters at two locations in the crater, in addition to geophysical monitoring (seismicity, gravity and deformation) (http://www.geowarn.ethz.ch/index.asp?ID=39). Visitors to Solfatara are warned about health hazards associated with the volcanic degassing.

A3. Albani Hills, Italy. The Albani Hills were formed by explosive volcanism in an extensional tectonic regime and are composed of sequences of volcanic deposits overlying sedimentary basement (Voltaggio and Barbieri 1995; De Rita and others 1995). Ciampino is a city located 30 km southeast of Rome within the Albani Hills volcanic complex. CO_2 of magmatic and crustal origin is emitted at the surface in the form of diffuse soil, spring, and vent degassing at various locations throughout the Albani Hills and within the city of Ciampino (Annunziatellis and others 2003; Beaubien and others 2003). Gas is hypothesized to leak up along major faults from deep pressurized reservoirs hosted by structural highs in carbonate basement rocks (Chiodini and Frondini 2001).

A continual risk posed by soil and vent CO_2 degassing to the local population in Ciampino is the migration of CO_2 into unventilated basements of buildings and low-lying areas. Also, several large sudden releases of CO_2 have been recorded during historic times, the most recent of which occurred in 1995 and 1999. On November 2, 1995, a large area (25-km^2) of the Albani Hills was affected by the sudden release of CO_2 from the soil and shallow water wells. Residents reported noisy emissions of pressurized gas from the heads of shallow (< 60 m deep) water wells, and anomalous gas in basements. On the same day, researchers carried out field surveys and observed a well in Ciampino discharging lethal levels of CO_2 (Quattrocchi and Calcara 1995). The water had a pH of 5.48 and an alkalinity of 15.83 mmol l^{-1}, which increased and decreased, respectively, on November 3. Other wells in the Ciampino area showed similar trends in CO_2 degassing from November 2 to 3. Due to high CO_2 concentrations, basements of nearby buildings were deemed off-limits on November 2, but became accessible on November 3 as the CO_2 dissipated. Two low-magnitude earthquakes occurred within 70 km of the study area on November 2 and 3; however, based on available data, the origin of the degassing event, its relationship to the earthquakes, and the total amount of CO_2 released are poorly understood. In September 1999, elevated CO_2 degassing occurred in conjunction with seismic activity, and 30 cows in a field within the city limits died as a result of CO_2 asphyxiation. It was hypothesized that the seismicty caused a decrease in the confining hydrostatic pressure and opening of faults, allowing for increased gas flow to the surface. Detailed descriptions of the 1995 and 1999 CO_2 releases can be found in Chiodini and Frondini (2001) and Beaubien and others (2004).

Chiodini and Frondini (2001) measured soil CO_2 fluxes in 1996 at the Cava dei Selci area (6000 m^2) in Ciampino and the Solforata area (55,000 m^2) located southwest of Ciampino and observed elevated fluxes distributed along linear trends corresponding to prominent faults. They estimated total CO_2 emissions from these areas to be ~74 t d^{-1}. Beaubien and others (2004) measured soil CO_2 concentrations in the Ciampino area ranging from 0.1 to 92.7 vol.%. Similar to CO_2 fluxes measured by Chiodini and Frondini (2001), they observed elevated CO_2 concentrations along linear trends paralleling major faults in the area, indicating that these structures provide pathways for upward gas migration. In addition, Chiodini and Frondini (2001) estimated the total rate of CO_2 dissolution into shallow groundwaters to be ~506 t d^{-1} in the Albani Hills region. Although

Beaubien and others (2004) found that some houses were built on soils with CO_2 concentrations > 70 vol.%, measured indoor CO_2 concentrations were typically < 1 vol. %, likely due to the Italian custom of maintaining open windows in homes during the daytime. To minimize risk associated with elevated CO_2 concentrations in homes, the University of Rome is working with the regional government and the local Civil Protection Agency to develop zoning bylaws, identify residential areas at risk, and develop public education programs (Beaubien and others, 2004).

Three main hydrogeologic units have been identified in the Albani Hills region (Boni and others, 1995). From depth to the surface, these include: (1) a calcareous-siliceous-marly basal complex constituting a multi-layered aquifer hosted in fractured carbonates interbedded with confining clay layers, (2) a clayey-marly intermediate complex that acts as a groundwater flow boundary due to its low permeability, and (3) the Albani Hills volcanic complex which displays wide variation in permeability and acts as a multi-layered aquifer with radial groundwater flow. Chiodini and Frondini (2001) conducted a geochemical study of groundwaters collected from 293 wells and 63 springs in the region and found high CO_2 partial pressures (average = 0.2 bar), indicating a high CO_2 leakage rate into the regional aquifers. HCO_3 is the major anion in most waters, while only a few samples are characterized by high Cl and SO_4 concentrations. The SO_4-rich waters in the northern part of the study area are associated with influx of deep sulfur-rich gases into shallow groundwaters, while the Cl-rich waters are located on the coastal plain and are associated with fossil seawater. The relative concentrations of cations in waters reflect interaction of CO_2-rich groundwaters with host rocks. In particular, many samples have high HCO_3, Ca, and Mg contents, which can be explained by the influx of CO_2-rich fluids from depth and subsequent interaction with sedimentary rocks.

A4. Clear Lake, California, USA. The Clear Lake volcanic-magmatic system is located in a rural area in northern California within a broad zone of deformation related to the San Andreas fault system. In this region, Coast Range ophiolite rocks and the Mesozoic Great Valley marine sedimentary sequence are thrust above coeval Franciscan Complex rocks (weakly metamorphosed subduction zone metagraywackes and argillites). These rocks are overlain by Tertiary marine and nonmarine rocks and late Pliocene to Holocene mafic to silicic Clear Lake Volcanics. Numerous strike-slip, thrust, and normal faults cut the region. The Clear Lake volcanic-magmatic system is thought to be related to the northward migration of the Mendecino triple junction and associated upwelling of the asthenosphere in a slabless window (e.g., Dickinson and Snyder 1979; McLaughlin 1981; Johnson and O'Neil 1984). Volcanism around Clear Lake is localized in regions of transtension associated with structures of the San Andreas fault system.

The Franciscan Complex hosts a geothermal system which includes several localized liquid-dominated reservoirs, with fluid temperatures up to 218°C at 503 m depth (Goff and others, 1995), the heat source for which is likely a large silicic magma body underneath the Clear Lake volcanic field. There are numerous surface thermal features (e.g., thermal and mineral springs, gas vents) in the area. Many of the springs are CO_2 rich, discharge along fault zones, and deposit carbonate travertine (e.g., Goff and others 1993). Most gases from thermal and non-thermal springs are composed of > 95% CO_2 (Bergfeld 1997). Based on isotopic analyses, CO_2 is primarily derived from thermal decomposition of metasedimentary rocks, with a minor contribution from magmatic sources (Bergfeld and others 2001). Bergfeld (1997) measured CO_2 fluxes from vents and soils and estimated that up to one t d^{-1} of CO_2 is released at the surface from individual geothermal reservoirs. Bergfeld (1997) observed that CO_2 emissions were highly focused, with fluxes decaying rapidly with distance from gas vents.

One person was killed in 1912 as a result of “gas poisoning“ when exploring an abandoned mining tunnel near the Bartlett Springs resort near Clear Lake (http://www.cagenweb.com/lake/lakobits.htm). The tunnel was known to contain gas that had previously killed small animals and birds. Also, three people have died (in 1878, 1981, and 2000) as a result of CO_2 asphyxiation/toxicity when bathing in a popular mineral pool on an island near the shore of Clear Lake’s Soda Bay (e.g., The Press Democrat, 2000; http://www.sfgate.com/cgi-bin/article.cgi?file=/news/archive/2000/09/26/national0057EDT0406.DTL). Gas concentration measurements made following the 2000 death showed that the air 6 to 8 inches above the water level was 60 % CO_2. The bath was subsequently closed to the public.

A5. Latera Caldera, Italy. Latera caldera is located in the Vulsini volcanic complex in Latium, central Italy. This volcanic complex is characterized by Quaternary pyroclastic flows, pyroclastics, lavas, and cinder cones ranging in age from 1 Ma to 55,000 years old (e.g., Locardi and others 1975; Varekamp 1979). Latera caldera hosts a water-dominated geothermal reservoir (200 to 230^{o}C) in metamorphosed carbonate rocks, the depth of which varies from 1000 to 1500 m (Cavarretta and others, 1985) due to faulting, folding, and uplift. CO_2 is the dominant gas in the geothermal reservoir (Cavarretta and others 1985), the source of which is thermal decomposition of carbonate rocks. The reservoir is sealed by overlying hydrothermally altered volcanic rocks (Cavarretta and others 1985).

CO_2 originating from the geothermal reservoir migrates vertically along major NW-SE and NE-SW trending fault zones and is emitted at the surface in Latera caldera in the form of diffuse soil, vent, and spring degassing. Soil and vent gas surveys have been conducted to measure CO_2 concentrations by gas chromatography; vent gases have CO_2 concentrations > 90%, and soil CO_2 concentrations range up to 97%, with an average value of 4.7% (Astorri and others 2002). These surveys have shown that elevated soil CO_2 concentrations and gas vents are restricted to small areas aligned along faults, indicating that gas flow is channeled along small gas-permeable pathways within the fault zones (Annuziatellis and others 2004). Vegetation is either lacking or is “stressed” in the areas surrounding gas vents (Annuziatellis and others 2004). Astorri and others (2002) assessed hazards associated with gas emissions in the Vulsini volcanic complex using soil gas measurements, geological data, geostatistical analysis, and Geographic Information Systems to create a risk map of the area. The highest risk was associated with the central Latera caldera area where both major faults and minimum sediment overburden occur.

A6. Mátraderecske, Hungary. Mátraderecske is a town in northern Hungary in the foreland of the Mátra Mountains, which are middle Miocene andesite volcanoes. Here, andesite, andesite tuff, and andesite agglomerates are underlain by basement limestone and shale, and are locally overlain by clays and sands (e.g., Tóth and others 1997). Major faults striking NE-SW are seismically active. Deeply derived gases (e.g., CO_2, CH_4) associated with geothermal activity migrate from a karst water reservoir at ~1000 m depth upwards along the faults and fractures within the andesite, and then move both laterally and vertically along bedding planes and faults, respectively, in the overlying sediments. Gas vents in Mátraderecske discharge CO_2, CH_4, and Rn and numerous CO_2-rich springs and wells are found in the area. CO_2 is used in medicinal 'spas'. Soil CO_2 fluxes have been measured up to ~1700 $g\ m^{-2}d^{-1}$, with average values of ~200 to 400 $g\ m^{-2}d^{-1}$ (NASCENT 2005). As a result of the CO_2 leakage, high CO_2 concentrations (up to 90 vol.%) can occur in basements of homes and have resulted in human deaths, most recently in

1995 (Tóth and others 1997). Residents of Mátraderecske have installed CO_2 detection devices and control systems (e.g., tubes and pumps) in homes to mitigate potential hazards (NASCENT 2005). Two homes were demolished in 1993 due to high CO_2 levels. The town supports an active public education program to inform residents and visitors of the hazards associated with CO_2.

A7. Dieng Volcanic Complex, Indonesia. The Dieng Volcanic Complex in Java, Indonesia, is composed of two or more stratovolcanoes and numerous small craters and cones, overlying sedimentary sequences of limestone, sandstone, and shale. Major E-W and NE-SW striking faults control the location of volcanic centers. In February 1979, an eruption began at the pre-existing, water-filled Sinila crater where dark gray clouds and hot mudflows were emitted from the crater (Modjo 1979). Gas emissions ceased from Sinila crater two days after the initial eruption. A new crater was also created nearby and contained a 71°C fumarole. The low temperatures (i.e., below the local boiling point of water) and gas-rich nature of discharges at Dieng led Giggenbach and others (1991) to propose that the eruptions were “pneumatic”, i.e., driven by gas at low temperature. A new fissure aligned with the two craters was also activated and on February 20, 1979, a lethal cloud of gas, likely predominantly CO_2 of magmatic origin, was released from the fissure (Allard and others 1989). The gas cloud killed 142 people as well as several rescue workers.

A8. Rabaul, Papua New Guinea. Rabaul is a pyroclastic shield volcano on New Britain Island, Papua New Guinea. Several large caldera-forming eruptions have occurred over Rabaul’s history and historical eruptions have formed intra-caldera cones (e.g., Newhall and Dzurisin 1988). In June 1990, toward the end of a 51-year non-eruptive period at Tavurvur cone,

CO_2 was released from a 25-m deep pit crater at Tavurvur. Three people were killed while attempting to collect bird eggs in the crater, and then three more people were killed when trying to rescue them. The release of CO_2 occurred suddenly (over the previous several days), as people collecting bird eggs in the crater a week earlier were unaffected. With the aid of SCUBA equipment, the bodies were recovered and a vent was found at the bottom of the crater wall from which gases were emitted at low temperature (48^oC). The thickness of the CO_2 layer at the bottom of the crater was observed to vary between 1.7 and 4.8 m during the month following the deaths, and when windy, the CO_2 cloud was completely dispersed. High levels of CO_2 were also observed in Tavurvur's crater in October 1981 when dead animals were discovered there (SI 1990).

A9. Lakes Monoun and Nyos, Cameroon. In 1984 and 1986, lethal gas bursts occurred at Lakes Monoun and Nyos, respectively, in Cameroon. These gas bursts have since been labeled as “limnic eruptions” (e.g., Tietze 1987). A limnic eruption occurs when a deep tropical lake becomes supersaturated with respect to CO_2 due to input of CO_2 into the bottom of the lake through volcanic degassing. Due to the increased bulk density of the bottom layer, large quantities of CO_2 can build up over years, leading to lack of seasonal turnover and a stably stratified lake. Under normal conditions, CO_2 may diffuse into shallow waters and escape gradually to the atmosphere as bubbles formed at shallow water levels. However, the rapid lake overturn triggered by a landslide, earthquake, strong wind, or cold descending rainwater can cause depressurization of CO_2-rich deep waters and nucleation of CO_2 in the deep water. Once the CO_2 begins to ascend, it becomes a self-sustaining fountain as CO_2-rich water is entrained with the ascending, expanding two-phase mixture.

Both Lakes Monoun and Nyos are located within the crater of an extinct volcano along the volcanic chain in the western highlands of Cameroon. At ~11:30 pm on August 15, 1984, people in villages near Lake Monoun reported hearing an explosive noise and feeling an earthquake. The following morning, a whitish cloud hung over the lake and surrounding area and people were found dead along the road near the lake with burns and skin lesions. Domestic and wild animals were also found dead in the area and vegetation was described as bleached and withered. A landslide scarp was observed from the eastern crater rim to the eastern lakeshore and vegetation at the east end of the lake was flattened, likely from a 5-m water wave caused by the displacement of lake water by the landslide. This landslide is hypothesized to have triggered the rapid turnover of Lake Monoun, leading to the limnic eruption and the deaths of 37 people. A detailed description of the events surrounding the eruption can be found in Sigurdsson and others (1987).

In the case of Lake Nyos, the limnic eruption occurred without warning during the evening of August 21, 1986 and was associated with a degassing process lasting approximately four hours. The cause of rapid lake overturn has not been clearly identified. Extensive damage to vegetation and soils resulted from 20-80 m directional waves. 240,000 tonnes of CO_2 were lost from the upper 100 m of lake Nyos (Giggenbach 1990) and the cloud of gas spilled over the crater rim, killing some people there. The gas flowed and accelerated down along two narrow valleys, preventing dispersion of the gas. Damage to vegetation was observed along the flow path of the gas and humans and animals in the cloud dropped unconscious, comatose, or dead almost immediately. The final toll was 1746 people, over 3000 cattle, and innumerable other animals killed up to 27 km away and 24 hours after the initial gas release. Detailed descriptions of the Lake Nyos disaster can be found in e.g., Freeth and Kay (1987), Baxter and Kapila (1989), LeGuern and others (1992), and Evans and others (1994). Today, in an effort to mitigate CO_2 buildup at depth and prevent future eruptions, both Lakes Monoun and Nyos are being degassed using vertical pipes extending from the lakes' surfaces to near the lakes' bottoms (e.g., Halbwachs and others 2004). These pipes activate controlled fountains of CO_2-water mixtures, safely venting CO_2 to the atmosphere.

A10. Laacher See, Germany. Laacher See is a lake-filled crater in western Germany, formed ~11,000 years ago as a result of an explosive volcanic eruption (Schminke 1989). Laacher See is part of the East Eifel Volcanic Field, which overlies the Rhenish shield and Rhine Graben rift zone. Numerous CO_2-rich mineral springs are found throughout the Eifel region, and discharge of gas (~ 99 vol.% CO_2) is visible within the lake water and on the eastern shore of Laacher See. Isotopic data indicate that the CO_2 is of deep mantle/magmatic origin (Griesshaber and others 1992; Giggenbach and others 1991). A bubble flux of mantle-derived CO_2 in lake water was estimated to be 4 g $m^{-2}d^{-1}$ and the yearly release of CO_2 to the atmosphere is about 5000 t (Aeschbach and others, 1996). The chemical composition and origin of gases in Laacher See are similar to Lake Nyos; as a result, concern has been raised that Laacher See may present a similar hazard from CO_2 buildup and subsequent catastrophic release (e.g., Giggenbach and others 1991). However, because annual lake turnover and vertical mixing occurs at Laacher See, the gases seeping into the lake bottom are released to the atmosphere at a much higher rate than they are at Lake Nyos and hazardous accumulation of CO_2 has been deemed unlikely (Aeschbach and others 1996).

A11. Paradox Basin, Utah, USA. The Paradox Basin, located in the Colorado Plateau area in southwestern Utah/southeastern Colorado, contains numerous actively producing oil, gas, and CO_2 fields. The Paradox Basin is filled with faulted and folded clastic and carbonate sedimentary rocks; its extent is defined by organic-rich Pennsylvania and Permian marine limestones, shales, and evaporites. The CO_2 reservoirs in the basin are vertically stacked and have accumulated within fault-bounded anticlines in sand-rich units that are also the dominant aquifers in the area. Shale or siltstone-rich capping units commonly provide seals.

Present day gas and water flow to the surface in the northwestern Paradox Basin is primarily controlled by the Little Grand and Salt Wash faults that cut north-plunging anticlines and provide high-permeability pathways for fluid flow. These faults are part of a set of west-northwest trending 70-80^o dipping normal faults in the basin and show evidence for Early Tertiary and Quaternary slip (Shipton and others 2004). Active CO_2 leakage and seepage along these faults is characterized by CO_2-rich springs, travertine mounds, gas seeps, and leaky well bores (abandoned oil exploration and water wells; see section B2 below). Fossil travertine mounds also run parallel to the Little Grand and Salt Wash fault traces, indicating extensive past CO_2-rich spring discharge. The source of the CO_2 is likely thermal clay-carbonate reactions in Paleozoic source rocks in the basin at depths greater than 1.5 km (e.g., Heath 2004; Shipton and others 2004). Anomalously high surface CO_2 fluxes up to ~100 g m^{-2} d^{-1} have been measured using the accumulation chamber method along the Salt Wash faults, primarily within small localized areas (Allis and others 2005). However, total CO_2 emission rates from soils and springs have not yet been quantified. No adverse effects of surface CO_2 discharge on people visiting the area or on ecosystems have been reported to date (Shipton and others 2004). Based on geological and geochemical data, Shipton and others (2004) proposed a model of fault-controlled fluid flow in the northwestern Paradox Basin. The shallow Navajo/Wingate sandstone aquifer contains low temperature CO_2-rich waters from which surface spring and geyser discharges are sourced. While shale units cap the aquifer, the Little Grand and Salt Wash faults cut the sealing units, and allow for fluid to move in the vertical direction due to the high hydraulic conductivity. Lower cross-fault permeability relative to up-dip permeability causes the faults to act as barriers to cross-fault fluid flow.

A12. Florina Basin, Greece. The Florina basin lies within the northern area of a NNW-SSE-trending graben that extends150 km from northern Greece to the Former Yugoslav Republic of Macedonia. This middle Tertiary graben, formed in metamorphic crystalline rocks, was subsequently filled with fluvial and lacustrine sediments (>1000 m thick) (Beaubien and others 2004). The Florina basin is flanked on the west side by a normal fault zone and metamorphic rocks intruded by granites, and on the east side by crystalline limestones, schists and gneisses. Moving eastward in the basin, sedimentary cover thins and changes from coarse clastics to sequences of sand, silt, clay, and lignite. Vertically stacked reservoirs of >99.5% CO_2 are located in limestone basement and overlying sandstone units, with the top of the upper reservoir located at only 300 m depth (Beaubien and others 2004). Sandstone reservoirs are capped by clayey sediments. CO_2 leakage at the surface in the Florina basin occurs as CO_2-rich springs throughout the area and, where basement limestones are exposed, as surface gas seeps. The Florina basin is seismically active, with earthquake magnitudes up to 5 on the Richter scale; the potential relationship between fluid migration and seismicity is being investigated (Beaubien and others 2004).

Two aquifers are present in the Florina basin. One is a confined aquifer in clastic sedimentary rocks capped by silts and clays that extends throughout most of the basin and hosts the CO_2 reservoir. The second is an unconfined aquifer hosted in karstic carbonates on the eastern and southern margins of the basin. To evaluate the effects of CO_2 leakage from depth on groundwater quality in the Florina basin, Beaubien and others (2004) conducted an investigation of the chemistry of waters from wells and springs throughout the basin. They analyzed major element concentrations in 132 samples and trace element concentrations in 17 of these samples and found that total dissolved solids ranged from 150 to 4230 mg L^{-1} and hardness ranged from 70 to 1950 mg L^{-1} as $CaCO_3$. Waters collected from shallow wells and springs were Ca-HCO_3 type, while those collected from deep boreholes were Mg-HCO_3 type. Most water samples were potable. However, samples collected close to the CO_2 field had higher total dissolved chemical constituents and hardness, and consequently were of poorer drinking water quality. Beaubien and others (2004) interpreted the spatial trends in the chemical compositions of groundwaters to reflect interaction of CO_2-rich groundwaters with host rocks along flow paths.

Appendix B: Summary Descriptions of Industrial Analogues

B1. Sheep Mountain, Colorado, USA. The Sheep Mountain CO_2 field is located in the Colorado Plateau area of southern Colorado. The CO_2 reservoir is located at 1000 to 1800 m depth in a northwest-trending anticlinal fold, bounded on the northeast side by a thrust fault (Allis and others 2001). The CO_2 reservoir units are the Cretaceous Dakota and Jurassic Entrada sandstones and are sealed by Cretaceous marine sediments capped by a laccolith (Allis and others 2001). The CO_2 originates from thermal decomposition of limestones (Caffee and others 1999).

Production of the Sheep Mountain CO_2 field began in 1975 and has continued at about 2×10^9 m^3 yr^{-1}. The produced gas is 97% CO_2 and total reserves are estimated to be 7×10^{10} m^3 (Allis and others 2001). In March, 1982, a production well blew out of control during drilling, resulting in freely flowing CO_2 at the well head and leakage of CO_2 from ground fractures on the west slope of Little Sheep Mountain directly above the drill site (Lynch 1983). The “kill” operation was complicated by the high CO_2 flow rate from the reservoir, which lifted the kill fluid (brine and mud) up the annulus. The well was brought under control in April, 1982 by the dynamic injection of drag-reduced brine followed by mud (Lynch 1983).

B2. Crystal and Tenmile Geysers, Utah, USA. A number of well bores drilled for water or oil exploration discharge CO_2-rich groundwater along the Little Grand Wash and Salt Wash faults in the Paradox basin of Utah (see section A11 above). Crystal Geyser is a cold-water geyser located on the eastern bank of the Green River in the footwall of the Little Grand Wash fault zone (Baer and Rigby 1978). Crystal Geyser erupts from the Glen Ruby #1-X oil exploration well that was drilled in 1935. The well was spudded into a 21.5 m thick travertine mound, drilled to a depth of 801 m, and then abandoned after oil was not found. Crystal Geyser currently erupts from the well bore to over 20 m high every 4-12 hours (e.g., Shipton and others 2004). Because this is an artesian well, the CO_2-charged water rises in the well, the pressure decreases, and explosive degassing of dissolved CO_2 occurs. As the CO_2-charged waters continue to flow to the surface, the process is repeated.

Gouveia and others (2005) measured atmospheric CO_2 concentrations on a grid 25 to 100 m away from Crystal Geyser, along with wind speed and direction. Based on Gaussian modeling of these data, CO_2 emission rate was estimated to be ~224 to 500 t d^{-1} during eruption events, and ~15 t d^{-1} during pre-eruptive events. They estimated the annual CO_2 emission rate from Crystal Geyser to be 12 kilotonnes. CO_2 concentrations were below human health and safety concerns, even within a few meters of the geyser.

Tenmile geyser is located near the northern extent of the Salt Wash faults. The geyser erupts infrequently to a height of several meters from an abandoned well drilled to a depth of 200m in the fault footwall (e.g., Shipton and others 2004). Other smaller geysers (e.g., the Woodside, Tumbleweed, and Chaffin Ranch geysers) also erupt occasionally from abandoned water and oil exploration wells drilled in the northern Paradox basin. No health or safety effects related to the geysers are reported in the literature.

B3. Florina basin, Greece. The Florina CO_2 field, located in the Florina basin (see section A12 above), is the only commercial natural CO_2 reservoir in Greece. The field has been in production over the last ten years, with production ranging from 20,000 to 30,000 t yr^{-1} over the past three years (e.g., Beaubien and others 2004). As summarized in NASCENT (2005), in 1990, the Department of Hydrogeology, IGME drilled an exploration well for mineral water to 559 m depth in the Florina basin. After the well was completed and the wellhead valve was closed, surface CO_2 leakage was observed 100 m from the well. The area of leakage moved toward the well, eventually creating a ~25 m^2 depression around it, and allowing the drill rig platform to collapse into the hole. A small lake formed in the hole and the area was fenced off. A small pool was later built for people to immerse their feet in; however, when one person attempted to swim in the pool and died as a result of CO_2 asphyxiation, it was closed by local authorities. In 2000, water was observed to still be flowing in the pool, while in 2003, the well and pool were dry, likely due to lowering of gas pressure in the reservoir and borehole collapse (NASCENT 2005).

B4. Torre Alfina Geothermal Field, Italy. The Torre Alfina geothermal field is located in northern Latium, central Italy. This field is water dominated, with a gas cap composed primarily of CO_2 overlying the reservoir. The cap rock on the reservoir consists of sequences of shales, marls, and limestones. In 1973, the first exploratory well (Alfina 1) was drilled through 20 m of volcanics and then through the cap rock to a depth of 663 m, at which point it blew out, producing over 300 t h^{-1} of fluid, primarily gas (Ferrara and Stefani 1978). After releasing ~25,000 t of CO_2 to the atmosphere, the well was shut in. Numerous areas of surface CO_2

emissions then appeared around the well and were attributed to a lack of production casing and CO_2 migration along permeable pathways in the cap rock and overlying volcanics. Due to the potential danger to the rig technicians and local residents associated with high CO_2 emissions, the well was completely cemented. Three boreholes were also drilled in an effort to focus subsurface CO_2 flow to a few points and release the CO_2 at a height above the ground surface where the hazards associated with the gas would be reduced. However, this was only successful at one of the boreholes.

Ferrara and Stefani (1978) conducted a survey of atmospheric CO_2 concentrations associated with the surface CO_2 emissions within a 250-m diameter area around the Alfina 1 well. Over a 53-day survey period, they measured CO_2 concentrations of up to ~50%. The highest values were measured closest to the ground surface (10 cm height above ground), in topographic depressions, and during periods of low wind speed.

Tables

Table 1. Summary of FEPs of natural leakage of CO_2 (see Appendix A for references).

Site	**CO_2 Source**	**Geologic model for accumulation**	**Event triggering leakage**	**Pathway for leakage**	**Type of surface leakage**
A1. Mammoth Mountain, CA USA	Magmatic + thermal decomposition of carbonates	Accumulation at ~2 km depth in porous/fractured rock under caprock	Seismic activity and reservoir pressurization	Faults and fractures	Fast, diffuse, vent, spring
A2. Solfatara, Italy	Magmatic + thermal decomposition of carbonates	Relatively shallow zone of fractured rock contains gas phase and overlies aquifers, then magma body at several km depth	No specific leakage event captured	Faults and fractures	Diffuse and vent
A3. Albani Hills, Italy	Magmatic + thermal decomposition of carbonates	Deep pressurized reservoirs in structural highs of sedimentary bedrock	Slow releases with several sudden large releases also occurring, possibly triggered by seismic activity	Faults and fractures	Diffuse, vent, spring/well, 1995 and 1999 events fast
A4. Clear Lake, CA, USA	Thermal decomposition of metasedimentary rocks, minor magmatic component	CO_2 derived from liquid-dominated geothermal reservoir hosted in marine metasedimentary rocks	No specific leakage event captured	Faults and fractures	Gas vents, springs
A5. Latera caldera, Italy	Thermal decomposition of carbonates	CO_2 accumulates in liquid-dominated, carbonate geothermal reservoir capped by hydrothermally altered volcanics	No specific leakage event captured	Faults and fractures	Diffuse, vent, spring
A6. Mátraderecske, Hungary	Geothermal/copper-zinc mineralization	CO_2 accumulates in karst water reservoir (~1 km depth)	No specific leakage event captured	Faults and fractures	Diffuse, vent, spring
A7. Dieng, Indonesia	Magmatic	Unknown	Volcanic, possibly “pneumatic”, eruptions	Fissure	Eruptive

Site	CO_2 Source	Geologic model for accumulation	Event triggering leakage	Pathway for leakage	Type of surface leakage
A8. Rabaul, Papua New Guinea	Magmatic	Unknown	Unknown	Fractures	Fast, vent
A9. Lakes Monoun and Nyos, Camaroon	Magmatic	Accumulation in deep lake and stable stratification	Rapid lake turnover triggered at Monoun by landslide; Nyos trigger unknown	NA	Eruptive (limnic)
A10. Laacher See, Germany	Magmatic	NA	Seasonal lake overturn and mixing	NA	Diffusive and bubbling from lake surface, diffuse from lake shore
A11. Paradox Basin, UT, USA	Thermal decomposition of carbonates	Reservoirs are vertically stacked, sandstone units, in fault-bounded anticlinal folds, capped by shale/siltstone units	No specific leakage event captured	Faults and fractures	Diffuse, gas seeps, springs
A12. Florina Basin, Greece	Thermal decomposition of carbonates	Reservoirs are vertically stacked, limestone and sandstone units (upper unit at 300 m depth), capped by silts and clays.	No specific leakage event captured	Slow leakage along rock discontinuities	Springs, gas seeps

Table 2. Summary of FEPs of industrial leakage of CO_2 (see Appendix B for references).

Site	CO_2 Source	Geologic model for accumulation	Event triggering leakage	Pathway for leakage	Type of surface leakage
B1. Sheep Mountain, CO, USA	Thermal decomposition of carbonates	Reservoir is anticlinal fold, bounded on one side by thrust fault, sandstone, ave. depth 1500 m, capped by marine sediments and a laccolith.	Well blowout	Well	Free flowing CO_2 gas from well, CO_2 leakage from fractures above drill site
B2. Crystal and Tenmile Geysers, Paradox Basin, UT, USA	Thermal decomposition of carbonates	Reservoirs are vertically stacked, sandstone units, in fault-bounded anticlinal folds, capped by shale/siltstone units	Well blowouts	Wells	Cold geysers
B3. Florina Basin, Greece	Thermal decomposition of carbonates	Reservoirs are vertically stacked, limestone and sandstone units (upper unit at 300 m depth), capped by silts and clays.	Well blowout	Well	CO_2 gas leakage from soils, water-filled pool formation around well
B4. Torre Alfina geothermal field, Italy	Geothermal	Geothermal reservoir with a gas CO_2 cap at ~660 m depth, capped by sequences of shales, marls, and limestones.	Well blowout	Well	Free flowing CO_2 gas from well, diffuse emissions from ground around well

Table 3. Additional aspects of CO_2 leakage associated with natural (N) and industrial (I) processes (see Appendices A and B for references).

Site	**Geographic setting/land use**	**Magnitude of surface CO_2 leakage**	**Consequences of release**	**Monitoring and remedial measures**
A1. Mammoth Mountain, CA USA (N)	Recreational area (U.S. national forest, ski resort)	~250 t d^{-1} from 480,000 m^2 area	Formation of tree kill areas, one person with symptoms of asphyxiation, one person died	Temporal and spatial monitoring of CO_2 concentrations and fluxes in tree kill areas; measurements of groundwater chemistry; public education
A2. Solfatara, Italy (N)	Recreational area (private park/campground) surrounded by urban area	1500 t d^{-1} from 0.5 km^2 area	No vegetation in degassing area.	Temporal and spatial monitoring of soil CO_2 fluxes, monitoring of heat release; monitoring of fumarole gas chemistry; seismic and deformation monitoring; public education
A3. Albani Hills, Italy (N)	Urban area	74 t d^{-1} as surface gas emissions (61,000 m^2 area) and 506 t d^{-1} as dissolved CO_2 in shallow ground water	High CO_2 concentrations in homes; deaths of livestock (1999 event); past human deaths	Measurements of soil CO_2 fluxes and concentrations; monitoring groundwater chemistry; identification of residential areas at risk, development of zoning bylaws, and development of public education programs
A4. Clear Lake, CA, USA (N)	Rural	~ 1 t d^{-1}	Four people killed	Measurements of soil and vent CO_2 fluxes and concentrations, mineral pool closed to public
A5. Latera caldera, Italy	Rural, small towns	Na	Vegetation stress or kill	Soil gas concentration surveys, hazard mapping
A6. Mátraderecske, Hungary (N)	Rural area, village	Average CO_2 flux ~ 200 to 400 g $m^{-2}d^{-1}$ (total degassing area unknown)	High CO_2 concentrations in homes, death of several people	CO_2 detection and control devices installed in homes, demolition of homes with hazardous CO_2 levels, public education
A7. Dieng, Indonesia (N)	Rural	Unknown	~145 people killed	Na

Site	Geographic setting/land use	Magnitude of surface CO_2 leakage	Consequences of release	Monitoring and remedial measures
A8. Rabaul, Papua New Guinea	Rural	Unknown	Three people killed, birds killed	Na
A9. Lakes Monoun and Nyos, Camaroon (N)	Rural, villages	Nyos: 240,000 t CO_2 in eruptive event	Loss of human (~1800 combined) and animal life (e.g., thousands of cattle), vegetation damage	Controlled lake degassing using pipes, monitoring of lake chemistry, public education
A10. Laacher See, Germany (N)	Rural	~14 t d^{-1}	Na	Monitoring CO_2 fluxes and concentrations from lake surface and shore
A11. Paradox Basin, UT, USA (N)	Rural	Soil CO_2 fluxes up to 100 g $m^{-2}d^{-1}$; total emission rate unknown	Na	Measurements of soil CO_2 fluxes; monitoring groundwater chemistry
A12. Florina Basin, Greece (N)	Rural, small towns	Unknown	Na	Measurements of groundwater chemistry
B1. Sheep Mountain, CO, USA (I)	Rural	Unknown	Na	Dynamic injection of drag-reduced brine followed by mud
B2. Crystal and Tenmile Geysers, Paradox Basin, UT, USA (I)	Rural	Crystal Geyser: ~33 t d^{-1}	Na	Measurements of atmospheric CO_2 concentrations
B3. Florina Basin, Greece (I)	Rural, small towns	Unknown	Death of one person	Leakage area closed off to people
B4. Torre Alfina geothermal field,	Rural	~25,000 t	Na	Cementation of exploration well; borehole installation to focus subsurface gas flow and vent CO_2 at height in

Site	Geographic setting/land use	Magnitude of surface CO_2 leakage	Consequences of release	Monitoring and remedial measures
Italy (I)				atmosphere; atmospheric CO_2 concentration monitoring