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Impacts of Carbon Dioxide Gas Leaks from Geological Storage Sites on Soil Ecology and Above-Ground Vegetation

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1. Introduction

The global annual carbon dioxide (CO₂) gas emissions, one of the major green house gases contributing to global warming, into atmosphere have increased to 31.5 Gt in 2008 (German renewable energy institute [IWR], 2009), of which little over two-third (~22 Gt) were emitted from manmade sources (Benson, 2005). Electricity production and transportation make up two-third of total manmade emissions while the rest is contributed from heating buildings and other industrial consumption. Our dependence on fossil fuels continues to be increasing with over 85% of the world's energy needs still coming from burning oil, coal and natural gas (Benson, 2005) and by the end of 21st century our demand for fossil fuel is projected to more than double. Some of the scenarios (e.g. with no action taken to limit emissions) suggest a doubling of CO₂ emissions by 2050. This increased energy demand is mainly driven by continued industrialization and improved quality of life in not only western countries (North America and Europe), but also in two of the largest populated countries in the world viz., China and India. This would further increase CO₂ gas emissions into atmosphere with a strong positive feedback on climate change. This demands urgent action to reduce or offset CO₂ emissions from fossil fuels. In this context, while the efforts are being made for cleaner and efficient use of fossil fuels, carbon capture and storage technology is being considered as one of the main short-term viable strategy to help mitigation climate change in coming decades (Bachu, 2000; Intergovernmental Panel on Climate Change [IPCC], 2005; Pacala et al., 2004; Van de Zwaan & Smekens, 2009).

1.1 Carbon capture and storage technology

The carbon capture and storage technology basically includes two approaches: (1) CO₂ gas is captured directly from the large and stationary source points (e.g. power plants, petroleum refineries, gas processing units & cement factories), concentrated into a nearly pure form, transported through pipelines and injected into geological storage sites (on- and off- shore) far below the ground surface (Bachu, 2000). This technology is called as "Carbon Capture and Storage" (CCS), and (2) atmospheric CO₂ gas is biologically fixed by growing vegetation (e.g. forest trees, biomass crops) and stored in above- and below-ground plant parts. This is referred to as "Carbon Sequestration" (CS) and these two approaches complement each

other as CCS approach, unlike CS, cannot capture CO₂ gas directly from the atmosphere. Hence, CCS technology is increasingly seen as one of the mechanisms that can make a useful contribution to the reduction of CO₂ emissions over the next 50 years (IPCC, 2005). Some estimates predict that CCS technology has the potential to capture and store CO₂ emissions from power generation by 80–90% (Department of Trade and Industry, UK [DTI], 2002). However, in order to have CCS that significant impact, CO₂ gas will have to be injected on a large scale (in Gt year⁻¹).

1.2 The geological storage sites and their storage capacity

Geological formations suitable for CO₂ storage are located in sedimentary basins where thick sediments have accumulated over millions of years (Benson, 2005). Such sites are oil and gas reservoirs, deep saline aquifers with suitable caprocks and deep unmineable coal beds. Some estimates suggest that depleted oil and gas reservoirs can store as much as 800 Gt of CO₂ gas (Freund et al, 2003). These sites are known to trap buoyant fluids such as CO₂ and CH₄ underground for millions of years. Hence, CCS technology intends to adopt the methods already used by oil / gas exploration and production, and enhanced oil recovery (EOR) schemes. Under EOR schemes CO₂ gas is injected into oil reservoirs to make it dissolve into the oil which reduces the viscosity of oil while increasing its volume to enhance reservoir pressure and production (Benson, 2005). For example, EOR scheme at Williston Basin oilfield, Canada started injecting ~5000 tonnes of CO₂ day⁻¹ in October 2000. The CO₂ gas is being transported through 330 km long pipeline from the lignite-fired Dakota Gasification Company plant site in North Dakota, USA (DTI, 2005). The saline aquifers are the reservoirs deep underground and contain saline water (not suitable for drinking) and the global storage capacity of these sites is estimated to be between 400 and 10,000 Gt of CO₂ (Freund et al., 2003). Whereas, the unmineable coal beds, which are located too deep beneath the ground making them uneconomical to explore, can also be used to inject CO₂ gas where the injected gas is absorbed onto the coal. The global storage capacity of unmineable coal beds is estimated to be around 148 Gt of CO₂ (Freund et al., 2003).

1.3 Potential risks of failures of CCS technology

Presently existing CCS technology suggest that geological formations selected for CO₂ storage needs to be located at a minimum depth of 800 m so that CO₂ gas is stored at supercritical state to trap large amounts of gas in a small volume. However, in order to implement CCS technology on large and commercial scale, it is essential to assess all the potential risks and provide evidence to inform governments and the public that potential risks are well understood and impact assessments are studied for long-term safety and control measures (Wei et al., 2011).

As the CO₂ gas is captured from the large production sites located on land (e.g. power plants), the gas needs to be transported through pipelines over a long distance. The first source of potential leakage, therefore, would be pipeline failures or small leaks from joints. The scale of leakage and the potential impacts on surrounding environment from such leakages depends on whether the pipeline is laid over or under the ground and whether the pipeline pass through built-up area or near large drinking water sources (e.g. inland lakes or drinking water reservoirs). Pipeline corrosion over a period of time is another issue that might cause gas leakage. CO₂ gas transportation via pipelines in a supercritical state is

reported to cause corrosion of steel pipes @ $0.01 \text{ mm year}^{-1}$. However, the corrosion rate further increases to 0.7 mm year^{-1} if free water was present in the pipeline (IPCC, 2005). If other gasses like hydrogen sulfide or hydrocarbons are mixed with CO_2 gas, then the chances of leakage and corrosion increase further (Klusman, 2003). Therefore, the pipelines require continuous surveillance for leakage or third party intrusions or encroachments. For example, the Cortez pipeline in Colorado, USA which is buried 1 m below ground, but passes through build-up areas is being air monitored once every two weeks (IPCC, 2005).

The leakage from geological storage sites may also occur due to failure of the sealing cap of injection well or migration of gas through geologic media and lead to slow but large releases either due to over-pressurization or slow releases via faults and fractures (Heinrich et al., 2003; Klusman, 2003). While the past evidence from oil and gas fields shows that the natural gases and fluids, including CO_2 gas, can be held intact underground for millions of years, incidences like the one of McElmo dome leakage (Gerlach et al., 1998; Stevens et al., 2000) demand complete evaluation of storage sites before selecting for gas injection (IPCC, 2005). Therefore, in order for CCS to be effective, the CCS technology must ensure that leakage is minimized from both sudden releases due to accidents or technical failures and slow leaks over longer period of time.

Perry (2005) reports that more than 600 natural gas storage reservoirs exist across the globe, but to-date on only 10 occasions significant leakage have occurred. These leakages were mainly attributed to failure of bore well integrity (5 times), leaks in the caprocks (4 times) and poor site selection (1 time). However, when it comes to long-term safety of CCS technology there are uncertainties as we lack the experience on the long-term fate (100 to 1000 years) and safety of large volume of CO_2 gas to be injected into geological formations (Celia et al., 2002). Some of the naturally occurring CO_2 springs and volcanic sites located across the world have been emitting CO_2 gas with no severe effect on our ecosystems or population, but the risks of CO_2 gas leakage from CCS transport pipelines or storage sites will be on larger scale as huge amounts of CO_2 gas is being handled under CCS schemes (IPCC, 2005). If leaks were to occur, the CCS technology would defy the very purpose to help mitigate climate change (Heinrich et al., 2003). While the existing CCS technology claims to reduce the risks of such leakages by applying safety systems in place and selecting safe geological storage sites (both on- & off-shore), there are chances that slow but continuous releases from CCS sites could go unnoticed as leaking CO_2 gas would quickly diffuse in the atmosphere (Heinrich et al., 2003). Therefore, it is important to understand the effects of CO_2 gas leaks on surrounding environments viz., marine life if gas were to be injected into off-shore geological sites and, vegetation and soil ecosystems if gas were to be injected into on-shore geological sites.

1.4 Effects of naturally occurring CO_2 leaks on soil geochemistry

Elevated soil CO_2 concentrations can cause changes in mineralogy composition together with changes in trace elements like As and Cr (Kruger et al., 2009; Stenhouse et al., 2009). Changes in cation exchange capacity (CEC), and the presence of oxides like CaO, MgO, Fe_2O_3 , and Mn_3O_4 have also been reported elsewhere (Blake et al., 2000; Billett et al., 1987; Goulding et al., 1998). Leakage of CO_2 may also reduce groundwater pH besides affecting taste, color or smell and cause significant deterioration in the quality of potable groundwater by altering groundwater chemistry (Stenhouse et al., 2009). CO_2 leakage rising

to sub-soil levels may also cause changes in subsurface microbial populations either by favoring some species or restricting others, depending on species type and site characteristics (Jossi et al., 2006; Tian et al., 2001).

1.5 Effects of naturally occurring CO₂ leaks on overlying vegetation

CO₂ is an odorless and non-toxic gas, and considered an integral part of our everyday lives. However, exposure to high concentrations of CO₂ poses danger to human beings, animals and surrounding environment, but such leaks may increase soil CO₂ concentrations in near surface and below vegetation canopies. Such a situation could have significant effects on above-ground vegetation and soil inhabiting organisms (e.g. earth worms, microorganisms), both in the short- and long-term. While plants in general are known to be more tolerant to elevated CO₂ gas, persistent leaks from geological storage sites may lead to accumulation of CO₂ gas in soil (near and sub surface). This may suppress root respiration, alter plant water / nutrient uptake capacity by altering soil pH towards acidity and ultimately affect above-ground biomass (Celia et al., 2002; Cook et al., 1998; Gahrooei, 1998; Miglietta et al., 1998; Sorey et al., 2000; Sowerby et al., 2000; Stephens & Hering, 2002). There are many studies where forest trees or perennial vegetation mortality from naturally occurring active volcanoes emitting CO₂ gas into atmosphere have also been documented (e.g. Macek et al., 2005; Stephens & Hering, 2002; Vodnik et al., 2006). In fact, to-date naturally occurring CO₂ springs and active volcanic sites are the ones quite extensively studied in Europe and America.

At Mammoth Mountain, USA, more than 30% by volume of soil CO₂ levels were measured at sites where tree mortality has occurred (Gerlach et al., 2001). At Bossoleto, Italy, soil CO₂ leaks increasing atmospheric CO₂ concentrations to as high as 75% by volume at night, but much lower during day time, were recorded (Van Gardingen et al., 1995). Low levels of CO₂ concentrations during day time, the period when plants are photosynthetically active, may have reduced the adverse effect of elevated CO₂ gas on trees and herbaceous plants or these plant species may well have adapted to elevated CO₂ gas after being exposed for long period of time (van Gardingen et al., 1995). While anaerobic conditions (anoxic or hypoxic) are harmful to plants, many species are known to adapt to such conditions, at least temporarily, by modifying their rooting system and supplying O₂ internally from leaves to roots (Vartapetian & Jackson, 1997). This may have been the case at Bossoleto, Italy where *Phragmites australis*, a wetland species adapted to temporary anoxic conditions was reported to be the most dominant plant cover (Van Gardingen et al., 1995).

Most of studies referred in above paragraphs including the ones reported elsewhere (Beaubien et al., 2008; Biondi & Fessenden, 1999; Vodnik et al., 2006;) have examined the effects of naturally occurring CO₂ leaks from active volcanoes / geothermal sites, and hot / cold CO₂ springs on ecosystems. At these environments the existing ecosystems have been exposed to elevated CO₂ for considerably long periods, thus the plant / tree species may have adapted (West et al., 2009). Therefore, the findings from these sites may not be representative of the effects of potential leakage from a CCS storage sites. Moreover, many of these sites release not only hot or cold CO₂ gas but also gas mixed with either volcanic ash or mineral particles or with other gasses like CH₄ (Bergfeld et al., 2006),

which makes it difficult to isolate the effect of CO₂ gas alone. Furthermore, the effects of slow release of CO₂ from CCS underground transport pipelines or geological storage sites on plant and soil inhabiting organisms are not well studied and needs better understanding (Lewicki et al., 2005). Past studies also suggest that not all the plant species respond similarly when exposed to elevated soil CO₂ concentrations (Van Gardingen et al., 1995), hence makes it difficult to define a “lethal CO₂ concentration level” as different vegetation types respond differently to anoxic stress or anaerobic soil environments due to severe dearth of O₂ level in the soil. Added to this, variations amongst the natural ecosystems and their surrounding environment make it difficult to gauge exposure levels (Sarah & Sjoersten, 2009).

Hence, understanding the risk of CO₂ leakage from storage sites and studying the effect of leaking gas on surface ecosystem is critical for multiple reasons. First, accurate data on the quantity of CO₂ that has been injected and stored is required for trading and accounting purposes; second, any leakage will negate the original purpose of the CCS technology and; third, the leaking CO₂ might damage surface ecosystems including above-ground vegetation and soil ecology. Findings from such studies would enable CCS technology to adopt full safety measures while transporting and injecting huge amounts of CO₂ gas into on-shore geological storage sites, and alleviate the public perceptions, if any, on long-term safety of CCS technology.

In order to test the response of overlying vegetation and soil ecology to gas leaks an experimental field facility, the Artificial Soil Gassing And Response Detection (ASGARD), has been established at the University of Nottingham, UK where gas can be artificially injected into the soil to simulate build up of gas concentrations and its slow release to soil surface (Photo 1). This facility has enabled to study some impacts of a controlled injection of CO₂ gas on a non-adapted pasture grass and field crops, and on soil ecology and chemistry. This chapter describes some of the main findings from studies carried out at the ASGARD site.

Between 2002 and 2005, the ASGARD site was used to investigate the effect of elevated concentrations of soil CH₄ on pasture grass, wheat and winter bean crops (Smith et al., 2005). The natural gas, a major source of energy supply in Europe, is mainly composed of CH₄ gas (78-95% by vol.). European natural gas sub-surface transportation pipelines are under regular helicopter surveillance to detect any gas leaks from pipeline joints, third party incursion and land slippage which may physically damage pipeline and gas supply (Smith et al., 2005). According to Baggott et al. (2003) the CH₄ gas leakage from UK natural gas transportation system alone amounts to 342 kilo tonnes year⁻¹, which is equivalent to 10260 kilo tonnes of CO₂ in terms of global warming potential. Thus, early warning system to detect CH₄ gas leaks would enable the surveillance system to take immediate control measures. Therefore, Smith et al., (2005) artificially injected CH₄ gas into the soil at ASGARD site, to simulate CH₄ leakage and monitored above-ground vegetation stress symptoms using remote sensing technology.

Since 2006 the ASGARD site is being used to inject CO₂ gas, initially by the British Geological Survey, UK (West et al., 2009) and later by Patil et al. (2010) and Sarah and Sjoersten, (2009) in 2007-08. Therefore, this chapter while describing the ASGARD site in

detail presents main findings of previous studies undertaken at this site. These studies were undertaken with multiple objectives: (1) to develop a field site where CO₂ gas could be artificially injected at a targeted rate into the soil to simulate build up of soil CO₂ concentrations in near-surface and its leakage into the atmosphere, (2) to monitor temporal and spatial variations in soil gas concentrations under different land cover, and (3) to study the response of vegetation(s), soil properties, and soil inhabiting organisms to elevated soil CO₂ concentrations.



Photo 1. The ASgard site. Both pasture and fallow plots with gassing pipes and measuring tubes can be seen.

2. Methodology

2.1 The study location and the ASgard site

The ASgard research facility is located on a flat and open field of permanent pasture at the Sutton Bonington campus of the University of Nottingham (52° 49' 60 N, 1° 14' 60 E, 48 m a.s.l.), approximately 18 km south of central Nottingham, UK (Figure 1). The site was previously used as a sheep pasture and had remained grassland for over 10 years until the ASgard facility was laid out. Long term temperature average (1971–2000) at this site shows January as the coldest month with maximum and minimum temperatures of 6.9 and 1.2 °C, respectively and July as the warmest month with maximum and minimum temperatures of 21.3 and 11.4 °C, respectively. The mean annual precipitation is 606 mm; most of it is received as precipitation, and is fairly uniformly distributed throughout the year (Sarah & Sjogersten, 2009). The ASgard site is positioned in such a way that it is not influenced by shade from trees or fencing.

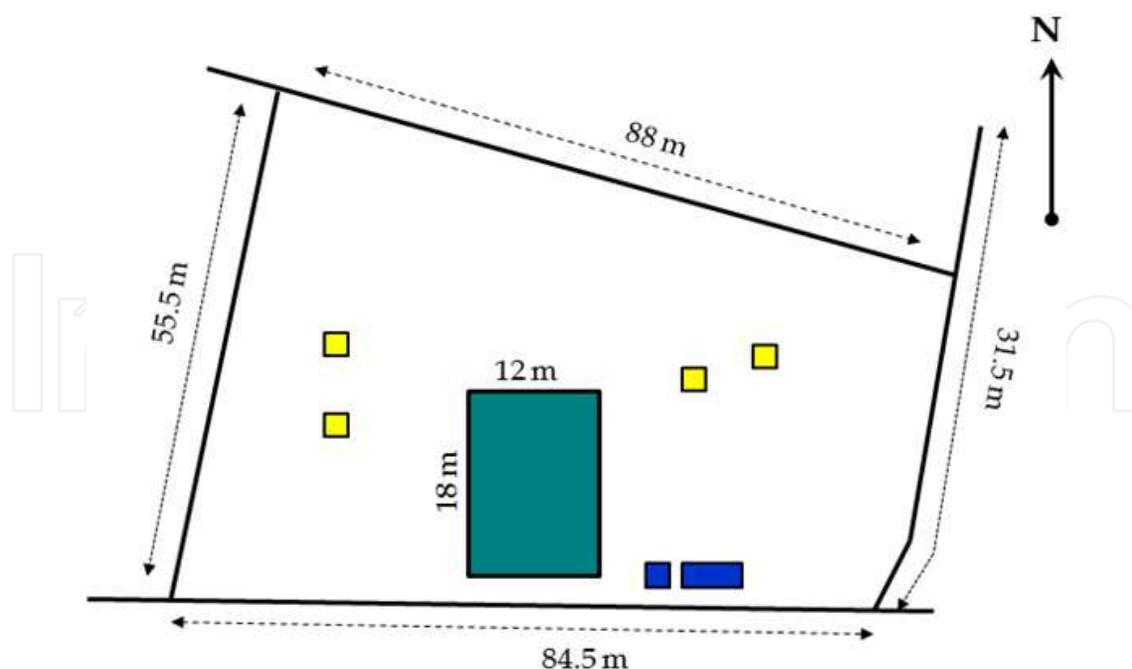


Fig. 1. Location of the ASgard field facility and the main experimental block. Green- main experimental plots with a total of 30 plots, and Yellow - 4 remote control area located >10 m away from the main experimental plots. Blue- gas cylinders and port-cabin which accommodated automated gas supplying hardware and software system.

2.2 Site mineralogy and soil characteristics

Geologically, the study area is characterized by up to 1.5 m of head deposit overlying mudstones of the Mercia Mudstone Group. Mineralogical analyses in 2006 showed that quartz was the dominant mineral (>90% of the total dry weight) followed by K-feldspar and albite as minor along with trace amounts of mica, kaolinite, chlorite and hematite (West et al., 2009). Mineralogical composition between the A horizon (0.15–0.30 m depth) and B horizon (0.45–0.50 m depth) were found to be the same (West et al., 2009). However, readers are directed to refer to Ford (2006) for detailed geological description of this site and its surrounding area. The soil type lies within the Worcester Series and comprises 0.3 m deep sandy clay loam over 0.7 m clay and marl horizon. The top soil layer (~ 0.1 m) contains 8.91% clay, 22.89% silt and 68.2% sand (West et al., 2009).

2.3 Experimental plots and gas supply system

In the year 2006 a total of 30 plots each of 2.5 m × 2.5 m in size were laid out in a rectangular grid patterns (5 × 6 plots) with 0.5 m pathways between each plot (Figure 2). Ten plots were kept under already established pasture grass and rest were planted with agricultural crops after removing the pasture grass from those plots (West et al., 2009). CO₂ gas was delivered into the pasture plots at a constant rate of 3 liters min⁻¹ for 19 weeks (May to September 2006). In the year 2007, Sarah and Sjogersten (2009) used 8 plots to plant commercial turf, previously planted with agricultural crops, but left untreated for more than 8 months before they began the study. The turf grass was composed of *Lolium perenne*, *Festuca rubra*, *Festuca rubra commutate* and *Poa pratensis* types. The CO₂ gassing was started 6 weeks after planting the turf grass. Of the total 8 turf grass plots, 4 plots were injected with CO₂ gas at a constant

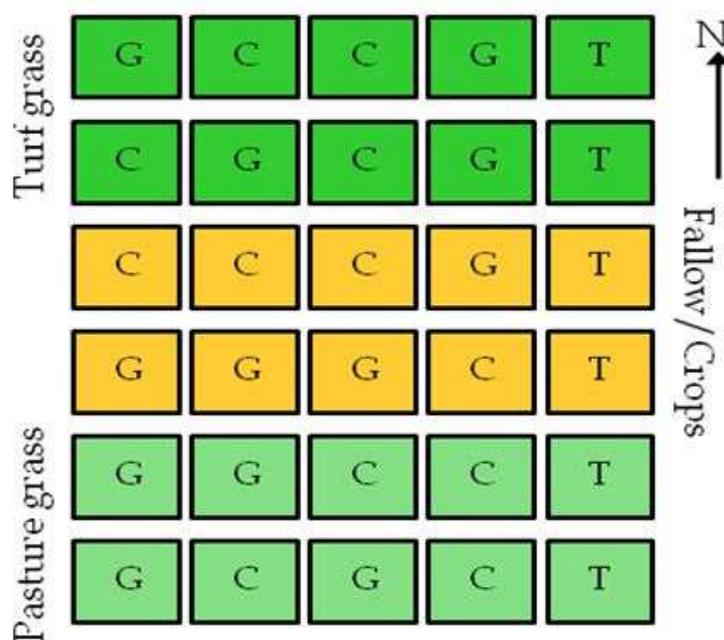


Fig. 2. Layout of 30 plots within the main experimental block. Light green plots- pasture grass, yellow plots- fallow and agricultural crops, and dark green - turf grass. G = gassed, C = un-gassed control and T = plots used only for testing the gassing system and all the T plots were not used to impose any of the treatments during study period.

The injection rate for all the gassed plots at ASGAR site since CO₂ gassing studies began varied from 1–3 liters min⁻¹, which equates to an annual injection rate of around 1–3 tonnes year⁻¹. This rate of gas injection is far less than the amount injected at some of the already existing off-shore storage sites. For example, Sleipner west field beneath the North Sea, Norway injects 1 million tonnes of CO₂ year⁻¹. Nevertheless, the injection rates selected at the ASGAR project site were constrained by the funding and the logistics put in place as well as for practical purposes.

2.4 Measurements on soil gas concentrations

Plastic tubes of 1 m long with 0.2 mm internal diameter were installed vertically into the soil to a depth of 0.3 m and at different distances from the center of plots on a diagonal transect in all the plots (gassed & un-gassed; Figure 3). The bottom end of each sampling tube (at 0.3 m depth) was sealed and the lower 0.15 m of the tube was drilled with 14 equally spaced holes (4.5 mm diameter). This portion of the tube was covered with fine meshed cloth from inside the tube to prevent outside soil clogging the holes. These holes enabled free diffusion of gas from surrounding soil into the tube so as to attain equilibrium with the soil gas concentration at 0.15 to 0.30 m depth. The top end of the tube was sealed with a plastic on/off valve connectable to a portable GA2000 Landfill Gas Analyzer (Geotechnical Instruments UK Limited) to measure soil CO₂ and O₂ concentrations (in % of total 100% by vol.). In addition, Patil et al. (2010) measured soil surface CO₂ efflux from pasture grass and fallow plots (ppm hr⁻¹) using Draeger tubes (Draeger Safety AG & Co., Germany,) placed in a grid spacing of 0.5 m × 0.5 m on the surface to monitor gas diffusive pattern within each plot and its horizontal spread. The Draeger tube system is an established method for measuring and detecting contaminants in the soil, water and air.

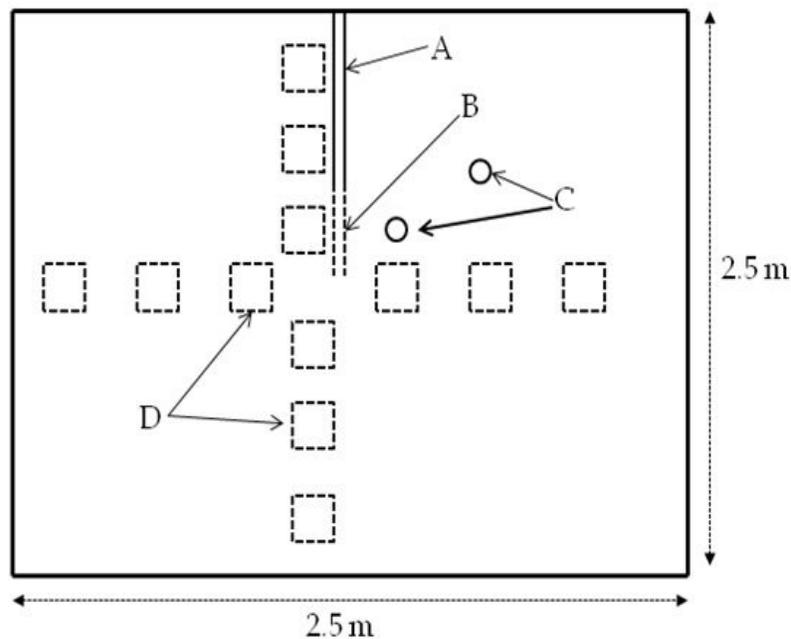


Fig. 3. Details of individual experimental plot showing the position of gas delivery pipe (A = above-ground portion, B = below-ground portion), gas measurement spots (C; one at 0.15 m & the other at 0.7 m away from center) and above-ground grass biomass sampling areas only in pasture plot (each of 0.2 × 0.2 m in size). This holds true for un-gassed plots but for the absence of soil gas measuring tube at 0.7 m away from centre of the plot.

2.5 Measurements on soil chemistry

West et al. (2009) analyzed soil samples from 0.15–0.30 m and 0.45–0.60 m depth, before and after gassing, for mineralogical (e.g. particle fraction) and geochemical (pH, organic carbon) content and changes due to gassing. Whereas, Patil et al. (2010) collected the soil samples from the top 0.3 m depth, one composite sample from each plot, three times during the gassing period at equal interval, and analyzed for pH and organic matter content. The holes left open after removing augered soil samples were re-filled immediately with local soil and marked to avoid repeated use of the same spots during subsequent sampling periods. Wei et al. (2011), on the other hand, used the top 0.12 m layer soil from the ASGARD site and incubated with CO₂ gas at varied levels of soil moisture under laboratory conditions to study the effect of CO₂ gassing on soil chemical properties and availability of mineral elements.

2.6 Measurements on soil inhabiting organisms

To study the effect of CO₂ gassing on soil-inhabiting organisms, earthworm activities were monitored by counting the number of their castings on the surface (Patil et al., 2010). Sarah and Sjögersten (2009) collected soil samples from the turf grass plots from the top 0.1 m depth and at different distance from the center of the plot. They did this on 3 occasions: before gassing began, and at 5 and 10 weeks after gassing. These soil samples were used to determine microbial biomass and microbial activity. West et al. (2009) also looked at soil bacterial population and adenosine triphosphate (ATP) concentrations, the latter as a measure of microbial activity in the soil.

2.7 Measurements on vegetation composition and growth

While West et al. (2009) did not collect destructive biomass samples, Sarah and Sjoergersten (2009) collected turf grass above- and below-ground biomass samples to record dry biomass. West et al. (2009) instead monitored botanical composition (% plant species cover) of the pasture plots before and after the gassing period both in gassed and un-gassed plots. Patil et al. (2010) monitored pasture growth by collecting only its above-ground biomass from 0.2×0.2 m patch (0.04 m^2) above soil surface taken at distances of 0.3, 0.6 and 0.9 m from the plot center in all four directions (as shown in Figure 2), making up four samples within each plot from each distance interval. Each time after collecting biomass samples the pasture grass plots were mowed and let the grass grow again, whereas, Sarah and Sjoergersten (2009) did not mow the turf grass. Between April through October 2007, the fallow plots had only bare soil with no vegetation cover and only soil gas concentrations were recorded using GA2000 Landfill Gas Analyzer as described in above paragraphs. On November 1, 2007 all the eight fallow plots were sown with winter bean (*Vicia faba* Cv. Clipper). The seeds were hand dibbled at 45 seeds per m^2 . First germination count (number of seeds emerged per plot) was recorded on December 3, 2007 and the same was repeated at regular interval until the germination / emergence process was complete or no additional seeds emerged from both gassed and un-gassed plots.

2.8 Measurements on pasture grass stress responses

Pasture and turf grass stress symptoms were also monitored by recording visual appearance of grass on the surface (e.g. drying, brown / yellow coloration) both in gassed and un-gassed plots. Furthermore, Patil et al. (2010) monitored physiological stress responses to CO_2 gassing by measuring moisture content in above-ground grass biomass after each sampling (as a difference between fresh and oven dried biomass) and leaf chlorophyll content. To measure leaf chlorophyll content without any destructive sampling, the SPAD 502 Chlorophyll Meter (Spectrum Technologies Inc., USA) was used. The SPAD meter instantly measures the amount of chlorophyll content in leaves, a key indicator of plant health. The SPAD meter was clamped over pasture grass leaf part for few seconds and the meter displays an indexed chlorophyll content reading (0–99.9). Lower the value means higher stress. A more detailed description of these methodologies and measurements are given elsewhere (Patil et al., 2010; Sarah & Sjoergersten, 2009; West et al., 2009).

3. Results and discussion

3.1 Soil gas leakage and migration pattern

The first objective of developing ASGARD field gassing facility was to achieve control over CO_2 gas injection into the soil at a targeted rate all through the study period. This was achieved successfully with the hardware and software logistics installed at the site. Furthermore, artificial gas injection at 0.5–0.6 m depth simulated gas diffusion and migration in the gassed plots (Patil et al., 2010; West et al., 2009). West et al. (2009), who injected CO_2 gas @ $3 \text{ liters min}^{-1}$ for three months in 2006, reported horizontal migration of gas at a roughly similar rate in all directions in the gassed plots. They also observed that while the injected CO_2 gas had clearly migrated upwards throughout all the gassed plots, larger lateral movement was recorded at depth. This may have been probably influenced by

the relative permeability of soil and the topographies of the boundaries between plots (West et al., 2009). The injected gas tended to move laterally beneath the soil beyond the boundaries of gassed plots as only the one-third amount of total injected gas was emitted at the surface from the gassed plots (West et al., 2009). However, in 2007-08 when CO₂ gas was injected at lower rates (1 liter min⁻¹) the lateral spread of diffused gas was relatively small, although the spread was much more in pasture plots than in fallow ones (Figure 4 & 5). This suggests that rate of leakage and the land use type (whether covered with pasture or left fallow) does influence the extent of surface flux and lateral migration of leaking gas. Hoeks (1972) suggests that the sub-surface injected CO₂ gas would migrate isotropically towards soil surface and creates a spherically symmetric gas plume, but that was not the case at ASGARD site (Figure 4 & 5). This may have been caused by the physical disturbance and loosening of soil along the path of inserted plastic pipe (Patil et al., 2010). Therefore, surface CO₂ flux rates recorded and its adverse effect on overlying vegetation were much higher in and around the entry point of plastic pipe (Photo 3). The diffusion and migration pattern of CO₂ gas seems to follow the pattern of CH₄ gas as reported by Adams and Ellis (1960) and Smith et al. (2005).

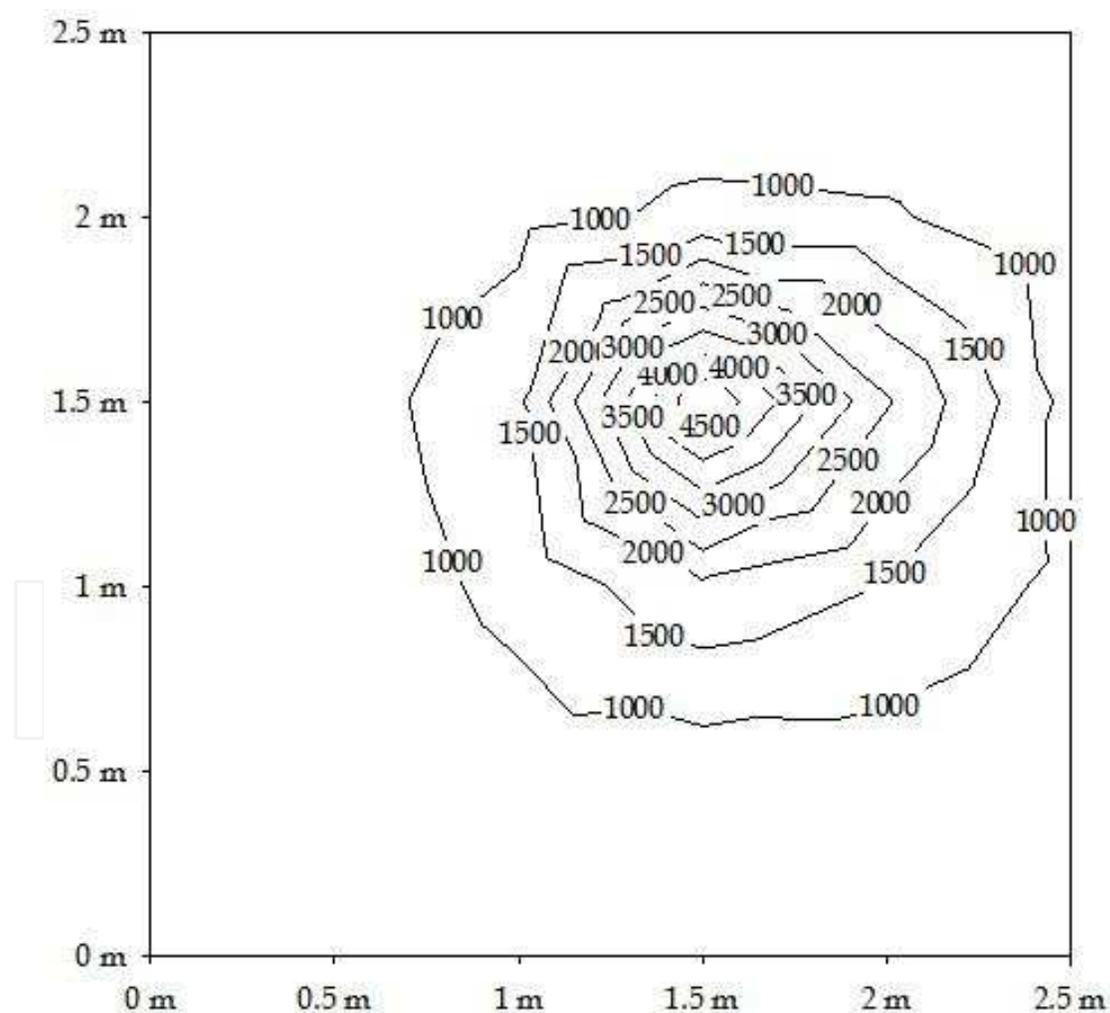


Fig. 4. Mean CO₂ efflux (ppm hr⁻¹) measured at 0.5 m × 0.5 m grid intervals at the soil-air interface in pasture plots using the Draeger tubes and shown in a 3-D contour map (source: Patil et al., 2010).

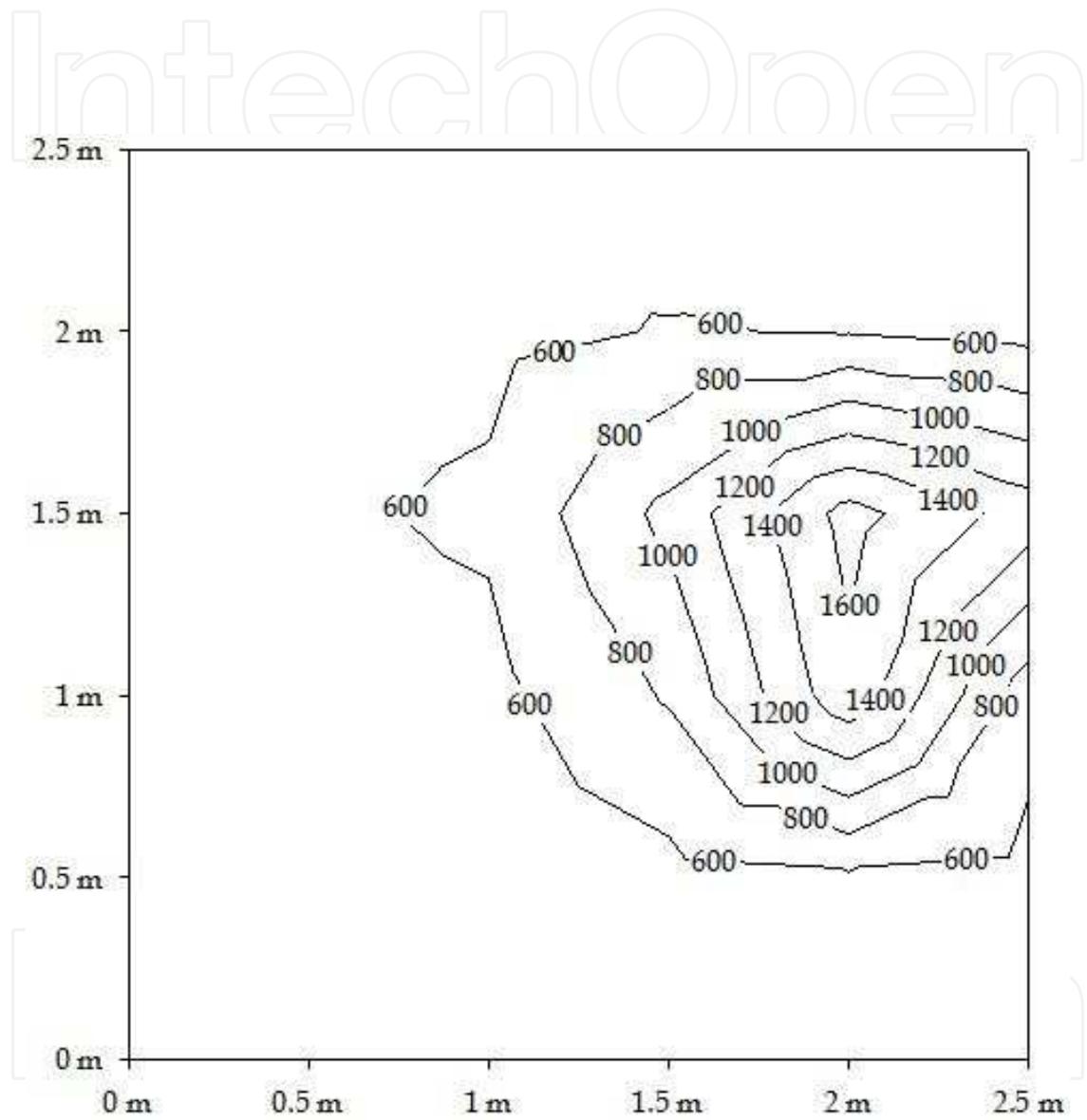


Fig. 5. Mean CO₂ efflux (ppm hr⁻¹) measured at 0.5 m × 0.5 m grid intervals at the soil-air interface in fallow plots using the Draeger tubes and shown in a 3-D contour map (source: Patil et al., 2010).



Photo 3. Vegetation in gassed pasture plots (top two) showing visual stress symptoms compared with non stressed un-gassed pasture plots (middle two), and winter bean emergence and seedlings growth pattern in gassed (bottom right) and un-gassed plots (bottom left).

3.2 Effect of land vegetation cover on soil gas concentrations

Gassing significantly increased the soil CO₂ concentrations in both pasture and fallow plots compared with their respective un-gassed pasture and fallow plots (Patil et al., 2010). In the gassed pasture plots, the maximum soil CO₂ concentrations were in the range of 19.5–76.3% with a seasonal mean of 45.7% (by vol. of the total 100%) from the measuring tubes that were 0.15 m from the center of the plots and significantly less, which ranged between 6.1–29.2% with mean of 11.5%, in measurement tubes at 0.7 m from the center as lesser amount of CO₂ migrated laterally below the soil surface. Similar trend was recorded from gassed fallow (bare soil) plots, although the seasonal high, low and mean CO₂ concentrations were on much lower side compared with gassed pasture plots. In contrast, soil CO₂ concentrations recorded from un-gassed plots were very low. From un-gassed pasture and fallow plots seasonal mean CO₂ concentrations of 1.9% and 0.7%, respectively, were recorded, but the soil O₂ concentrations reached as high as 20.8%. This clearly showed

a significant negative relationship ($r^2=-0.95$) between soil CO₂ and O₂ concentrations as soil O₂ gas was displaced by injected CO₂ gas, since the latter one is heavier than former one (Patil et al., 2010). The difference in soil CO₂ concentrations between gassed pasture and gassed fallow plots also suggests that build up of injected CO₂ gas in near-surface and its diffusion / lateral migration are influenced by the land use type. Presence of vegetation tended to hold more gas due to the presence of root biomass, where as bare soil tended to release the leaking gas quickly into the atmosphere. This may have been to do with difference in soil aggregation. Pasture plots were never ploughed or tilled for over 10 years. This may have helped the pasture to develop thickly matted rooting system closing the bigger soil pores while creating larger proportion of micro pores compared with the broken soil (with more of macro pores) in fallow plots due to ploughing and cultivating with agricultural crops. Wei et al. (2011) reported that when soil was exposed to 100% CO₂, the gas is either absorbed by the soil water present in the pore space or filled the micro pores between the soil particles. This suggests that pasture soil with more of micro pores tends to hold more gas and build up CO₂ concentrations compared with loosely aggregated soil from fallow plots or the soil cultivated with seasonal crops.

When it comes to CO₂ gas migration beyond the plots of gassing, Patil et al. (2010) recorded slightly higher levels of soil CO₂ concentrations in both un-gassed pasture and fallow plots compared with the pasture plots located far away from the main treatment plots (as remote control plots). This could only be possible with sub-surface lateral migration of diffusing CO₂ gas from gassed plots to adjacent un-gassed plots (Patil et al., 2010), which again shows that even with low levels of sub-surface gas leakage (e.g. 1 liter min⁻¹) the diffusing gas can move laterally beneath the surface over quite a distance and affect the overlying vegetation and soil ecology. Therefore, if CO₂ leaks were to occur from geological storage sites located >800 m deep via cracks / faults in caprocks the gas would start diffusing upwards and spread in a funnel like shape occupying large area by the time gas reaches soil surface. This leak, if goes unnoticed, could affect large patch of land and its surrounding ecosystem.

3.3 Effect CO₂ gassing on pasture composition

The baseline botanical characterization, recorded in 2006 before gassing study was initiated, showed a range of monocotyledonous (e.g. grasses) and dicotyledonous (e.g. dandelions, thistle, plantain, chickweed, mallow, clover) plant species in all the pasture plots. However, three months after gassing the % composition changed only in gassed plots (West et al., 2009). Grass was the dominant species at the center of the plot where the soil CO₂ concentrations were much higher (> 75% of the total 100% by vol.) than at the edges of the plots. Whereas, towards the edges of the gassed plots where CO₂ concentrations were around 45% at 0.2 m depth, grass was the dominant species. In contrast, un-gassed (control) pasture plots had more species composition and higher proportions of minor plant groups than the gassed plots even at the end of the injection period. This suggests that grass species tended to be more tolerant to higher soil CO₂ concentrations than the non-grass or broad leafed species found in this perennial pasture (West et al. 2009). Similar responses were reported from a Mediterranean pasture at a natural CO₂ vent (Latera, Italy) where Beaubien et al. (2008) studied the effects of venting CO₂ gas on the shallow ecosystem.

3.4 Effect of CO₂ gassing on pasture grass stress symptoms and growth

Despite being tolerant to elevated CO₂ concentrations, the grass turned yellow or brown and patches of bare earth was exposed as no vegetation (including perennial grass) grew in and around the point of entry of gassing pipeline, the patch where the soil CO₂ concentrations reached as high as 75% at 0.2 m depth (West et al., 2009). Similar visual stress symptoms on pasture and turf grass, respectively, were observed by Patil et al. (2010) and Sarah and Sjogersten (2009) when CO₂ gas was injected @ 1 liter min⁻¹ and also when CH₄ gas was injected @ 100 liters hr⁻¹ in 2002-03 (Smith et al., 2005). While the grass close to the point of entry of gassing pipe turned yellow and died, a small patch of grass in a circular pattern around the dead grass showed much shorter growth, looked yellow and dry, but not dead yet. Whereas, the pasture towards the edges of the plots looked green and less affected as the soil CO₂ gas concentrations recorded towards the edges of the plot were much lower.

The observations on above-ground biomass, chlorophyll content and moisture content of pasture grass followed the same pattern; significantly lower values at the centre and higher values at the edges of gassed plots (Patil et al., 2010). This pattern of effect on overlying vegetation very much followed the pattern of soil CO₂ gas migration below the surface (Figure 4 & 5). Previous studies carried out at sites of naturally occurring CO₂ springs / vents and or volcanic sites have shown that elevated soil CO₂ concentrations reduce plant growth, disrupt plant photosynthesis, inhibit root respiration mainly due to severe dearth of soil O₂ levels, and even kill the vegetation (Cook et al., 1998; Macek et al., 2005; Miglietta et al., 1998; Pfanzen et al., 2007; Vartapetian & Jackson, 1997; Vodnik et al., 2006). Previous studies on leaking CH₄ gas have also caused the same stress symptoms on above-ground vegetation as both CO₂ and CH₄ gases displace O₂ gas from the soil (Arthur et al., 1985; Hoeks, 1972; Smith et al., 2005; Smith, 2002) thus depriving the plant roots off O₂ for respiration, which in turn affects other plant functions viz., water and nutrient uptake, evapotranspiration, photosynthesis and ultimately plant growth. In fact, Adamse et al. (1972) suggested that for the proper functioning of a healthy root system, a minimum soil O₂ concentration of 12-14% is required, whereas at ASGARD site in the gassed plots this was not the case. Macek et al. (2005), Vodnik et al. (2006) and Pfanzen et al. (2007) studied plant responses in relation to measured soil CO₂ concentrations at a natural CO₂ spring in Slovenia. In their studies soil CO₂ concentrations reached as high as 100% near vents, but atmospheric concentrations barely exceeded ambient concentrations (360-500 ppm) due to fast dispersion of leaking CO₂ by winds on a flat terrain. The study by Macek et al. (2005) considered root respiration in seven plant species and found that only when exposed to very high CO₂ concentrations did it inhibit root respiration, but the effects were highly variable amongst different plant species. This suggests that sensitivity of plants to elevated soil CO₂ concentrations differs with plant species as some species are more sensitive than others. The study by Vodnik et al. (2006) noted that leaf chlorophyll content was negatively correlated with soil CO₂ concentration, whereas Pfanzen et al. (2007) noted that plants exposed to high soil and air CO₂ concentrations contained lower levels of nutrients in their vegetative parts and did not flower.

3.5 Effect of CO₂ gassing on winter bean crop

Smith et al. (2005) while studying the effect of leaking CH₄ gas on crops (wheat and winter bean) observed that in the plot area with the highest CH₄ concentrations most seeds

germinated, but did not grow further. However, towards edges of plots, an area approximately 0.5 m in diameter, showed reduced growth with yellow leaves. Similarly, in this study significant adverse effect of CH₄ gas on chlorophyll content and leaf area of grass, wheat and bean was also reported. When it comes to CO₂ gassing, significantly lower number of winter bean seeds emerged / grew into seedlings in gassed plots compared with un-gassed plots (Patil et al., 2010). Even a very low level of leakage with 1 liter min⁻¹ gas injection had lethal effect on bean seeds emergence. Plants are known to be more sensitive to anaerobic conditions especially during early growth stages (Hoeks, 1972) and that might be the reason why CO₂ gassing had lethal effect on winter bean seed emergence and seedling growth compared with the response of well established pasture grass observed by Patil et al. (2010). Schollenberger (1930) while studying the effect of CH₄ leaks on crops noted that leaking gas pipeline killed all the oat seedlings within the range of 1.0–1.3 m while stunting the seedling growth up to 4–5 m away from pipeline and beyond which no injury appeared. Godwin et al. (1990) observed wheat being more tolerant to CH₄ leaks compared with oil seed rape, which again suggests that crops differ in their sensitivity to gas leaks. In fact, this differential sensitivity could be used in early warning system of gas leaks, especially from under-ground pipeline, by growing highly sensitive crops along the path of transportation pipeline.

3.6 Effect of CO₂ gassing on soil mineralogy and chemistry

No significant changes in the mineralogical composition of soils from gassed and non-gassed plots were recorded during the 16 weeks injection period (West et al, 2009). However, soil Ca concentrations, in general, decreased, but the largest reductions were recorded in the soil samples collected close to the injection point, which also recorded the highest CO₂ concentrations (West et al, 2009). Wei et al. (2011) suggested that elevated soil CO₂ concentrations enhance weathering of minerals, thus it would be possible to assess the impact of CO₂ leaks on soil mineralogy only if the studies were carried out for longer period of time (in years). With regards to soil pH, soil CO₂ gassing @ 3 liters min⁻¹ for only 16 weeks reduced the soil pH in gassed plots and the drop in soil pH was drastic near the point of entry of gas delivering pipeline (West et al., 2009). Among the soil layers, soil samples collected from gassed 'A horizon' recorded the largest reduction in pH (by 0.5 units) after only 16 weeks of gassing (West et al, 2009). Similarly, Patil et al. (2010) also recorded lower soil pH both in gassed pasture and fallow plots in comparison with their respective un-gassed control plots. This could be attributed to acidification of soil water due to dissolution of leaking CO₂ gas (Celia et al., 2002) and was corroborated by the findings of Wei et al. (2011), where the latter reported that absorption of CO₂ gas would occur either by reacting with soil pore water or by filling the pore space, thus increased soil moisture increases soil CO₂ build up in the soil. This process further leads to the formation of H₂CO₃ which, in turn, lowers the pH of soil solution. Soils in general have a buffering capacity and when pH of soil solution was lowered in the presence of absorbed CO₂, clay minerals start to weather to neutralize the lowering pH by releasing minerals (to exchange with H⁺ ions) leading to an increase in the CaCl₂-exchangeable concentration of Al. Thus, increase in uptake of CO₂ by the soil solution leads to increased Al mobilization in moist soil (Wei et al, 2011). However, Al concentrations reported in their study were much lower than plant tolerance limits, which range between 40 μM and 60 μM depending on species (Poschenrieder et al, 2008; Taylor et al, 1998). In addition to Al, Wei et al. (2011) also reported increase in CaCl₂-

exchangeable concentrations for Mg, K, Ti, V, Cr, Mn, Fe, Co, Cu, Rb, Sr, Mo, Cs, Ba, Pb, Th and U, while the metal concentrations for Zn and Cd decreased. Whereas, total organic carbon (TOC) concentrations in the 'A horizon' increased in both gassed and non-gassed plots by the end of the summer growing season, but at the injection depth TOC concentrations were found to be on lower side in the gassed plot compared with the un-gassed plots (West et al., 2009). This suggests that elevated soil CO₂ concentrations lower soil pH and TOC, although different soil horizons responded differently depending on their buffering capacity to changes in pH and chemical components. However, these gassing studies were carried out for a very short period (few months) and variations in soil carbon observed in these studies show only the rough indications of changes in soil chemistry which, in this case, might have been of temporary in nature influenced by factors not controlled during the study period (e.g. seasonal temperature, above-ground vegetation and other climatic conditions). Therefore, further investigation by continuing gassing over long period of time needs to be undertaken.

3.7 Effect of CO₂ gassing on soil inhabiting organisms

CO₂ gassing significantly increased the earth worm casts in gassed pasture plots compared with un-gassed pasture plots, but no earth worm activities were noticed on both gassed and un-gassed fallow plots (Patil et al., 2010). Smith et al. (2005) also reported higher worm casts in grass plots injected with natural gas. While the higher earth worm casting on gassed pasture plots indicate increased activities, but surprisingly enough the absence of earth worm casting on both gassed and un-gassed fallow plots begs question which the authors fail to clarify. Therefore, this needs to be looked at in detail to understand the causation. When it comes to soil bacterial population CO₂ gassing drastically reduced their number in gassed plots. The ATP concentrations, a measure of microbiological activity, were also reported to be below detection limits at the center of the gassed plots where CO₂ concentrations reached maximum of 87% at 0.15–0.30 m depth (West et al, 2009).

Sarah and Sjögersten (2009) observed a tendency for reduced respiration in the soil exposed to elevated CO₂ concentrations, not significant though, compared with the soil in un-gassed plots within a period of 10 weeks. Soil moisture content seemed to have negative significant influence on microbial respiration. This negative effect of higher soil moisture on soil respiration, Sarah and Sjögersten (2009) report, was not anticipated as increased soil moisture generally results in increased microbial respiration up to the point of anoxia (Wardle and Parkinson 1990; Davidson et al. 2000). One possible explanation could be that higher soil water content reduced the O₂ supply (anoxic condition) while increasing the share of CO₂ concentrations in soil pores owing to the latter's leakage from the center of the plot. Such a soil environment would inhibit microbial respiration in the same way when soil water content reaches saturation (Davidson et al. 2000). Sarah and Sjögersten (2009) also looked at carbon source utilization rate as an estimate of change in microbial community metabolism, which however, did not differ between the soil from gassed and un-gassed plots in a 72 hr incubation study.

However, findings from the atmospheric CO₂ concentrations enrichment studies (not the soil concentrations) suggest that longer period of time is required to see any noticeable changes in microbial communities. For example, Griffiths et al. (1998) recorded no difference in soil microbial communities in a less than a month long study whereas, Grayston et al.

(1998) observed changes in bacterial community in a study carried out for four long years. Therefore, to understand the actual and long lasting effects on soil chemistry, organic matter, microbial population / their diversity, the gassing needs to be continued for longer period.

4. Conclusions

The ASGARD site developed at the University of Nottingham, UK successfully injected CO₂ gas into the soil at a targeted rate, simulated build up of soil CO₂ concentrations near soil surface and enabled measurement of soil concentrations and its effect on vegetation and soil biogeochemistry. The CO₂ gassing studies from the ASGARD site, despite being carried out for short period of time, showed the potential ecological risks of CO₂ leakage from geological storage sites on agro-ecosystems. Surprisingly enough, even the low levels of gas leakage with 1–3 liters of CO₂ gas injection min⁻¹ significantly increased the soil CO₂ concentrations in a very short period of time by displacing the soil O₂ and adversely affected the growth of pasture and turf grass, severely hindered the germination and establishment of winter bean crop, lowered soil pH, TOC and microbial population while increasing the activities of earthworms. These studies also showed that different plant species have different tolerance capacity to soil CO₂ concentrations. Monocotyledonous species (e.g. grass types) tended to be more tolerant compared with dicotyledonous species (e.g. beans & broad leaf species). Therefore, some of the more sensitive plant species (e.g. non-grassy species) could be used to grow along the path of CCS transportation pipelines in early warning system to detect gas leaks.

Another limitation of studies carried out at the ASGARD site was that the CO₂ gas was injected at a very low rate (1–3 liters min⁻¹) and at a shallow depth (0.5–0.6 m) compared with CCS schemes where amount of gas injected each minutes would be in tonnes and at > 800 m deep. Therefore, while the ASGARD site based studies increased our understanding of the effects of below ground CO₂ leaks on agro-environment, long-term studies to evaluate the potential long-term consequences on ecosystem are needed to be carried out on larger scale for decision making and management. In CCS schemes the upwards movement of gas from the deep storage sites, possibly via cracks and faults in the caprocks, and its further diffusion and migration before reaching the soil surface would naturally enable the gas to spread on much larger area. Moreover, under such a situation factors like quality of selected site, amount of gas injected, the state and pressure under which it is held beneath the caprocks, geochemistry of the path of gas movement and issues related to hydrology needs to be studied in detail in addition to the impacts on overlying vegetation and environment. Therefore, further gassing studies needs to be carried out on larger scale and continued for longer period to better understand the long-term impacts.

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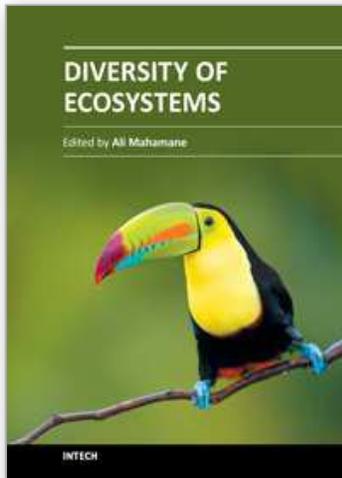
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The ecosystems present a great diversity worldwide and use various functionalities according to ecologic regions. In this new context of variability and climatic changes, these ecosystems undergo notable modifications amplified by domestic uses of which it was subjected to. Indeed the ecosystems render diverse services to humanity from their composition and structure but the tolerable levels are unknown. The preservation of these ecosystemic services needs a clear understanding of their complexity. The role of research is not only to characterise the ecosystems but also to clearly define the tolerable usage levels. Their characterisation proves to be important not only for the local populations that use it but also for the conservation of biodiversity. Hence, the measurement, management and protection of ecosystems need innovative and diverse methods. For all these reasons, the aim of this book is to bring out a general view on the function of ecosystems, modelling, sampling strategies, invading species, the response of organisms to modifications, the carbon dynamics, the mathematical models and theories that can be applied in diverse conditions.

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