Available online at www.sciencedirect.com

SciVerse ScienceDirect

Energy Procedia 37 (2013) 3521 – 3528

Energy Procedia

GHGT-11

Potential environmental impacts of CO_2 leakage from the study of natural analogue sites in Europe

F. Ziogou[a]*, V. Gemeni[a], N. Koukouzas[a], D. de Angelis[b], S. Libertini[b], S. E. Beaubien[b], S. Lombardi[b], J. M. West[c], D. G. Jones[c], P. Coombs[c], T. S. Barlow[c], S. Gwosdz[d] and M. Krüger[d]

[a] *Centre for Research & Technology Hellas/Chemical Process and Energy Resources Institute, Thessaloniki, 57 001, Greece*
[b] *Dipartimento di Scienze della Terra, Universita` di Roma ''La Sapienza'', Rome, Italy*
[c] *British Geological Survey, Keyworth, Nottingham, NG12 5GG, UK*
[d] *Bundesanstalt für Geowissenschaften und Rohstoffe, Hannover, Germany*

Abstract

Sites of natural CO_2 leakage provide opportunities to study the potential environmental impacts of such leakage on near-surface ecosystems. As part of the FP7 RISCS (Research into Impacts and Safety in CO_2 Storage) project a geochemical, botanical and microbiological study have been conducted on a natural CO_2 vent in Florina, Greece and the findings are compared with the results drawn from Latera, Italy and Laacher See, Germany. Plant and microbial communities appear to have adapted to long-term CO_2 exposure. Therefore the findings may not be representative of the effects of potential leakage from man made storage sites.

Keywords: Vegetation; Bacterial communities; CO2 Geological Storage; Terrestrial CO2 vents; Soil – gas concentration

---

1. Introduction

The United Nations Intergovernmental Panel on Climate Change (IPCC) has concluded that 50% to 80% cuts in global CO_2 emissions by 2050, compared to 2000 levels, will be needed to limit the long-term global mean temperature rise to 2.0°C to 2.4°C [1]. The development of carbon capture and storage

---

* Corresponding author. Tel.: +30-2310-498391; fax: +30-2310-498392.
E-mail address: ziogou@certh.gr

doi:10.1016/j.egypro.2013.06.245

(CCS) technologies is considered as a potential option in the portfolio of required measures to stabilise atmospheric greenhouse gas concentrations at a time of rapidly growing energy needs. Additionally, public acceptance of CCS is widely recognised to be an important factor affecting the feasibility of commercial deployment of this climate change mitigation option. Consequently, the health, safety, and environmental risks associated with potential CO_2 leaks from storage reservoirs need to be evaluated and appropriate monitoring programmes established to provide confidence in the technology.

The effects of naturally occurring CO_2 leaks on vegetation and soil inhabiting organisms have been addressed in relatively few studies, including Mammoth Mountain (California, USA) [2] and Stavesinci (NE Slovenia) [3], [4]; however, considerable work has now been undertaken in Europe at sites in Italy (Latera) [5] and Germany (Laacher See) [6]. The current study assesses the impacts of a natural CO_2 vent on a pasture field located within the Florina basin in Greece, the first such study in a European mountainous environment. Similar methods to those used at Latera and Laacher See were used at Florina and the results from all three sites are compared in this paper. The goal of this study is to integrate the botanical, geochemical and microbial results from these natural sites to better understand how local differences can influence and potentially modify the impact of a CO_2 leak.

The Florina basin is a NNW-SSE trending graben in the NW part of Greece formed by Neogene coarse clastic sediments. The overlying, 800-1000 m thick lacustrine deposits consist of conglomerates, marls, sandstones, and marl limestones with clayey caprocks. Natural CO_2 accumulations alternate with lignite seams in these sediments at various levels. Carbonate rich springs and CO_2-rich gas vents occur throughout the Florina basin, resulting from a slow upwelling of magmatic-hydrothermal CO_2 along faults and fractures. In contrast, the other two sites both occur in extinct volcanic calderas. Here, CO_2 is produced via upper mantle degassing (Laacher See, [6]) or thermo-metamorphic reactions (Latera, [7]), after which it leaks towards the surface along fault and fracture systems and is released to the atmosphere from spatially restricted gas vents.

Research into the impact of CO_2 leakage on the Florina pasture ecosystem consisted of two phases. First, a regional grid of soil gas and CO_2 flux measurements was conducted in July 2011 to define the leakage distribution and orientation. Second, in September 2011, a detailed, 25m-long transect was chosen based on these results and measured every 0.5 m for soil gas concentrations, CO_2 flux, botany, and soil microbiology. Methods used were similar to those applied at both Latera [5] and Laacher See [6], thereby facilitating comparison.

2. Methods

The CO_2 flux measurements were performed using the closed loop accumulation chamber method [5]. This method involves the accumulation of CO_2 that is migrating from the soil to the atmosphere within an open-faced chamber; the increasing concentration over time within this chamber (measured using a non-destructive infrared analyser) combined with the physical dimensions of the chamber itself are used to calculate the flux of CO_2 for that point. Soil gas samples were collected using a 6 mm diameter stainless steel probe that was pounded to the desired depth using a co-axial hammer. On the regional grid samples were collected only at 70 cm depth, whereas those along the transect were sampled at 20, 50 and 70 cm depth. All points were analysed directly in the field for CO_2 using a hand-held infrared analyser, all points along the transect were analysed in the field for O_2, CO, and H_2S, while all 70 cm deep samples along the transect and a portion of the regional grid samples were analysed in the laboratory for CO_2, O_2+Ar, N_2, light hydrocarbon gases using a gas chromatograph and total helium using a mass spectrometer.

The botanical survey was conducted along the entire length of the transect, visually defining the percentage cover of identified plant groups at 0.5 m intervals using a 0.5 m x 0.5 m quadrat. Field flora books were used to identify plant species [8] and digital photographs were taken of each quadrat for a complete visual record. To support these results, water content measurements were also conducted in soil collected at depths of 15-30, 45-60 and 65-70 cm, once every metre.

To assess the CO_2 induced effects on microbial metabolic pathways and populations, samples were collected at 65-70 cm depth at three transect points having CO_2 concentrations that were high (100% at 1.25 m within the vent core), moderate (8-10% at 11.25 m within the transitions zone) and low (<0.9% at 20.25 m within background conditions). The aim is to investigate potential metabolic rates of e.g. anaerobic methane production in soil incubations and the microbial community composition using quantitative real time polymerase chain reaction analyses (qPCR). The qPCR analyses first involved the extraction of high molecular weight DNA from frozen soil samples via cell lysis and DNA purification. Specific fluorescent probes were used targeting the ubiquitous 16S rRNA genes of bacterial or archaeal organisms, which were then quantified by real-time qPCR. The anaerobic methane production activity was determined using a gas chromatograph equipped with a flame ionization detector, as described in [9], [12].

3. Results

3.1 Soil gas concentrations and CO2 flux

The regional survey results clearly defined NE-SW and NW-SE anomaly trends that align parallel to the main faults of the Florina Basin. Soil gas CO_2 anomalies defined wide features, whereas soil gas CH_4 and He were spatially more restricted in correspondence with CO_2 flux anomalies. The anomalies consist of individual gas vents formed by a core with high flux and CO_2 concentrations near 100% surrounded by a transition zone of gently decreasing CO_2 concentrations but rapidly decreasing CO_2 flux rates. Reactive soil gas species like CH_4 are only found within the essentially anoxic core of the vents. Based on this distribution, anomalies of soil gas CO_2 tend to merge because of their wider extent whereas those of CO_2 flux and soil gas CH_4 tend to be more isolated. These results were used to choose an appropriate gas vent on which to conduct the transect.

The gas geochemistry results from the transect are presented in Figure 1. The CO_2 flux data are presented with both linear and log scales (Fig. 1a), illustrating three distinct zones: 0-3.25 m in the vent core with very high values from 2,000 to 10,000 $gm^{-2}d^{-1}$; 3.25-8.25 m where values drop rapidly from 700 to about 40 $gm^{-2}d^{-1}$; and 8.25-25 m where values remain relatively stable from 40 to 20 $gm^{-2}d^{-1}$. Whereas soil gas CO_2 at 20 cm follows a similar pattern, in that it reaches near background values by about 10 m (Fig. 1b), concentrations at 50 and 70 cm do not reach background levels (c. 1%) until about 20 m from the start of the profile. CO_2 concentrations in the core of the gas vent for the two deeper samples are near 100% while those at 20 cm depth are often over 90% (Note that laboratory analyses of the 70cm deep samples gave slightly lower CO_2 concentrations in this interval, likely due to the qualitative nature of field-based IR detectors in the high concentration range). The O_2 concentration values, not shown, are the exact opposite to those of the CO_2, with conditions being essentially anoxic in the vent core. Finally, both CH_4 and He (Fig. 1c) sampled at 70 cm depth exhibit highly anomalous values in the vent core (from 0-7m), followed by a very rapid drop to background values over less than a metre. This abrupt transition interval corresponds with CO_2 concentrations <50%, CO_2 flux values <500 $gm^{-2}d^{-1}$, and O_2 concentrations

>9%. All parameters show small-scale spatial variations, illustrating the spot nature of gas release as controlled by local, near-surface variability in soil permeability.

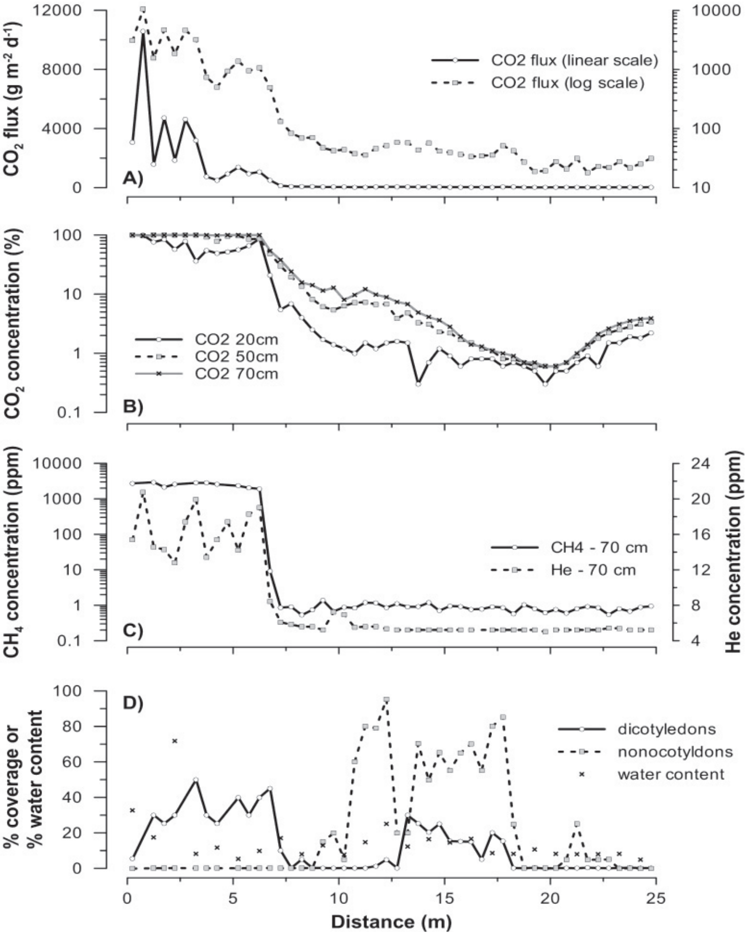

Fig.1. Results obtained from the 25 m long transect at the Florina study site: A) CO_2 flux plotted on both linear and logarithmic scales; B) soil gas CO_2 concentrations at 20, 50, and 70 cm depths measured with a hand-held infrared analyser; C) soil gas CH_4 and He at 70 cm depth; and D) plant cover and soil water content.

3.2 Botanical surveys

The botanical survey showed a long-term adaptation of some plant species to the hypoxic or anoxic conditions of the naturally CO_2-enriched environment (Fig. 1d). From the centre of the vent to 8.5 m along the transect, where CO_2 concentrations range between 99.7-4 % at 20 cm depth and 99.9-13 % at 50 cm depth, only dicotyledonous plants *Minuartia glomerata* and *Polygonum aviculare* were observed and thus can be considered as bioindicators of high CO_2 in soil. The CO_2 flux range here varied from around 70 to 10.600 $g/m^2/d$ with a slight correlation coefficient of -0.63 with the soil CO_2 concentration. The soil oxygen decrease below 10% in this interval (strong negative relationship between soil [CO_2] and [O_2]

with a Pearson correlation coefficient of -0.99) indicates the ability of these plant species to adjust respiration (metabolism) to oxygen deficiency and high CO_2 conditions [3]. At a distance of 9 m from the centre of the vent, concentrations of CO_2 reach the background values of <2% at 20 cm depth. At this point, monocotyldenous plants (such as *Cynodon dactylon*) predominate and *Minuartia glomerata* is not observed although other dicotyledonous plants *(e.g. Astragalus*) are present.

Soil water content (Fig. 1d) at the depth of 15-30 cm is relatively constant along the transect indicating limited effect of elevated soil CO_2 concentrations on soil moisture at the depth of 15-30 cm. Many studies have shown that at sites where elevated CO_2 concentrations limited plant growth, the moisture of the upper soil layers remain higher compared to soils with normally developed vegetation due to the lack of transpirational water loss [10]. Other studies suggested that soil moisture can decrease due to increased plant growth and root biomass depending on the plant species [5].

3.3 Microbiological analyses

Analyses of the CH4 production rates revealed the influence of different CO2 concentrations on the methane production rates. As it can be noticed in Fig. 2 these rates were with 0,016 µmol gdw-1 d-1 at the CO2 vent (100% CO2) three times higher than at the medium site with 8-10% CO2 while no methane production could be detected at the reference site (<0,9% CO2).

In addition to the activity analyses, cell numbers of *Bacteria* and *Archaea* were determined using qPCR. Trends of increasing copy numbers along the transect corresponding with decreasing CO_2 concentrations (Fig. 2) could be observed for both, *Bacteria* and *Archaea*. The numbers of *Bacteria* increased from $3{,}0*10^9$ to $3{,}7*10^9$ gene copies gdw^{-1} of soil from the reference site and vent centre and those for *Archaea* increased from $7{,}6*10^8$ to $1{,}5*10^9$ gene copies gdw^{-1}. Similar trends have been observed for both, activity and community analyses at Laacher See [6] and Latera [12].

The results so far show changes in the activity and community composition as a consequence of continuous CO_2 release. The successive replacement of O_2 with CO_2 in the soil along possibly leads to an increase of important anaerobic metabolic pathways like methane production, sulfate reduction and the anaerobic CO_2 production (mineralization). In fact, increasing CH_4 production rates with increasing CO_2 concentrations indicate high abundance of anaerobic methanogens [12], [6]. In contrast, the gene copy numbers of *Archaea* showed no increase with high CO_2 concentrations. Copy numbers of *Archaea* were highest at the reference site with background CO_2 concentrations and were lower at the vent centre. Similar results could be observed for *Bacteria*. One explanation for the detected results might be a CO_2 induced shift in the microbial community composition for the benefit of anaerobic microorganisms which successively replace aerobic microorganisms. The cell numbers won’t be necessarily affected by changes within the populations.

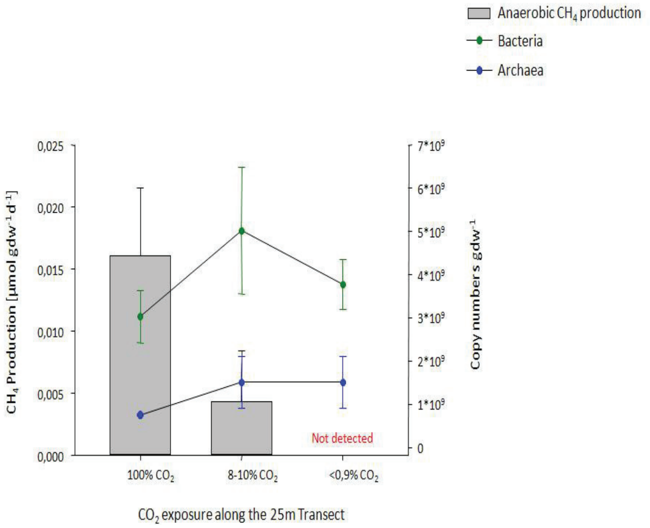

Fig. 2: The variation of the microbial activity and community composition in the soil samples of the CO_2 vent, the transition zone and the reference site of the transect in Florina basin

4. Discussion

Near surface gas geochemistry results along the Florina transect are in many respects very similar to those observed at the Latera site, including a gas vent core with high CO_2 flux, high CO_2, CH_4, C_2H_6, and He concentrations, and very low O_2 levels that is surrounded by a transition zone where flux rates decrease rapidly, concentrations of CH_4, C_2H_6, and He decrease very abruptly over an interval of less than 1 metre, and CO_2 concentrations (at least at the deeper levels) decrease relatively slowly. As discussed in [5], the wider CO_2 concentration distribution is probably due to the dense nature of this gas relative to air, the very narrow distribution of He is due to its very low density, whereas that of CH_4 is likely related to the minimum CO_2 flux rate needed to maintain O_2 concentrations low enough to prevent microbial oxidation. The one principle difference observed between these two sites is the high levels of H_2S in the gas vent core at Latera, in contrast to its almost complete absence at the Florina site. This fact removes one extra variable that could potentially impact on plant growth, thus focusing this work on the impact of elevated CO_2 values alone.

At the Laacher See, soil gas and CO_2 flux measurements present similar findings. Three main zones of higher CO_2 concentrations and fluxes were identified along the traverse: Between locations 11–17 m, 21–28 m, and 30–42 m, the latter representing the so-called centre of the vent where concentration values were greater than 90 vol% CO_2 in 60 cm depth. As the extension of natural CO_2 vents is limited, in less than 15 m from the centre of the vent CO_2 concentrations and fluxes decrease sharply to background values. [9]. Helium anomalies are narrower compared to CO_2 ones, similar to gas geochemistry results along the Florina and Latera transects. The results of the gas surveys conducted at Laacher See highlight also the occurrence of several CO_2 releases along an N-S axis, which is consistent with the known striking thrust of the basement [13], [9].

The observation that dicotyledonous species appear be more tolerant to very high CO_2 concentrations than monocotyledonous plants in this adapted CO_2 rich environment is similar to the findings from the CO_2 vent at the Laacher See where Polygonatum arenastrum was the only observed dicotyledonous plant between 25 and 50 m along the transect when CO_2 concentrations were between 10–35% at 15 cm depth [6]. However, the botanical survey at Latera showed that the greatest impact on vegetation was observed within 6 m of the vent centre, where CO_2 concentrations at 20 cm depth were over 95%, trace reduced gases (CH_4, H_2S, and H_2) present and CO_2 flux rates exceeded 2000–3000 g m-2 d-1. However, at this site, monocotyledonous plants (e.g. grasses) appear to tolerate elevated CO_2 concentrations [5].

As part of the RISCS project similar observations at the controlled injection sites Asgard Field Site, UK and Grimsrud, Norway suggest that monocotyledonous plants (e.g. grasses) are inherently more tolerant to elevated CO_2 [11].

The microbial activity measurements revealed differences in their spatial distribution for CO_2-rich and reference soils. The reduced aeration of the soil due to elevated CO_2 concentrations and fluxes in CO_2 vents, and the consequently anaerobic and more reduced conditions in the soil lead at the CO_2 vent in Latera to strongly decreasing microbial cell numbers with increasing CO_2 concentrations [12]. On the other hand, anaerobic microbial activities and communities, like sulphate-reduction or methanogenesis, were positively correlated with higher CO_2 levels. The same was observed for the Florina soils, where methane production was strongly stimulated. However in contrast to the studies at Latera, the quantification of 16S rRNA genes in the surface soils at the Florina as well as the Laacher See site showed only minor differences in the overall distribution of archaeal and bacterial gene copy numbers between the sites. In summary, these results indicated a CO_2-induced shift in the environmental conditions leading to more anaerobic and potentially acidic microenvironments.

5. Conclusion

Impacts of CO_2 gas vents on the near-surface ecosystem of natural analogues appear to be highly localized under the prevailing extreme CO_2 regime. The spatial variations of soil CO_2 concentration and fluxes are generally controlled by a complex interplay of factors such as the migration pathway at depth, the physical and chemical properties of the vadoze zone, the features and hydrogeology of the near surface deposits etc. Therefore, soil gas analyses and flux measurements will be required for the baseline characterization of the migration pathways for soil gases and for the design of any near-surface gas geochemistry monitoring program of CO_2 geological storage sites.

The botanical results indicate species-specific response to high CO_2 concentrations depending on soil properties, mineralogical composition and temporal and spatial soil [CO_2] patterns. However the speed of ecosystem's reactivity to short-term leaks in non-adapted systems such as a CO2 geological storage site is not well investigated up to now.

The outcome from the microbiological analyses at the terrestrial CO_2 vent sites suggest changes in the soil microbial community and significant environmental changes caused by high CO_2 concentrations. Elevated CO_2 concentrations will lead to a shift in the microbial community composition towards anaerobic and acid tolerant microorganisms as well as an ecosystem adaption to the CO_2 induced soil biogeochemistry. This included significant effects on metabolic rates but less pronounced effects on the bacterial and archaeal cell numbers. Further activities will focus on the diversity of anaerobic Bacteria and Archaea as well as the detection and identification of important soil microorganisms like ammonia oxidizing microorganisms and fungi at the different CO_2 concentrations [12], [6].

Naturally occurring CO_2 deposits provide unique natural analogues that can be used to assess the resulting impacts of the gas release on human health and safety, ecology, surface water, groundwater and the effectiveness of remedial measures. However, at these environments the existing ecosystems have been exposed to elevated CO_2 for considerably long periods, thus the plant/tree species may have adapted. Therefore, the findings from these sites may be either typical of and transposable to various different sites or they may not exhibit characteristics similar to the conditions that would occur with potential leaks from anthropogenic CO_2 storage [11].

Acknowledgements

RISCS is funded by the EC 7th Framework Programme and by industry partners ENEL I&I, Statoil, Vattenfall AB, E.ON and RWE.

References

[1] IPCC, Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. In: Solomon, S. et al. (Eds.). Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, pp. 996 .

[2] Stephens JC, Hering JG. Factors affecting the dissolution kinetics of volcanic ash soils: dependencies on pH, CO2, and oxalate. Appl Geochem 2004; 19(8): 1217 -1232.

[3] Macek I , Pfanz H, Francetic V, Batic F, Vodnik D. Root respiration response to high CO2 concentrations in plants from natural CO2 springs. Environ Exper Bot 2005; 54: 90-99.

[4] Vodnik D, Kastelec D, Pfanz H, Macek IBT. Smallscale spatial variation in soil CO2 concentration in a natural carbon dioxide spring and some related plant responses. Geoderma 2006; 133: 309–319.

[5] Beaubien S E, Ciotoli G, Coombs P, Dictor M C, Krueger M, Lombardi S, Pearce J M, West JM. The impact of a naturally occurring CO2 gas vent on the shallow ecosystem and soil chemistry of a Mediterranean pasture (Latera, Italy). Int J. Greenhouse Gas Control 2008; 2: 373-387.

[6] Kruger M, West J, Frerichs J, Oppermann B, Dictor M C, Joulian C, Jones, D., Coombs, P., Green, K., Pearce, J., May, F., & Moller, I. Ecosystem effects of elevated CO2 concentrations on microbial populations at a terrestrial CO2 vent at Laacher See, Germany. *GHGT-9, Energy Procedia 1* 2009; pp. 1933-1939.

[7] Annunziatellis A, Beaubien SE, Bigi S, Ciotoli G, Coltella M, Lombardi S. Gas migration along fault systems in the Latera natural analogue (central Italy): implications for CO2 geological storage. Int. J. Greenhouse Gas Control 2 2008; (3): 353–372.

[8] Lafranchis T and Sfikas G. Flowers of Greece. Paris, France: Diatheo; 2009

[9] Krüger M.,.Jones D, Frerichs J, Oppermann B, West J, P. Coombs, K. Green, T. Barlow, R. Lister, R. Shaw, M. Strutt, and I. Möller I. Effects of elevated CO2 concentrations on the vegetation and microbial populations at a terrestrial CO2 vent at Laacher See, Germany. *International Journal of Greenhouse Gas Control* , 2011, 5:1093-1098.

[10] Vodnik D, Videmšek U, Pintar M, Maček I, Pfanz H.. The characteristics of soil CO2 fluxes at a site with natural CO2 enrichment. *Geoderma 150* 2009; 32–37

[11]West JM., Pearce JM., Coombs P., Ford, J.R., Scheib, C., Colls, J.J., Smith, K.L., & Steven, M.D. The impact of controlled injection of CO2 on the soil ecosystem and chemistry of an English lowland pasture. *Energy Procedia 1* 2009; pp. 1863−1870.

[12] Oppermann BI, Michaelis W, Blumenberg M, Frerichs J, Schulz H M, Schippers A, Beaubien S.E., Krüger, M. Soil microbial community changes as a result of long-term exposure to a natural CO_2 vent. *Geochim. Cosmochimi. Acta 74; 2010*: 2697-2716.

[13] Gal F, Michel B, Gilles B, Fridiric J, Karine M. CO2 escapes in the Laacher See region, East Eifel, Germany: Application of natural analogue onshore and offshore geochemical monitoring. International Journal of Greenhouse Gas Control ;2011, 5: 1099–1118