

Diffuse soil CO₂ flux to assess the reliability of CO₂ storage in the Mazarrón-Gañuelas Tertiary basin (Spain)

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Abstract

Geological storage of CO₂ is nowadays internationally considered as the most effective method for greenhouse gas emission mitigation, in order to minimize its effects on the global climatology. One of the main options is to store the CO₂ in deep saline aquifers at more than 800 m depth, because it achieves its supercritical state. Among the most important aspects concerning the performance assessment of a deep CO₂ geological repository is the evaluation of the CO₂ leakage rate from the chosen storage geological formation. Therefore, it is absolutely necessary to increase the knowledge on the interaction among CO₂, storage and sealing formations, as well as on the flow paths for CO₂ and the physico-mechanical resistance of the sealing formation. Furthermore, the quantification of the CO₂ leakage rate is essential to evaluate its effects on the environment. One way to achieve this objective is to study of CO₂ leakage on natural analogue systems, because they can provide useful information about the natural performance of the CO₂, which can be applied to an artificial CO₂ geological storage.

This work is focused on the retention capacity of the cap-rock by measuring the diffuse soil CO₂ flux in a site selected based on: i) the presence of a natural and deep CO₂ accumulation; ii) its structural geological characteristics; and iii) the nature of the cap-

rocks. This site is located in the so-called Mazarrón-Gañuelas Tertiary Basin, in the Guadalentin Valley, province of Murcia (Spain)

Therefore the main objective of this investigation has been to detect the possible leakages of CO₂ from a deep saline aquifer to the surface in order to understand the capability of this area as a natural analogue for Carbon Capture and Sequestration (CCS).

The results obtained allow to conclude that the geological sealing formation of the basin seems to be appropriate to avoid CO₂ leakages from the storage formation.

1. Introduction

The scientific community has general accepted that long-term extrapolation in terms of safety of a deep geological storage of toxic industrial wastes, such as high activity radioactive wastes, industrial and mining wastes and even greenhouse gases, can not be satisfactorily done on the basis of short term researches in the laboratory [1]. Therefore, countries affected by these problems have developed methods of investigation which include both short-term tests in the laboratory, where the variables are controlled, as the study of natural analogues.

Although the studies about CO₂ natural accumulations are not yet sufficiently developed, some authors [2,3] have included in their works the existing CO₂ reservoirs in the world and the experimental reactions between CO₂ and the storage formations [4]. Moreover, in the last decade there are many works focused on the evaluation of the safety of a CO₂ geological storage by means of the study of CO₂ leakage natural analogues [5-11].

Regarding Spain, there's one current important project cofunded by the Ministry of Science and Innovation and FEDER European Funds, whose main objective is the global study of the several CO₂ natural analogues in all over the country. Among them, the natural analogue of storage, and natural and artificial leakage of CO₂ located in the – Gañuelas-Mazarrón Tertiary basin (Province of Murcia) is being studied by the CIEMAT reseach team (Fig. 1). The CO₂ diffuse flux in the soil by means of a WEST-

SYSTEMS fluxmeter has been performed in the above-mentioned site, in order to know whether the cap-rock is able to retain possible escapes of CO₂ at the surface.



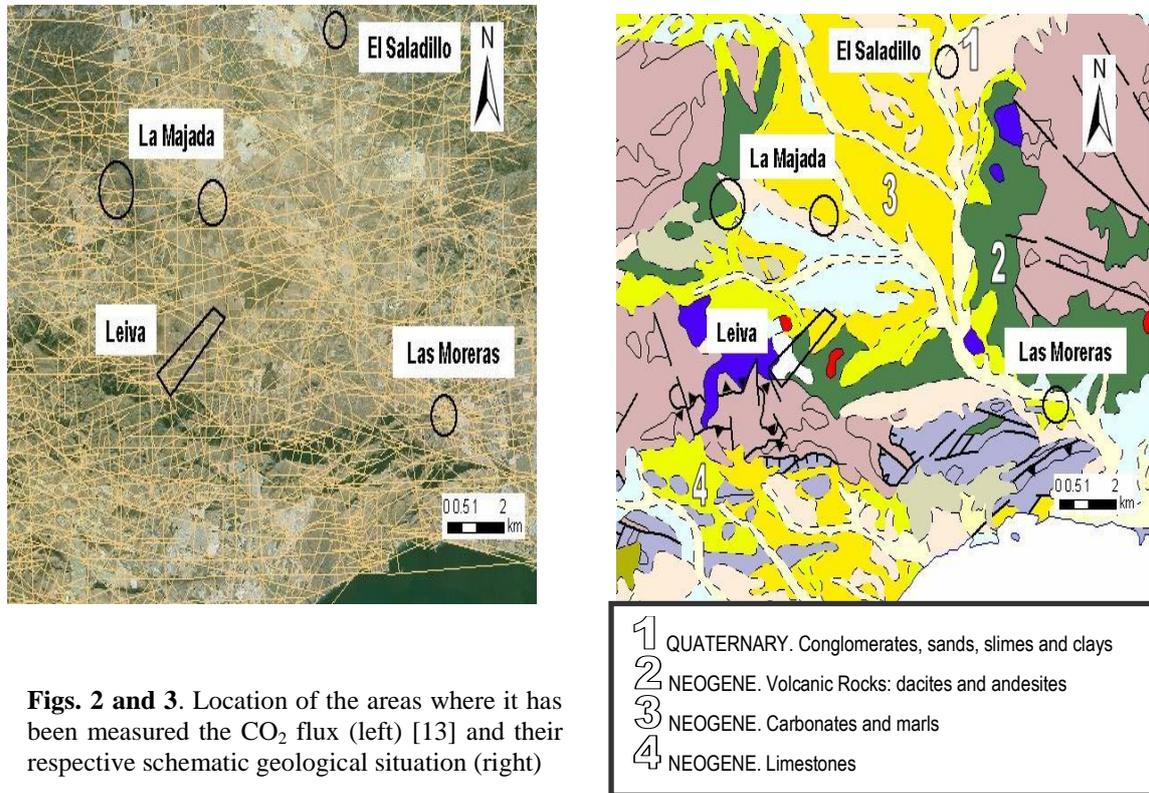
Fig. 1. Geographical location of the study area (red square)

2. Experimental section

In the Gañuelas-Mazarrón Tertiary basin, according to the structural geological features [12,13], four areas were selected for a comprehensive CO₂ flux study. They are located at the intersection of high density lineaments (Fig. 2) that should likely correspond to preferential leakage paths of deep-seated CO₂. These areas are: Las Moreras, La Majada and Leiva (Fig. 3), which are at the contact between the Tertiary basin and the Triassic surroundings mountains, and the El Saladillo place, situated inside the Gañuelas-Mazarrón basin.

The equipment used for CO₂ flux measurements is that licensed by West-System and consists in an accumulation chamber from where the soil gas is forced to be pumped through an IR cell set at the wavelength of CO₂. The increase of CO₂ with time allows the measurement of the flux by means an algorithm that takes into account the pressure and temperature data collected in the field [14].

The CO₂ soil fluxes were carried out in September 2009 and March 2010 during dry and meteorologically stable periods in order to avoid the possible influence of variations induced by environmental parameters on soil degassing. Laboratory experiments were performed to assess both, the reliability of CO₂ flux measurements and the calibration of the instrument [14].



Figs. 2 and 3. Location of the areas where it has been measured the CO₂ flux (left) [13] and their respective schematic geological situation (right)

3. Results and Discussion

In September 2009 the CO₂ flux soil was computed for a surface of ~52,700 m² in Las Moreras; ~86,800 m² in La Majada; ~179,600 m² in Leiva; and ~136,000 m² in El Saladillo. In these areas, 127, 277, 257 and 187 evenly distributed measurements were done, respectively. In March 2010, the investigation in La Majada and Leiva areas was enlarged with 93 and 94 measurements, covering additional surfaces of ~39,000 m² and 30,000 m², respectively.

The measured ϕCO_2 at Las Moreras oscillates from 0.007 to 0.929 moles m⁻² day⁻¹, with an average value of 0.262 moles m⁻² day⁻¹, while at El Saladillo they were spanning between 0.020 and 1.103 moles m⁻² day⁻¹, with an average value of 0.353 moles m⁻² day⁻¹. At La Majada a large interval of variation was observed in September 2009, ranging from

0.007 to 7.503 moles m⁻² day⁻¹, with an average value of 0.877 moles m⁻² day⁻¹; whereas, in March 2010, a lower interval, between 0.025 and 1.425 moles m⁻² day⁻¹, was observed, being its average value of 0.456 moles m⁻² day⁻¹. Finally, at Leiva the ϕCO_2 values varied between 0.024 and 1.490 moles m⁻² day⁻¹, with an average value of 0.391 moles m⁻² day⁻¹ (September 2009) and between 0.041 and 1.074 moles m⁻² day⁻¹ with an average value of 0.310 moles m⁻² day⁻¹ (March 2010).

In order to better constrain the total ϕCO_2 and the CO₂ spatial distribution overall the investigated areas, the values are divided in populations according to the method proposed by Sinclair [15]. The diffuse ϕCO_2 values in the four investigated areas were lower than 1.0 moles m⁻² day⁻¹, whereas values up to 7.5 and 1.49 moles m⁻² day⁻¹ were measured in September 2009 at the La Majada and Leiva areas, respectively. It is worthy to mention that ϕCO_2 values higher than 1 moles m⁻² day⁻¹ were only sporadically recorded.

4. Conclusions

On the basis of the diffuse soil CO₂ degassing surveys carried out in September 2009 and March 2010, the general picture emerging from the present study is that in the area under study, although characterized by a complex geological setting, the efficiency of the cap-rock, as sealing formation, in the Gañuelas-Mazarrón Tertiary basin does not allow any relevant CO₂ leakages at the surface. That is, in terms of CO₂ soil flux, the Tertiary sedimentary deposits filling the basin act then as an impermeable layer through which the escape of CO₂ is not jeopardized. This is strongly supported by the measurements of the ϕCO_2 carried out by means of the accumulation chamber method. The investigated areas have generally low ϕCO_2 . They are basically comparable to those observed in cultivated areas worldwide, with very few exceptions that can possibly be related to structural weakness or fault zones. Nevertheless, this statement is not sufficiently supported by the available data. It is however matter of fact that the geological sealing formation results to be effective and efficient in case of any leakage of CO₂.

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References

- [1] Petit JC. Reasoning by analogy : rational foundation of natural analogue studies. *Appl. Geochem* 1992; Supplementary Issue 1:9-12.
- [2] Czernichowski-Lauriol I, Sanjuan B, Rochelle C, Bateman K, Pearce J, Blackwell P. The underground disposal of carbon dioxide. In: Holloway S, editor. *Inorganic Geochemistry. Final Report of Joule II Project N° CT92-0031*.
- [3] Pearce JM, Holloway S, Wacker H, Nelis MK, Rochelle C, Bateman K. Natural occurrences as analogues for the geological disposal of carbon dioxide. *Energy Converse and Management* 1996;37:6-8.
- [4] Pearce JM, Rochelle C. CO₂ storage: mineral reactions and their influences on reservoir permeability. A comparison of laboratory and field studies. Elsevier; 1999.
- [5] Czernichowski-Lauriol I, Pauwels H, Vigouroux P, Le Nindre YM. The french carbogaseous province: an illustration of natural processes of CO₂ generation, migration, accumulation and leakage. *Greenhouse Gas Control Technologies. Vols I and II, Proceedings 2003*;411-416.
- [6] Hawkins, DG. No exit: thinking about leakage from geologic carbon storage sites. *Energy* 2004;29:1571-1578.
- [7] Beaubien SE, Lombardi S, Ciotoli G, Annuziatellis A, Hatziyannis G, Metaxas A et al. Potential hazards of CO₂ leakage in storage systems-Learning from natural systems. *Greenhouse Gas Control Technologies* 2005;7:551-560.
- [8] Nordbotten JM, Celia MA, Bachu S, Dahle HK. Semianalytical solution for CO₂ leakage through an abandoned well. *Environmental Science & Technology* 2005;39: 602-611.
- [9] Oldenburg CM, Lewicki JL. On leakage and seepage of CO₂ from geologic storage sites into surface water. *Environmental Geology* 2006;50:691-705.
- [10] Riding JB. The IEA Weyburn CO₂ monitoring and storage project - Integrated results from Europe. *Advances in the Geological Storage of Carbon Dioxide: International Approaches to Reduce Anthropogenic Greenhouse Gas Emissions* 2006;65:223-230.

[11] Lewicki JL, Birkholzer J, Tsang CF. Natural and industrial analogues for leakage of CO₂ from storage reservoirs: identification of features, events, and processes and lessons learned. *Environmental Geology* 2007;52:457-467.

[12] Pérez del Villar L, Pelayo M, Recreo F. Análogos Naturales del Almacenamiento Geológico de CO₂ (Fundamentos, Ejemplos y Aplicaciones para la Predicción de Riesgos y la Evaluación del Comportamiento a Largo Plazo). CIEMAT; 2007.

[13] Pérez del Villar L. Memoria Científico-Técnica del periodo 2008-2009 del PSE-120000-2008-6 (PSS-120000-2008-31). Línea de Análogos Naturales: "Resultados preliminares del estudio de los análogos naturales estudiados en: la región de La Selva (Girona), Valle del Alto Guadalentín (Murcia-Almería), Alicún de las Torres (Granada), Alhama de Aragón-Járaba (Zaragoza) y Castilla León" CIEMAT; 2009.

[14] Nisi B, Vaselli O, Lelli M, Tassi F, Rodrigo-Naharro J, Pérez del Villar L. Diffuse CO₂ flux and dissolved gases in the Mazarrón-Gañuelas area (Guadalentín Valley). Report PSE; 2010.

[15] Sinclair AJ. Selection of threshold values in geochemical data using probability graphs. *Geochem. Expl.* 1974;3:129-149.