International Journal of Greenhouse Gas Control 21 (2014) 113–129

Contents lists available at ScienceDirect

International Journal of Greenhouse Gas Control

journal homepage: www.elsevier.com/locate/ijggc

Main drivers of diffusive and advective processes of CO_2-gas exchange between a shallow vadose zone and the atmosphere

E. Garcia-Anton[a,*], S. Cuezva[b], A. Fernandez-Cortes[a], D. Benavente[b], S. Sanchez-Moral[a]

[a] Department of Geología, MNCN-CSIC, C/José Gutiérrez Abascal, n.2, 28006 Madrid, Spain
[b] Department of Ciencias Tierra y Medio Ambiente, Universidad de Alicante, 03080 Alicante, Spain

ARTICLE INFO

Article history:
Received 25 July 2013
Received in revised form 23 October 2013
Accepted 6 December 2013
Available online 28 December 2013

Keywords:
Diffusion
Advection
CO_2 mass balance
Gaseous CO_2 transport mechanisms
Vadose zone

ABSTRACT

A multiparametric study of Altamira cave conditions was performed to identify mechanisms that affect CO_2. A daily survey was used to better understand the role of the shallow vadose system as a source/sink of this gas. Airborne particles were monitored to distinguish the air movement that was joined to $\delta^{13}CO_2$ and were also used as a proxy of the origin of the CO_2. A gas transport model has been created based on the interaction of three air masses (soil–cave–exterior), which is driven by soil-derived CO_2 diffusion to the cave and by the advective mixing of the cave with exterior air. The diffusive process increases cave CO_2 and decreases $\delta^{13}CO_2$. The advective mixing induces a decrease in CO_2 and an increase in the isotopic signal. The diffusive flux depends on soil CO_2 production; the advective flux is driven by outer–inner density gradients, and both depend on the degree of exchange between air masses. Consequently, external conditions, such as temperature and humidity, regulate gas interchange. The created process-based model permits the quantification of CO_2 fluxes. The consequence of the degassing stage is the release of light CO_2 ($\delta^{13}C$ quantified in −24.82‰) into the exterior air ($\delta^{13}C$ measured in −11.34‰). The migration of gas in the vadose zone may influence many environmental processes, and therefore, the contribution of shallow underground systems to surface CO_2 exchange and to the isotopic signal of troposphere should be accounted for.

1. Introduction

The region that is located between the soil surface and the groundwater table, which is called the vadose zone, has traditionally been studied within a hydrologic context (Hopmans and Van Genuchten, 2005). However, the vadose zone atmosphere may contain much CO_2 that occupies pores, cracks and voids of soil, bedrock or unconsolidated sediment (Benavente et al., 2010; Kell, 2012). This CO_2 source has traditionally been neglected or underestimated in studies regarding the net carbon balance in terrestrial ecosystems (Serrano-Ortiz et al., 2010). Furthermore, these shallow vadose environments show significant seasonal, and even daily, variations in CO_2 concentration, which involve the exchange of much CO_2 (g) with the lower troposphere and its role as a depot and/or emitter (Cuezva et al., 2011; Bourges et al., 2012).

Within the complex set of biological, physical and chemical processes that are involved in the interstices of soil and bedrock (subsurface), the migration of gas movements in the vadose zone plays a crucial role in many environmental processes. The ongoing interest in below-ground CO_2 capture and storage (CCS) as one potential mitigation strategy to reduce human CO_2 atmospheric emissions has emphasised the need for more knowledge regarding the geological storage capacity (Post et al., 2012; Nickerson and Risk, 2013). Assessments are needed to ensure that there is no CO_2 leaking from the storage formation and seeping out of the subterranean environment (Cohen et al., 2013). In this regard, a complete understanding of the medium- and short-term gaseous CO_2 transfer processes through the subterranean environment is key.

Ultimately, the mechanisms that control the isolation, recharge and storage processes of gases in the subsurface environment must be identified, particularly, the ventilation/venting processes of these subterranean environments and the resulting release/loss of stored gaseous CO_2 to the Earth's atmosphere. Shallow caves are favourable sites to investigate the transport mechanisms that control gaseous exchange processes at the subsurface because these caves are easily accessible natural macropores that are close to the surface. Thus, recent attention has been given to the role of the double membrane system (host rock and soil), which envelops the air that is contained in caves in the uppermost vadose zone. The role of macro- and micro-fissure rock networks has been taken into account in cave ventilation processes (Baldini et al., 2006; Bourges et al., 2006; Nachson et al., 2012). Other studies have revealed a complex process of gas exchange within a karstic subterranean environment that is controlled by the blockage of airways, such as

---

* Corresponding author. Tel.: +34 914111328 1178; fax: +34 915644740.
E-mail address: elena.garcia@mncn.csic.es (E. Garcia-Anton).

1750-5836/$ – see front matter © 2014 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.ijggc.2013.12.006

thin fractures and connected pores, by water, following an increase in the water saturation of soil and rock by vapour condensation or infiltration (Fernandez-Cortes et al., 2011, 2013). In the short-term, the interaction pattern of the soil porous system with daily humidity fluctuations determines the daily cyclic operation of this double membrane (circadian pattern) and the CO_2 subsurface storage or emission processes (Cuezva et al., 2011; Maier et al., 2010). However, CO_2 transport mechanisms that act at a daily scale are not fully resolved. In addition, the quantification and daily balance of these subsurface CO_2 flows and their relevance to regional CO_2 remain unknown.

The stable isotopic composition of gaseous carbon dioxide is a useful tool for understanding carbon cycling processes and has been widely used to determine the contributions of multiple carbon sources and the mechanisms of soil gas transport. The isotopic composition of soil CO_2 is a window through which we may understand an array of chemical reactions, as well as physical and biological processes, in the soil environment (Amundson et al., 1998). $\delta^{13}C$ isotopic analyses allow for the identification of carbon contributions to the soil CO_2 efflux, as well as the relative contribution of soil carbon pools to the overall ecosystem respiration (Bowling et al., 2008). Specifically, these analyses allow us to distinguish and quantify the contributions of autotrophic and heterotrophic sources to soil respiration (Ekblad and Högberg, 2001; Formanek and Ambus, 2004; Vargas et al., 2011). Additionally, the prevailing mechanism of transport and of the soil CO_2 efflux process can be ascertained, particularly providing information about the relative contributions of diffusion and advection (Cerling et al., 1991; Kayler et al., 2010; Bowling and Massman, 2011). Equivalent isotopic approaches are promising experimental techniques to obtain direct quantitative links to the sources of CO_2 and to the mechanisms that drive gas transport and the transfer of C in soil–cave systems (Breecker et al., 2012) and in the atmosphere–soil–vadose subsurface.

This study aims to model and quantify carbon/CO_2(g) transference processes in the vadose subsurface environment, which is crucial to assess the carbon sequestration or release in these terrestrial ecosystems. To accomplish this aim, we present a study that is based on a combination of the continuous multi-parameter monitoring of atmospheric characteristics (main climatic data and gas composition) and the stable carbon isotopic ($\delta^{13}CO_2$) data, in all three media that are involved (cave–soil–troposphere). Furthermore, a suspended aerosol study is used to discern air movement inside the cave at different times.

2. Site, materials and methodology

2.1. Field site description

The study takes place in the Altamira cave (43°22′40″N; 4°7′6″W, Cantabria Province, Spain), which is a shallow vadose karst cavity that is characterised by remarkable stable environmental conditions (Quindos et al., 1987; Sanchez-Moral et al., 1999; Cuezva et al., 2009). This cave, due to its relatively small size, good accessibility, no tourist impact (Saiz-Jimenez et al., 2011), and sealed entrance is a suitable natural laboratory for gas and microclimatic monitoring under non-disturbed environmental conditions. The main entrance is closed by a metal gate with a highly insulating heat insulation core (slotted surface <4%), which acts as the initial barrier to stop the exchange of energy and matter with the outside. In addition, a second door isolates the Entrance Hall from the rest of the cavity (primarily Polychrome Hall and Walls Hall, Fig. 1). The cave is in the upper vadose area of the karstic system, under a hill 161 m.a.s.l. at a depth of 3–22 m (8 m on average) below the surface. The cavity has a single entrance in a topographically higher position (152 m.a.s.l.) and includes several main rooms that have a downward trend from the outside access to the deepest part of the cave (Fig. 1). The main cave chamber, where the microenvironmental study was performed (Polychromes Hall), is situated 60 m from the cave's entrance, which is at a lower topographic level (146.5 m.a.s.l.) to the surrounding chambers. The rock layer over the chamber averages 7.5–8 m thickness.

The host rock in the Altamira Cave is a thin to medium, parallel bedded, Cenomanian (Upper Cretaceous) limestone succession from 13.5 to 15 m thick. The overlying soil above the cave is a heterogeneous and discontinuous artificial soil with little development (30–70 cm). The soil is silicate-based and poorly differentiated (a surface horizon "A" and, directly beneath this soil, a subsurface petrocalcic horizon). A developed plant cover (meadow vegetation, C3 plants) and high organic carbon were derived from this soil (10–15%).

A GIS-based geological model, which was developed using detailed Digital Elevation Models (Elez et al., 2013), provides information regarding the primary distribution of discontinuity planes: a well-marked stratification system (N18°, 8.5° E) and a primarily vertical or sub-vertical strike system. In outcrop points at the surface, these discontinuities must be direct exchange channels with the outside atmosphere through which gaseous exchange fluxes occur. In this sense, we must take into account the adjacent set of sinkholes, which are located to the east of the cave, as another possible means of direct exchange with the outside atmosphere (Garcia-Anton et al., 2013).

In this geographical area, the climate is moderately oceanic and humid, with an annual precipitation approximately 1400 mm and a mean annual temperature and relative humidity approximately 14 °C and 85%, respectively. Cave air is characterised by a highly stable temperature and humidity throughout the year, with an indoor relative humidity permanently near saturation and mean annual temperature near 14 °C, with 1.5 °C annual thermal amplitude (Cuezva et al., 2009). Relatively high levels of air CO_2 are registered during winter, which sometimes exceed 5000 ppm, and lowest values near 500 ppm during summer (from June to October), due to the most effective cave ventilation during this warmer and drier period (Sanchez-Moral et al., 1999; Kowalski et al., 2008), with an almost homogeneous spatial distribution of pCO_2-air along the cave (Garcia-Anton et al., 2013).

2.2. Micro-environmental monitoring

Gas and microenvironmental monitoring were performed during the warm and dry season (September 2011). Inside the cave, a micro-environmental monitoring station recorded microclimatic data in the Polychrome Hall (Fig. 1). The monitoring station was composed of an 8-channel, 16-bit datalogger (COMBILOG TF 1020, Theodor Fiedrich & Co., Germany) with a suite of probes for the following parameters: air temperature and relative humidity (HygroClip S3, which combines a Pt100 1/10 DIN temperature sensor and a humidity sensor, Rotronic), atmospheric pressure (Vaisala BAROCAP PTB 100, silicon capacitive, Finland), and CO_2 concentration (ITR 498 ADOS, Germany). The station scanned each sensor every 10 s and recorded the 15-min averages. A Radim 5WP Radon monitor (SSM&SISIE-Prague) was employed to measure the concentration of radon gas (^{222}Rn) in the air every half hour. Outside the cave, a weather station with two autonomous dataloggers stored 15-min means of the air temperature and relative humidity (HOBO U23 Pro v2, Onset, Bourne, MA, USA), as well as solar radiation and soil temperature (at 5 and 25 cm depth) (HOBO U12, Onset, Bourne, MA, USA, equipped with the following set of probes: pyranometer PYR-SA 2,5V, Apogee instruments, TMC20-HD of Onset and ECHO EC-10 of Decagon Devices, for radiation and soil temperature, respectively). Rainfalls were registered by an autonomous