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Review

Hidden, abiotic CO_2 flows and gaseous reservoirs in the terrestrial carbon cycle: Review and perspectives

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ABSTRACT

This review article analyzes different abiotic processes that could contribute to the global carbon cycle on short time scales, beginning with high rates of net CO_2 release or uptake measured over ecosystems by the FLUXNET community. The two main abiotic interpretations for these "anomalous" measurements are weathering processes and subterranean cavity ventilation. After analyzing their mechanisms and drivers, we evaluate their possible relevance and contributions in the studies mentioned above. Analyzing weathering (calcite dissolution and precipitation) chemistry and using a geochemical model, we conclude that CO_2 dissolution processes could explain the measured CO_2 release following dry season rain events, but their contribution is far from sufficient to explain large magnitudes of daytime CO_2 emissions or annual CO_2 uptake measured in some desert ecosystems. In this context, we hypothesize and evaluate a further abiotic mechanism: the role of subterranean cavities as a temporal depot of CO_2, along with their seasonal ventilation. A first approximation estimates that the subterranean CO_2 pool (and its potential ventilation) could represent more than half of the total CO_2 content of the atmosphere. Therefore, the non-negligible potential contribution to the net ecosystem carbon balance requires further investigation towards a better understanding of its drivers.

Contents

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1. Introduction

The increase in atmospheric CO_2 concentrations over the last four decades demands an improved understanding of the carbon cycle to accurately predict climate change and determine the main processes involved in the carbon cycle. The global carbon cycle depends on feedbacks among a number of sources and sink processes that operate on both short and long time scales (Boucot and Gray, 2001). Processes occurring over short periods (decadal or less) include photosynthesis, respiration, air–sea exchange of carbon dioxide and humus accumulation in soils (Berner, 2003), while the exchange of carbon between rocks and the surficial system (ocean, atmosphere, biosphere and soils) operates mostly at longer time scales (centuries or longer).

The annual increase of the atmospheric CO_2 concentration is only half that expected considering CO_2 emissions due to anthropogenic activities, implying a terrestrial or oceanic sink absorbing CO_2 on short time scales (annually). Isotopic studies reveal that air–sea CO_2 exchange is too small to explain the "missing sink" (Tans et al., 1990) which must therefore be accounted for by terrestrial ecosystems. Micrometeorological measurements are currently estimating net ecosystem CO_2 exchange around the globe on "flux towers", forming a FLUXNET community (Baldocchi et al., 2001). The flux tower community interprets CO_2 fluxes as "net ecosystem exchange" (NEE), a biological flux defined as the sum of photosynthetic and respiratory components (Falge et al., 2002; Reichstein et al., 2005; Stoy et al., 2006; Valentini et al., 2000), neglecting non-biological processes which are therefore not taken into account in ecosystem-scale carbon cycle research. However, a recent publication highlights the need to include other processes than photosynthesis and respiration and suggests the use of the term net ecosystem carbon balance (NECB) instead of NEE (Chapin et al., 2006). In addition, some other studies over carbonate ecosystems reveal a possible contribution of abiotic, perhaps geochemical, fluxes to net CO_2 exchange, with magnitudes relevant at least on short time scales (hourly, daily and annually) (Stone, 2008; Wohlfahrt et al., 2008; Xie et al., 2008). Furthermore, an apparent controversy about the role of geochemical processes (precipitation and dissolution processes acting as sink or source of CO_2) in the measured NECB is exhibited in the literature (Eshel et al., 2007).

This review article analyzes these abiotic processes that could be involved in the carbon cycle on short time scales and thus contribute to the "missing sink". In Section 2 we present without evaluation some interpretations regarding the high rates of net CO_2 release or uptake (including uptake at night) measured and published by the flux tower community (hereafter: "anomalous" CO_2 fluxes). In Section 3 these abiotic processes are described and evaluated (resolving contradiction in the literature) in order to determine the viability of their contribution to measured CO_2 at half-hour time scales. Finally we analyze the possible influence of abiotic processes at different spatial scales.

2. Flux tower indications of non-biological CO_2 fluxes

This section reviews the literature regarding abiotic interpretations of net CO_2 exchanges observed over carbonate substrates. Beginning with the publication of Emmerich (2003) concerning the behavior of CO_2 fluxes over high-carbonate soils, numerous studies have mentioned possible abiotic influences on net CO_2 exchange, but with inconsistency regarding their sign. Emmerich (2003) attributed CO_2 release measured after dry season rain events to equilibrium reactions occurring in carbonate soils. Acid rain events were associated with a rapid release of CO_2 due to carbonate dissolution at low pH. Later, when the soil profile dried, the loss of water from the soil solution caused CO_2 release. In a concordant study, long-term CO_2 flux measurements in the Chihuahuan desert of New Mexico revealed large daily CO_2 emissions in association with rain events during summer (Mielnick et al., 2005). These authors concluded that an abiotic CO_2 source (dissolution of carbonates) may provoke a portion of the measured CO_2 emissions.

Other "anomalous" results, while less explicit in terms of possible abiotic influences, have emerged from monitoring of desert communities. Low rates of nighttime carbon uptake where measured occasionally in a desert shrub community located in Baja California (Mexico; Hastings et al., 2005). These were attributed to failures in the eddy covariance measurements due to low wind speed or even to the presence of CAM photosynthesizing plants. Also, the NECB estimated for a Mojave Desert grassland ecosystem – assimilation exceeding 100 g m^{-2} and similar to that of some temperate forests – was attributed to expansion and growth of cryptobiotic crust organisms (Wohlfahrt et al., 2008). However, these crust species are neither sufficiently active nor extensive to explain such a magnitude of CO_2 uptake, particularly at night (Stone, 2008).

Other recent publications demonstrate that abiotic exchange processes can temporally dominate the ecosystem carbon exchange with the atmosphere in areas with carbonate soils. Kowalski et al. (2008) revealed large CO_2 release during the dry season in two different carbonate ecosystems located in North and South of Spain. Concurrent belowground micro-environmental conditions and aboveground micrometeorological measurements corroborated the hypothesis of an underground, abiotic CO_2 source; these authors concluded that carbonate precipitation, together with ventilation of subterranean cavities could explain dry season CO_2 emissions. Inglima et al. (2009) demonstrated a higher contribution of soil inorganic carbon release (40% of the total soil CO_2 efflux) during dry soil conditions in a carbonate Mediterranean ecosystem. Rain events produced a decrease of the relative inorganic contribution due to the strong enhancement of the organic flux (inorganic contribution less than 15% after irrigation). Finally, other scientists have highlighted the potential relevance of deserts in the global carbon cycle. Large magnitudes of CO_2 uptake have been observed, both from soil chambers in the Gubantonggut Desert (Xie et al., 2008) and also with open- and close-path eddy systems in the Mojave Desert (Jasoni and Arnone, 2005; Wohlfahrt et al., 2008) including net carbon uptake even at night. These two publications were cited by Stone (2008) to suggest that barren ecosystems could represent the long-sought missing carbon sink. Although there are many suggestions regarding abiotic processes involved in such CO_2 uptake, the true mechanisms are still unknown (Schlesinger et al., 2009).

To summarize, Table 1 shows the different interpretations regarding "anomalous" CO_2 fluxes measured over carbonate ecosystems by the flux tower community. The two main abiotic explanations for these CO_2 measurements are weathering processes (dissolution and precipitation of carbonates) and subterranean cavity ventilation. In the section below we explain these mechanisms and their drivers and evaluate their possible relevance to the studies mentioned above. Furthermore, we hypothesize and evaluate a further abiotic mechanism that could be involved in CO_2 uptake by some deserts, namely deep cavities and macropores as storehouses of CO_2 (prior to their possible ventilation).

3. Abiotic processes involved in net ecosystem CO_2 exchange

3.1. Geochemical weathering processes

Silicate and carbonate weathering processes that are considered important sources and sinks of CO_2, operate at differing time scales and need to be evaluated individually (Boucot and Gray, 2001). Recalling that the main objective of this review is to seek an

Table 1
Summary of "anomalous" CO_2 fluxes measured over carbonate ecosystems by the flux tower community and their interpretations.

Reference	Ecosystem and location	Observation	Explanation
Emmerich (2003) *Agric. Forest Meteorol.*	Semi-arid shrubland/grassland (Arizona, USA)	Large CO_2 release after dry season rain events CO_2 release when the soil is dry	Dissolution of carbonates Removal of water from soil solution
Mielnick et al. (2005) *Journal of Arid Environ.*	Desert grassland (New mexico, USA)	Large CO_2 release after rainfall events during dry season	Dissolution of carbonates
Hastings et al. (2005) *Global Change Biol.*	Desert shrubland (Baja California, Mexico)	Low rates of carbon uptake at night	No turbulence; CAM photosynthesizing plants
Wohlfahrt et al. (2008) *Global Change Biol.*	Mojave desert (Nevada, USA)	Annual CO_2 uptake similar to temperate forest or grassland	Crust organisms
Xie et al. (2008) *Environ. Geol.*	Gubantonggunt Desert (Western China)	Soil CO_2 uptake	Absorption by alkaline carbonate soil
Kowalski et al. (2008) *Agric. Forest Meteorol.*	Semi-arid shrubland and grassland (Southeastern Spain)	Large CO_2 release when soil is dry, windspeed dependence	Precipitation of carbonates; subterranean ventilation
Inglima et al. (2009) *Global Change Biol.*	Mediterranean ecosystems (Pianosa Island, Italy)	Decreased relative inorganic CO_2 release after precipitation events	Strong enhancement of the organic flux

explanation for ecosystem CO_2 exchange measured with micrometeorological techniques at half-hour time scales, we can eliminate silicates weathering directly. The rates of chemical weathering of most silicates in surface environments are slow with mean lifetimes from 10^2 to 10^7 years. Data from dissolution rates and corresponding theoretical mean lifetimes of the most common silicates are given by Lasaga et al. (1994) and Brantley et al. (2008). Therefore, weathering rates of silicates contribute in the global geochemical cycle of C at long time scales but should not be significant over timescales ranging from hours to years and need not be considered as a possible contribution to CO_2 fluxes measured by the flux tower community. By contrast, the reactions rate of precipitation and/or dissolution of carbonates are very fast. Laboratory and field studies indicate that only weeks or months are needed for fresh, undersaturated waters to reach equilibrium by calcite dissolution (Herman and White, 1985; Plummer et al., 1979) depending mainly on pH and temperature conditions.

Thus, weathering processes that occur in carbonate substrates imply consumption or emission of CO_2 and therefore short-term contributions to the net ecosystem CO_2 carbon balance. However, there is no agreement in the literature about the role of carbonate weathering processes in CO_2 cycling (Eshel et al., 2007). Specifically, some authors argue that precipitation of solid carbonates should be considered as a CO_2 sequestration process (Emmerich, 2003; Entry et al., 2004; Inglima et al., 2009; Serna-Pérez et al., 2006), while others argue that precipitation corresponds to a CO_2 source while dissolution of solid carbonate should be considered a CO_2 uptake mechanism (Entry et al., 2004; Gombert, 2002; Kowalski et al., 2008; Liu and Zhao, 2000; Oh and Richter, 2004; Schlesinger, 2000). The explanation for this disagreement is found in the confusion of two concepts: ecosystem CO_2 exchange and the soil carbon pool. In weathering processes both concepts are involved since geochemical reactions, which occur in the aqueous phase, affect carbon in both gaseous and solid phases. In the following section we will demonstrate that precipitation of calcite implies long-term net carbon sequestration in the soil, but also short-term CO_2 release from the substrate to the atmosphere. On the other hand, dissolution implies CO_2 uptake from soil air (reducing respiratory CO_2 release to the atmosphere) and at the same time net carbon release by rocks to the soil solution in the form of bicarbonate.

3.1.1. Theory: dissolution and precipitation chemistry

On short time scales, calcite dissolution and precipitation are mainly controlled by the reactions occurring within the ternary system water (H_2O), carbon dioxide (CO_2) and calcite ($CaCO_3$) (Kaufmann and Dreybrodt, 2007).

Large magnitudes of CO_2 accumulate in the soil due to respiration of plant roots and associated soil micro-organisms, resulting in soil CO_2 partial pressures 10–100 times higher than those of the atmosphere (Amundson and Davidson, 1999). The amount of CO_2 dissolved in the soil solution is directly proportional to the partial pressure of that gas in equilibrium with the solution (Henry's law of equilibrium; half-time on the order of minutes):

$$CO_{2(g)} \overset{K_{HC}}{\Leftrightarrow} CO_{2(aq)} \qquad K_{HC} = \frac{[CO_{2(aq)}]}{p_{CO_2}} \tag{1}$$

where p_{CO_2} is the partial pressure of CO_2 above the solution and K_{HC} is the temperature-dependent Henry's law constant (0.03 mol of CO_2 l^{-1} atm^{-1} at 298 K). However, the rate of CO_2 degassing from water (Eq. (1) to the left) is slower than its rate of gaseous uptake from the atmosphere (Cole et al., 1994), especially in undersaturated water where CO_2 reacts rapidly in the soil solution to form dissolved inorganic carbon (DIC) through the following reactions (with a half-time of less than 1 s):

$$CO_{2(aq)} + H_2O \Leftrightarrow H_2CO_3 \Leftrightarrow H^+ + HCO_3^- \Leftrightarrow 2H^+ + CO_3^{2-} \tag{2}$$

The relative amounts of these different species of DIC in the soil aqueous phase depend on the pH. Carbonic acid (H_2CO_3) is the dominant species at pH values lower than 6.35 while bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) dominate at pH values between 6.35 and 10.33 and higher than 10.33 respectively.

It is important to highlight that these processes occur in all soils.

In addition, in carbonate soils, the dissolution or precipitation of calcite takes place and plays an important role in buffering the system against acidification or basification through the following reaction:

$$CaCO_3 + H^+ \Leftrightarrow Ca^{2+}HCO_3^- \tag{3}$$

Eqs. (1)–(3) can be summarized (Plummer et al., 1979) as:

$$H_2O_{(aq)} + CO_{2(g)} + CaCO_{3(s)} \Leftrightarrow 2HCO_{3(aq)}^- + Ca^{2+}{}_{(aq)} \tag{4}$$

Due to buffering, pH values in carbonate soils are around 7 or 8 and the main DIC species in the soil solution is bicarbonate (HCO_3^-). In terms of net CO_2 exchange, Eq. (4) specifies that for each molecule of $CaCO_3$ dissolved a molecule of atmospheric CO_2 is consumed. In this context, we highlight recent articles published in Nature and Science that proposed the potential capacity of dissolution processes as an economical and favorable means of storing CO_2 via injection of CO_2 into deep geological strata (Aeschbach-Hertig, 2009; Gillfillan et al., 2009; Orr, 2009). On the other hand, stochiometry requires that one molecule of CO_2 be released for every molecule of $CaCO_3$ deposited to the surface (Eq. (4)). Thus processes like evapotranspiration, which enriches aqueous concentrations by removing pure water and (dry) seasonal reduction of the CO_2 in the soil pore space, both provoke

the deposition of $CaCO_3$ from the aqueous solution and the release of CO_2 to the atmosphere (Eq. (4) to the left).

Globally and at long time scales, weathering processes are essentially balanced as far as carbon dioxide is concerned (Berner, 2003; Lasaga et al., 1994) and dissolution of carbonate outcrops on the continents is balanced by precipitation of carbonate mineral in the aquatic system. However, at annual and seasonal scales the net predominance of dissolution or precipitation processes could be relevant to local net ecosystem CO_2 exchanges. Ecosystems with annual net calcite dissolution processes act as a local geochemical sink for atmospheric CO_2. Soil CO_2 is used to dissolve the rock (Eq. (4) to the right) decreasing CO_2 emissions to the atmosphere. In addition, calcite dissolution implies carbon loss from soil, as otherwise stable calcite carbon is included in the soil solution and leaches out as bicarbonate. Thus, in these ecosystems there is a local uptake of CO_2, but nonetheless a loss of carbon from the soil carbon pool. However, over longer periods the local atmospheric CO_2 geochemical sink will be compensated elsewhere by the reverse reaction (calcite precipitation) in aquatic systems.

On the other hand, weathering processes in arid ecosystems with predominance of calcite precipitation are more complex. During the growing season, production of CO_2 via respiratory processes is used to dissolve the rock decreasing CO_2 emissions from the soil air. However, due to water limitations, bicarbonates do not leach out and are stored in the soil. During the dry season however, the carbon contained in bicarbonates is now emitted again as CO_2 due to precipitation processes (Eq. (4) to the left). In addition, extra inputs of Ca^{2+} due to atmospheric deposition or silicate weathering combined with the negative water balance result in more calcite precipitation during the dry season than dissolution during wet season. The formation of these secondary carbonates (caliche) due to extra input of Ca^{2+} can also occur in arid ecosystems with non-carbonate parent material. The summarizing Eq. (4) shows that two molecules of bicarbonate, previously formed during the growing season by dissolution of two molecules of CO_2 (Eq. (1)), react with one molecule of Ca^{2+} to form one molecule of calcite and release one molecule of CO_2. Thus, at long time scales, caliche formation contributes to soil carbon sequestration (Marion, 1989; Schlesinger, 1985) although at short time scales it implies local CO_2 release.

3.1.2. Drivers and resulting seasonality of calcite weathering processes

Calcite dissolution and precipitation result from the action of governing chemical laws. The two main factors that control both processes are the spatial distribution of carbonate outcrops around the world and the climatically determined intensity of chemical solution processes (Gombert, 2002). According to the first main factor these processes occur in carbonate systems that outcrop on 10.4% of the water-free Earth (Dürr et al., 2005) and characterize 13.8 m km^2 in the world. However, the magnitude and dominance of dissolution versus precipitation processes are controlled by environmental changes related to climate location, meteorological seasonality and biological activity.

Some studies have indicated that these weathering processes are also very sensitive to seasonal fluctuations of CO_2 in the soil pore space as a result of plant activity and of water availability (Liu and Zhao, 2000; Schlesinger, 1985). In this context, a modified version of a geochemical model (Goddéris et al., 2006, 2009) including carbonate dissolution/precipitation was used to estimate the annual totals of calcite weathering considering different scenarios of annual net rainfall and annual biological CO_2 production for a sparse Mediterranean shrubland (Serrano-Ortiz et al., 2009; Table 2). Decreasing the actual values of rainfall and biological CO_2 production (2 and 10 times respectively) leads to significant increases in the annual net calcite precipitation (around three times higher), with greater sensitivity to water than to CO_2. By contrast, increasing these two drivers (4 and 10 times respectively) resulted in annual net weathering instead of precipitation. Since these environmental variables exhibit geographical and seasonal patterns, they affect the behavior and intensity of global geochemical processes.

Table 2
Estimated annual totals of calcite weathering ($g C m^{-2}$) considering different scenarios of annual net rainfall and annual biological CO_2 production. The WITCH geochemical model was applied to a semi-arid ecosystem with a productivity of ca. 200 $g C m^{-2} year^{-1}$ and rainfall of ca.180 mm $year^{-1}$ (100% in the table, bold style) using measured half-hourly meteorological forcing data of 2005. Negative values represent calcite dissolution (net CO_2 uptake) and positive values represent calcite precipitation (net CO_2 release).

		Biological CO_2 production		
		10%	100%	1000%
Rainfall	400%	−0.38	−1.32	−3.20
	100%	0.70	**0.30**	−0.48
	50%	0.98	0.97	0.87

However, although weathering processes are mainly controlled by environmental variables and biological CO_2 production, recent studies demonstrate that micro-organisms developing in soil and subterranean environments also might be able to induce precipitation carbonates, via biomineralization processes (Braissant et al., 2002; Cuezva et al., 2009; Portillo et al., 2009).

3.1.3. Can weathering processes explain the "anomalous" CO_2 fluxes?

According to the arguments in the section above, the "anomalous" CO_2 fluxes measured in some arid ecosystems (Table 1) cannot be attributed solely to weathering processes. The summarizing Eq. (4) reveals that on short time scales calcite dissolution implies loss of $CaCO_3$ (via bicarbonate formation) and CO_2 uptake from the atmosphere, reducing CO_2 emissions from the soil, whereas precipitation processes imply release of CO_2 to the atmosphere and soil carbon sequestration. Thus, the large magnitude of annual CO_2 uptake measured in some deserts (Xie et al., 2008; Wohlfahrt et al., 2008) and the reported CO_2 release measured half-hourly in some arid ecosystems after rain events (Emmerich, 2003; Mielnick et al., 2005), cannot be explained by a contribution of (CO_2 consuming) calcite dissolution.

However, CO_2 dissolution processes, together with reactions in the soil solution (Eqs. (1) and (2)), occur with a half-time of minutes and could explain the CO_2 uptake or release measured after rain events. These reactions show that immediately after a rain event, a series of rapid chemical reactions begins in the soil contributing to uptake of CO_2 from soil air. The half-times of these reactions are only minutes and decrease with increasing CO_2 partial pressure (Langmuir, 1997). Subsequent carbonic acid formation and dissociation Eq. (2) are also very fast, so that we can assume that the complete reaction of H_2CO_3 formation is fast enough to attain equilibrium within a few minutes. Usually, the residence time of meteoric water in the soil significantly exceeds this time scale and the magnitude of CO_2 contained in the soil air is anywhere from 10–100 times that of the atmosphere (Amundson and Davidson, 1999; Boucot and Gray, 2001). If rainwater infiltrates into the soil sufficiently and percolates across the entire soil profile down to the C horizon (parent material), the CO_2 dissolved in the water is sequestered, at least temporarily, from exchange processes between soil and atmosphere. On the other hand, if rain falls after a dry season, the water retained in the upper part of the soil (O and A horizons) and evaporated at the end of the rain event, quickly releases previously dissolved CO_2 to atmosphere, yielding no net change in ecosystem carbon stocks. This last process, as Emmerich (2003) suggested, together with crust respiration after light rain pulse events (<2 mm) (Cable and Huxman, 2004), could explain the CO_2 release measured during the

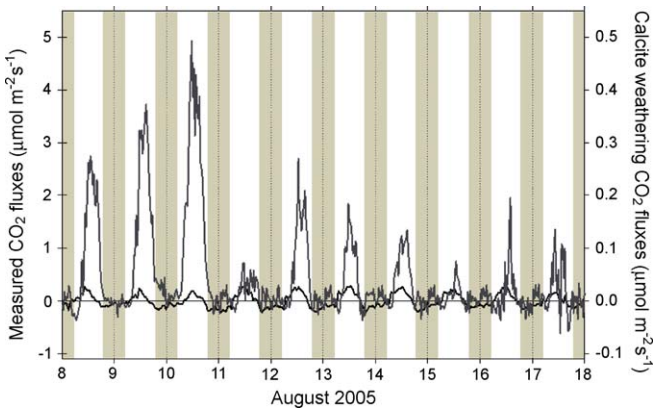

Fig. 1. Half-hourly CO_2 fluxes during a dry period without biological activity. The gray line (left axis) represents net CO_2 fluxes measured with an eddy covariance system while the dark line (right axis) represents CO_2 fluxes calculated with the WITCH geochemical model where positive values imply CO_2 release due to calcite precipitation processes. Nighttime period correspond to gray bands.

dry season after rain events and can even occur in other arid ecosystems with no carbonate parent soil material.

Also, calcite precipitation appears to be insufficient to explain the large magnitudes of CO_2 release over karst systems measured during dry periods (Kowalski et al., 2008). To show this, the WITCH model (Goddéris et al., 2006) was used to quantify the contribution of geochemical processes to these fluxes. The model reveals that during a dry period (plant senescence and soil drying) where biological contributions are considered negligible (Serrano-Ortiz et al., 2009) geochemical processes play an important role in the ecosystem carbon balance, but their contribution is far from sufficient to explain the large magnitude of the daytime CO_2 emissions (Fig. 1).

Consequently, we hypothesize that other abiotic processes may decouple the magnitude and timing of ecosystem CO_2 exchange from the biological and geochemical CO_2 sources and sinks. These processes could be subsurface storage of CO_2 (Boucot and Gray, 2001; Richter and Markewitz, 1995), together with subsequent degassing processes (Mörner and Etiope, 2002; Weisbrod et al., 2009).

3.2. The role of cavities and cracks as a subsurface storehouse of CO_2 and ventilation processes

3.2.1. Theory: CO_2 infiltration and subterranean precipitation processes

After rain events, infiltrating water dissolves the soil CO_2, acting as a geochemical CO_2 sink by reducing the CO_2 emissions and percolates downward. If the parent soil material contains carbonates, the CO_2-enriched water seeping through fissures in the bedrock, is thermodynamically undersaturated with respect to carbonate minerals and can therefore dissolve calcium carbonate from the bedrock according to reaction (4) with the consequent consumption of CO_2 and production of two molecules of bicarbonate. When this DIC-rich solution reaches an air-filled cave, degassing occurs until equilibrium is established with the partial pressure of CO_2 in the cavity, causing precipitation of calcium carbonate and release of CO_2 to the underground environment.

A second mechanism transporting CO_2 downwards could be molecular diffusion during the wet period, when soil CO_2 production is higher and exchanges with the atmosphere is limited by the water-filled pores. Cavities near the surface can thus accumulate high concentrations of soil-derived CO_2 (Bourges et al., 2001; Wood, 1985) that is isolated from soil–atmosphere exchange flows. The high CO_2 levels in caves, currently 10–100 times (Renault, 1968) the 0.04 vol.% typical at the surface, represent direct evidence of a notable downward carbon transit through karst structures (Bourges et al., 2001). On the other hand, part of the CO_2-enriched water can continue to infiltrate into deeper parts of the karst system and even reach the water table. This process of transfer of CO_2 from the soil to underground cavities is most effective in climates where the wet and cold seasons coincide. Then, soil and atmosphere hold more moisture and evaporation processes are less effective, allowing higher rates of infiltration. Moreover, solubility of CO_2 in water increases sharply with decreasing temperature (Eq. (4) to the right).

3.2.2. Theory: ventilation versus diffusion in the degassing processes

Diffusivity plays a major role in the exchange of CO_2 between surface soil and atmosphere. Diffusion of CO_2 is defined as the net transport that results from random molecular motions mixing against gradients in the molar fraction (Kowalski and Serrano-Ortiz, 2007); according to Fick's law, transport is oriented from high to low molar fraction regions, with a magnitude proportional to the molar fraction gradient. Soil respiration and carbonate precipitation act as sources of CO_2 causing gradients in the CO_2 molar fraction of soil pore airspace, against which diffusion can effect transport between soil and atmosphere. Given that soil pores can be filled with either air or water, it is important to recognize that diffusion is much faster for the gas phase (Jones, 2000). In addition, diffusive transport is determined by soil structure and porosity and soil water content (SWC) influencing water-filled pore space (WFPS) (Van Diest and Kesselmeier, 2008).

However, in karst systems characterized by carbonate rocks, cracks, pores and cavities with high capacity to store CO_2 belowground, ventilation processes can dominate the CO_2 exchange between the atmosphere and the subsurface. Ventilation is a transport process due to net movements of air in and out of an enclosed space. This process occurs belowground in the karst system and determines temporal variations of CO_2 (and other gases, notably radon) in caves and macropores (Fernandez-Cortes et al., 2009; Sanchez-Moral et al., 1999). Fig. 2 shows variations in gas concentration inside the Altamira cave in northern Spain, with ^{222}Rn representing a quantitative index of the effects of natural ventilation. Trace gas concentrations rise when the cave is poorly ventilated, but fall during enhanced air exchange with the outside (Kowalski et al., 2008). The similar pattern of variation between ^{222}Rn and CO_2 concentration indicates that ventilation processes determine variations in both gases.

3.2.3. Drivers controlling cave ventilation

The behavior of ventilation processes in caves is controlled by the degree of connection between the cavities and the above-ground system. Most studies related to variations in cave atmospheres due to ventilation processes correspond to caves adapted for tourism, where the control of CO_2 levels is crucial for

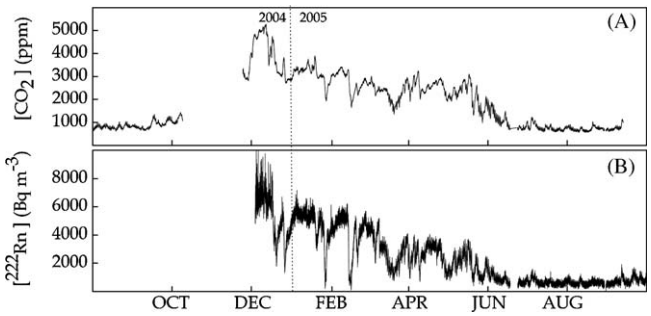

Fig. 2. Time series of (A) CO_2 and (B) ^{222}Rn concentrations inside the Altamira cave (Spain). Adapted from Kowalski et al. (2008).

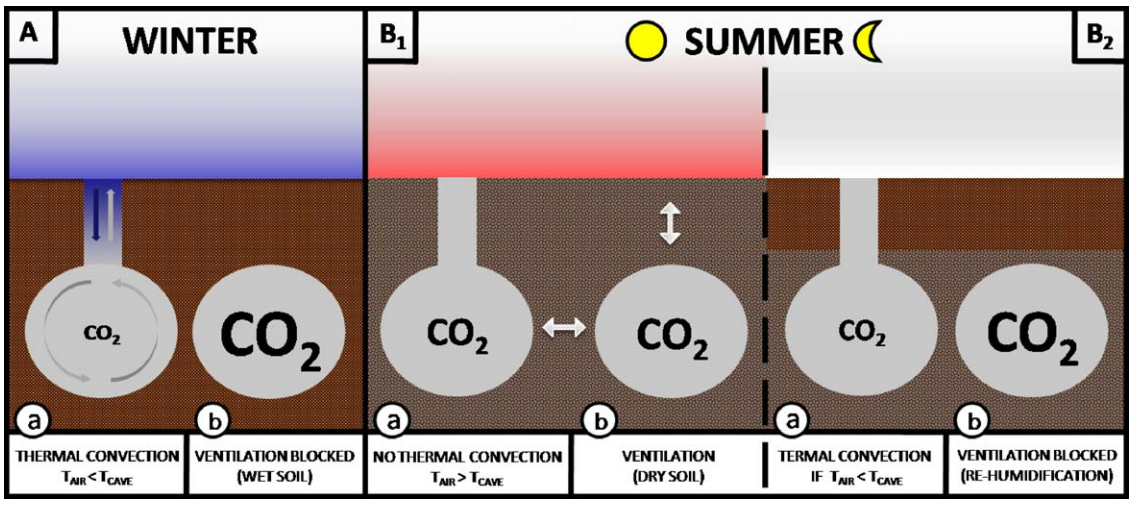

Fig. 3. Seasonal behavior of ventilation processes in a hypothetical belowground karst system composed of two cavities: (a) well connected with the external atmosphere and (b) hidden and inaccessible, but intermittently communicating with (a) and with the external atmosphere. Temporal and spatial CO_2 values are represented by font size.

the cave's conservation (Fernandez-Cortes et al., 2009; Lario et al., 2006). These tourist caves are usually well connected with the external atmosphere and the processes determining ventilation rates are well known (Baldini et al., 2006; Forbes, 2000). However the behavior of ventilation processes occurring belowground between interconnected macropores, fissures and cavities that are not directly connected to the atmosphere is still unknown.

Variations of CO_2 concentrations in well connected caves are characterized by switching between two ventilation regimes driven by changes in the external air temperature (Buecher, 1999; Milanolo and Gabrovšek, 2009). When the external air temperature is lower than the cave temperature, the dense, cold air from the exterior descends into the cave, displacing the warmer cave air which rises and exits. During this period CO_2 concentrations reach their minimum values (close to atmospheric values of CO_2) due to the high cave ventilation. At higher external air temperatures, the cold air inside the cave is denser than the outside air and is therefore trapped inside the cave (assuming the cave has no lower exit); exchange with the external atmosphere is blocked. Thus, in open caves ventilation processes follow a seasonal pattern related to the changes in external air temperature, with ventilation more efficient in winter.

However, the behavior of ventilation processes considering the whole belowground karst system (interconnected macropores, fissures and cavities) appears to follow other patterns. Fig. 3 shows a hypothetical belowground karst system composed of two cavities: the first (a) well connected with the external atmosphere and the second (b) hidden and inaccessible, but intermittently communicating with the first. In the figure, temporal and spatial variations are represented by font size. Gaseous CO_2 in the system is always more abundant in the more isolated, hidden cavity (Ek and Gewelt, 1985). When the external air is cooler than the karst system (Fig. 3A), cold air descends into cavity (a), which is well ventilated and thus has minimum values of CO_2 concentrations. Winter ventilation for such well connected caves is driven by thermal convection. By contrast, the hidden cave is isolated because the pores and fissures that connect to the external atmosphere are blocked by the more abundant water and this cave amasses its maximum values of CO_2.

During summer (Fig. 3B), the two types of cavities (well connected and isolated) communicate somewhat but are at different points in their respective seasonal cycles. During daytime (Fig. $3B_1$), there is a connection between cave (b) and the external atmosphere, because of the drying of the soil; cave (b) represents a spatial maximum of CO_2, despite being at its seasonal minimum. Under these circumstances, CO_2 emissions are observed to be well correlated with evapotranspiration and windspeed (Kowalski et al., 2008). In addition, ventilation transports CO_2 between the karst cavities from (b) to (a). This, along with the fact that thermal convection is suppressed (stable temperature gradient) results in an increase in the CO_2 concentration for the cool cave (a). However, during night time the re-humidification of the soil observed during summers (Kosmas et al., 2001) could limit the nocturnal ventilation for the hidden cavity (Fig. $3B_2$) This explains why hidden cavities show contrasting ventilation patterns versus well connected cavities (most touristic caves), which act as "staging areas" for exchange between the hidden cavities and the external atmosphere.

In summary, during wet winters CO_2 concentrations increase in hidden caves whereas during the dry period ventilation occurs and belowground CO_2 is released to the atmosphere. The magnitude of ventilation will depend on the pressure pumping driven by wind speed and enabled by evapotranspiration. This ventilation hypothesis of hidden cavities is supported by some published studies related to the behavior of touristic cavities not directly connected with the atmosphere such as Candamo (Hoyos et al., 1998), Altamira (Lario et al., 2005; Sanchez-Moral et al., 1999) and Castañar de Ibor caves (Lario et al., 2006).

3.2.4. Can cavity storage and ventilation explain the "anomalous" CO_2 fluxes?

In this section, we suggest that subterranean storage and ventilation processes may contribute to ecosystem CO_2 exchange measured over soils that contain cavities, macropores and fissures belowground – i.e., where the parent soil material contains carbonates. However, we do not discount the possibility that this can matter in other ecosystems with neither carbonate bedrock nor macropores (caves). Immediately after rain events, ecosystems with a deep vadose zone could temporarily store CO_2 below ground via processes of soil CO_2 dissolution, subsequent infiltration and perhaps later outgassing.

The magnitude of CO_2 ventilated from the lithosphere to the atmosphere will depend on the karst system storage capacity, cave geometry and source mechanisms affected in part by meteorological conditions (Ek and Gewelt, 1985; Faimon et al., 2006; Forbes, 2000). The amount and rate of CO_2 entering the cave follows an annual cycle, depending on the rate of the drip water entering the cave and biologic activity and diffusivity in the surface soil (Buecher, 1999). Therefore, in most caves CO_2 has a predominant organic origin and is thus less abundant in low productive areas. Maximum values of CO_2 stored in cavities can vary from less than

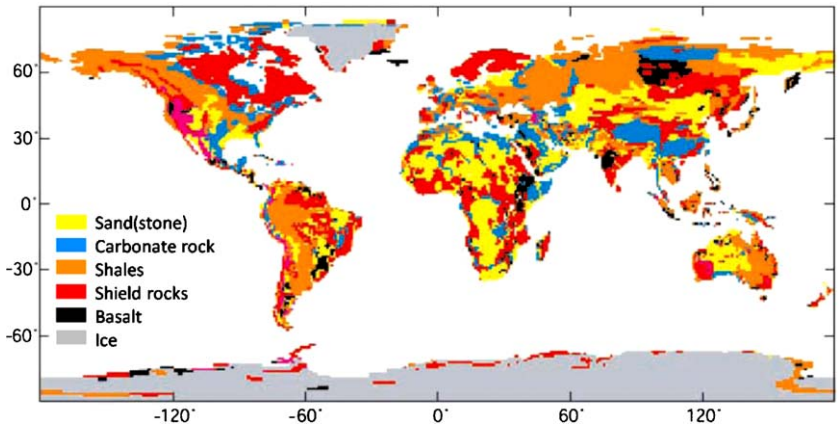

Fig. 4. Present-day exposures of the six major rock types on land area (adapted from Suchet et al., 2003, with permission).

600 ppm in Polar Regions (Ek and Gewelt, 1985) to more than 50,000 ppm in Mediterranean areas (Vadillo et al., 2007). Although soil respiration is considered the primary source of cave CO_2, other mechanisms must be considered including: carbonate precipitation processes inside the cave (Dreybrodt et al., 1997); deep-seated CO_2 seepage from porous reservoirs (usually igneous in origin; Bergfeld et al., 2001); production of CO_2 from respiration by cave micro-organisms (Sanchez-Moral et al., 2003); abundant CH_4 immediately oxidized to CO_2 (Czepiel et al., 2003); underground rivers rich in CO_2 (Chiodini et al., 2000); and anthropogenic contributions (cave visitors). These maximum values can approach atmospheric CO_2 concentrations when ventilation peaks.

Given the enormous capacity of karst systems to store CO_2 and release it by ventilation (Fernández et al., 1986; Lario et al., 2005, 2006), this mechanism may explain some CO_2 emissions detected aboveground using micrometeorological techniques (Kowalski et al., 2008). However, due to the complexity and peculiarity of each karst system, as well as the variety of meteorological conditions (rainfall events, wind speed or temperature) that determine the degree and timing of ventilation, further research is needed in order to quantify the magnitude of this contribution. In this context we highlight recent publications describing the use of "flux towers" and other technologies to detect abiotic (volcanic) CO_2 emissions (Lewicki et al., 2008, 2009; Rogie et al., 2001).

4. Upscaling: the importance of abiotic fluxes in regional CO_2 budgets and at different timescales

Weathering processes occur in ecosystems with carbonate soils but also in arid ecosystems with a negative water balance and inputs of Ca^{2+} that form of secondary carbonates (caliche). Some studies (Gombert, 2002; Liu and Zhao, 2000) have estimated a net annual contribution ranging from 3 to 8% of the total annual atmospheric CO_2 sink. This contribution can vary depending on region and specific climatological conditions. Thus, at annual scales, the fact that these processes are not included in national surveys of CO_2 cycling may cause errors for specific countries with abundant carbonate soils like China (Gurney, 2009; Piao et al., 2009). However, globally and over long-term, carbonate rock dissolution and precipitation are considered in balance as far as carbon dioxide is concerned (Berner, 2003; Lasaga et al., 1994) and thus, should not be included in the long-term CO_2 balance. The net bicarbonate leached out due to the annual predominance of dissolution processes is emitted to the atmosphere via CO_2 in the reverse reaction that occurs elsewhere in aquatic systems. In addition, at regional scales, caliche formation in arid ecosystems can also contribute to the annual carbon balance by acting as a pool of soil carbon. However, this process can be considered negligible at annual time scales in terms of the ecosystem carbon balance (carbonate accumulation rates less than 1 g C m^{-2} $year^{-1}$; Marion et al., 2008). Thus these processes need not be taken into account in inverse modeling calculations to estimate regional atmospheric CO_2 fluxes (House et al., 2003) but should be considered as an important pool of soil carbon over longer time scales (million of years).

Karst system storage and ventilation are phenomena that are well known by cave geologists (Bourges et al., 2001), but their implications for regional CO_2 budgets are still unknown. Fig. 4 shows the distribution of carbonate rock globally and thus identifies potential hotspots for CO_2 emissions by ventilation processes. As an initial and crude approximation, we take the total volume of fissures and cavities – assuming averages of 100 m depth to the water table and 10% porosity – together with an average of its maximum and minimum seasonal contents of CO_2 (20,000 ppm and 400 ppm respectively; standard temperature and pressure) to estimate maximum possible gas-phase storage in karst systems (and potential ventilation) at 2×10^{15} g C. Since this represents 60% of the total C content of the atmosphere, cavities can be considered as a temporal depot for CO_2 coming from different processes (mainly weathering and respiration) that should have negligible influence on long-term (e.g., decadal) CO_2 cycling. However, seasonal or even annual differences in degasification together with changes in rain events and duration of dry seasons can contribute to prominent changes in CO_2 emissions due to ventilation processes. In addition, the potential presence of hotspots in regions with karst systems should be considered when interpreting inverse model applications.

5. Conclusions and outstanding questions

Abiotic processes, such us weathering and storage/ventilation of karst systems, should be considered as mechanisms that, together with biological processes (photosynthesis and respiration), can contribute to the annual Net Ecosystem Carbon Balance (NECB). However, the annual contribution of these two abiotic processes to the NECB can vary depending on the predominant processes, ecosystem location and climatic conditions and may be negligible for other carbonate and semi-arid ecosystems. In this context we note several studies in semi-arid Arizona (Potts et al., 2008; Scott et al., 2004, 2006, 2009) reporting no anomalies, perhaps because moist soils (riparian zone; monsoon precipitation) inhibit ventilation processes. Nonetheless, a first approximation estimates that the subterranean CO_2 pool could represents more than half of the total CO_2 content of the atmosphere. Therefore, the non-negligible role of cavities as a temporal depot of CO_2 coming from different processes, along with seasonal

ventilation, requires further investigation towards a better understanding of its drivers.

Not only quantification of NECB, but also its determining processes are requisite information to enable management for sink optimization. Concerning storage and ventilation processes of subterranean systems, more knowledge needs to be gained on topics related to: (1) the dimension and potential capacity of subterranean CO_2 storage, (2) the drivers controlling the residence time of CO_2 and (3) the possible contribution of other subterranean depots like aquifers. Thus, for an accurate interpretation of carbon cycling over carbonate and karst ecosystems it is imperative to complement micrometeorological studies with other methodologies in order to discriminate between biological and abiotic components of CO_2 fluxes. In this context, radon measurements can be used as a quantitative index of the natural storage/ventilation in cavities (Fernández et al., 1986; Lario et al., 2006) to determine the duration of CO_2 storage and subsequent emissions. Finally, stable carbon isotopic analyzes (Stevenson and Verburg, 2006; Yakir and Sternberg, 2000) together with the implementation of biogeochemical modelling, could be applied to discern among different processes involved in the NECB.

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