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Analysis of Carbon Dioxide Variations in the Atmosphere of Srednja Bijambarska Cave, Bosnia and Herzegovina

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Abstract The results of one year's monitoring in Srednja Bijambarska Cave (Bosnia and Herzegovina) are presented and discussed. Temporal variations of the carbon dioxide (CO₂) concentration are controlled by the switching between two ventilation regimes driven by outside temperature changes. A regression model with a simple perfectly mixed volume applied to a cave sector ("Music hall") resulted in an estimate of ventilation rates between 0.02 h⁻¹ and 0.54 h⁻¹. Carbon dioxide input per plan surface unit is estimated by the model at around 50×10^{-6} m h⁻¹ during the winter season and up to more than 1000×10^{-6} m h⁻¹ during the first temperature falls at the end of summer (0.62 µmoles m⁻² s⁻¹ and 12.40 µmoles m⁻² s⁻¹ for normal conditions respectively). These values have been found to be related to the cave ventilation rate and dependent on the availability of CO₂ in the surrounding environment. For airflow close to zero the values of CO₂ input per plan surface have a range in the order of magnitude of a few units ×10⁻⁶ m h⁻¹. Based on two experiments, the anthropogenic contribution from cave visitors has been calculated, at between 0.351_{CO2} min⁻¹ person⁻¹

Keywords Carbon dioxide · Cave climate · Show caves · Ventilation

1 Introduction

Carbon dioxide (CO_2) plays a key role in limestone dissolution and deposition of speleothems. Changes in partial pressure of CO_2 in the cave environment can enhance limestone

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precipitation, turn the equilibrium toward aggressive solutions or augment the effect of corrosion by condensation. Therefore the control of the additional CO_2 input originating from tourist visits has been recognized as a potential issue for the conservation of caves. The concentration of CO_2 has been included by Cigna (2002) in the list of important parameters for monitoring systems in show caves. With the growth of studies that use speleothems as a proxy for paleoclimate there is an increase in interest in understanding how cave climate and thus the variability of carbon dioxide in the underground atmosphere influences speleothem growth and composition (Spötl et al. 2005; Baldini et al. 2006b; Fairchild and McMillan 2007).

The concentration of carbon dioxide in caves has been recorded extensively (for example see Dragovich and Grose 1990; Cigna 1996) to assess the tourist impact on the cave environment. Nevertheless, there is still a lack of data that enables quantitative treatment of spatial and temporal variations of CO₂. Recently, high resolution CO₂ maps were presented to identify the sources and sinks in a cave (Baldini et al. 2006a). Faimon et al. (2006) used a perfectly mixed reactor model to interpret the temporal variation of CO₂ concentration in Císařská Cave (Czech Republic). The scope of the present work is to link together a conceptual model of the cave climate and carbon dioxide temporal and spatial distributions while also considering possible anthropogenic contributions to this variability.

2 Site Description

The Bijambare area (declared protected landscape in 2003) is located about 40 km north of Sarajevo in Bosnia and Herzegovina (Fig. 1). Srednja Bijambarska Cave is used as a show cave but due to reconstruction work the number of visitors during the study period was negligible. The cave entrance (6m high and 10m wide) is located at 960 m at the bottom of a small vegetated depression. Around 30 m below the cave entrance, there is an active swallow hole where the Brodić creek sinks at the contact between impermeable rocks and the massive limestone (Middle Trias—Anisic). The thickness of the cave ceiling is about 30–40 m. The surface is characterized by coniferous forest with occasionally alpine pastures, while the average annual outside temperature has been estimated as 6.2°C with a total precipitation at about 917 mm (COOR, 2007, p. 5). The cave (Fig. 1) can be divided into two sections:

The main channel—Horizontal (except for the initial 30 m where it descends for around 15 m) gallery, about 180 m long with a relatively uniform cross-section of $60-80 \text{ m}^2$.

The "Music hall"—The final room named "Music hall" is the largest part of the cave, 60 m in length, 32 m wide and 2.5–12 m in height (Malez 1968).

The connection between these two parts is a short, narrow passage that was partially enlarged by removing the floor sediments during alterations for tourism.

3 Materials and Methods

The cave is equipped with a monitoring system to measure the impact of cave visitors and consists of an infrared cell probe measuring the carbon dioxide concentration (C), two remote pT100 probes for the temperature (T_1 and T_3) and a forced ventilation wet-bulb and dry-bulb system measuring the relative humidity (results not included) and which provides another measurement point for the temperature (T_2). All probes are connected to a central datalogger (Elog Model) through compensated cables. The whole system was manufactured by LSI-Lastem, Italy, factory-calibrated and installed at the site just before the beginning of the monitoring period (11 October 2006 to 18 November 2007).



Fig. 1 Map of Srednja Bijambarska Cave with location of measuring stations

All instruments located inside the cave were continuously powered and have an acquisition rate of 1 min. However, the datalogger recorded only the average and standard deviation of 10 measurements (with the exception of a short period in January when the original data were retained in memory). The probes were positioned 1 m above ground and at least 1 m from the nearest wall as suggested by Cigna (2002).

The outside temperature (T_{out}) was recorded every hour from 28 October 2006, with the thermometer located less than 1,000 m from the cave entrance. Values of the outside temperature before 28 October were estimated based on data available from the Sarajevo meteorological station (510 m) and corrected for the site location using a lapse rate of 6.25 K km⁻¹. From May 23 to July 3, data collection in the cave was suspended due to a malfunction of the electrical supply system.

A handheld CO_2 meter (Telaire-7001) was used for measuring the carbon dioxide space profile in the cave and intercalibrated with a fixed instrument during each measurement session.

All the parameters collected are listed in Table 1 (location of probes is shown in Fig. 1).

4 General Monitoring Results and Discussion

4.1 Cave Microclimate Overview

An overview of the general cave microclimate, with all data recorded by the monitoring system, is given in Fig. 2. Periods when the outside temperature was higher than the inside temperature are shown in the upper graph as darker areas.

	Abbreviation	Description	Characteristics	Location
Temperature	T_1	Cave Pt100 probe	Res. 0.01°C – Acc. ±0.08°C	1
	T_2	Cave Pt100 probe	Res. $0.01^{\circ}C - Acc. \pm 0.16^{\circ}C$	2
	T_3	Cave Pt100 probe	Res. $0.01^{\circ}C - Acc. \pm 0.08^{\circ}C$	3
	Tout	Outside temp. (Tinytag-Gemini)	Res. $0.1^{\circ}C - Acc. \pm 0.5^{\circ}C$	Outside
Carbon dioxide	С	Infrared CO ₂ probe	Res. 1 ppm – Acc. ±75 ppm	2
	None	Infrared CO ₂ probe	Res. 1 ppm – Acc. ± 50 ppm	Portable

 Table 1
 Measured parameters and instrument characteristics: resolution (Res.) and accuracy (Acc.)

(Telaire-7001)



Fig. 2 Variation of the measured parameters during the monitored period. Darker areas in the upper graphs represent periods when the outside temperature is higher than the cave temperature

Based on the collected data and field observations, and data from the literature (Baučić and Ržehak 1959; Pašić et al. 1962; Malez 1968), a conceptual model of the cave climate can be proposed. The cave temperature (T_{cave}) is less than the estimated yearly average outside temperature because, due to its morphology, it acts as a "cold trap" allowing stable thermal stratification during warm periods. Similar behaviour was described for the Dobšinská ice cave (Piasecki et al. 2005) and for l'Aven d'Orgnac (Bourges et al. 2001, 2006). Two regimes can be visualized:

Regime 1—When the outside temperature T_{out} is lower than the cave temperature (e.g., during December), external cold and dense air descends by gravity into the cave displacing the relatively warmer cave air. The warm air flows backward to the entrance passing under the cave ceiling (Fig. 3a). The temperatures T_1 and T_2 follow the outside fluctuations with amplitude decreasing with distance from the entrance. During this period CO₂ concentration reaches minimum values, around 580–590 ppm due to the high cave ventilation.



Fig. 3 Conceptual model of cave climate: (a) "regime 1"; (b) "regime 2"; (c) schematic representation for modelling purposes

Regime 2—During warm periods when T_{out} is greater than the cave temperature (e.g., from 20 to 30 October), the cold internal air is denser than the outside and is thus trapped inside the cave, and circulation with the external atmosphere is inhibited (Fig. 3b). However a local circulation between "Music hall" and the main channel may persist for a while due to the differences in temperature in these two parts of the cave.

The temperatures T_1 , T_{dry} and T_2 slowly increase and do not respond to the outside daily temperature fluctuations. In the same warm periods CO₂ accumulates inside the cave, reaching values of almost 2,200 ppm (August–September).

During days when cave temperature lies between the daily maximum and minimum external temperatures, a transition between the two regimes occurs during the 24-h period. The changes in ventilation rate produce typical carbon dioxide transient relaxation/accumulation curves.

4.2 Carbon Dioxide Spatial Variability

A first detailed profile of CO_2 concentration made on April 1, 2007 is shown in Fig. 4a. In this period of the year, the winter season, with a predominant "regime 1" condition, was ending. Entrance concentration is higher than the typical value for the atmosphere (447 vs. 380 ppm) because of the location (bottom of the depression) and abundance of vegetation.

Clearly two different regions with diverse carbon dioxide levels are present. The main channel has very low concentration, close to 500 ppm, with change in concentration versus



Fig. 4 Spatial variability of carbon dioxide concentration: (a) recorded on April 1, 2007; (b) recorded on September 17, 2007

distance from the entrance of 0.2 ppm m⁻¹. CO₂ abruptly increases after the narrow passage leading to the "Music hall", where the concentration is around 700 ppm but a slope one order of magnitude higher (2.2 ppm m⁻¹) is found in the environment following the narrow passage. Similarly, Baldini et al. (2006a) indicate that, in the Ballynamintra Cave in Ireland, major spatial changes in CO₂ concentration generally occur after tight passages. A low slope in the concentration versus distance relationship can be indicative of a well-mixed environment. In Baldini et al. (2006a) and in Ek and Gewelt (1985) values of the slope of 34.29 ppm m⁻¹ (cave with numerous constrictions) and 5.3 ppm m⁻¹ (cave with large and wide passages) were reported.

Analysis of the carbon dioxide spatial variability showed the presence of roughly two units that coincide with the two morphological sectors of the cave: the "Music hall" and the main channel. The narrow passage between them controls the exchanges of mass and energy.

For the opposite pattern, the profile recorded on 17 September 2007 (Fig. 4b) represents the cave's atmospheric situation after the summer season and thus after a period with a predominance of "regime 2". Carbon dioxide composition is rather uniform along the whole length of the cave (slope of 0.2 ppm m^{-1}) while the transition from the external composition (around 380 ppm) to the internal composition (around 1,200 ppm) occurred almost completely in the first 20 m of cave. This situation clearly depicts the effect of stable stratification of the internal atmosphere and the inhibition of air exchange with the outside environment.

5 Modelling

5.1 Model Description

We propose a simple model for the temporal variability of carbon dioxide in the "Music hall". Following Faimon et al. (2006) we consider three flows of CO_2 exchange (Fig. 3c):

- CO_2 from soil (J_S) — J_S is the natural input of carbon dioxide per unit of cave plan surface originating from biological activity in the soil layer and entering the cave environment by degassing from percolating water and gravity seepage through rock fractures. Although this flux is dependent on the partial pressure of CO_2 (p_c) in the cave atmosphere (Spötl et al. 2005; Baldini et al. 2006b), this dependency is not included in the model. The simplification is acceptable if the equilibrium partial pressure in the epikarst is always much higher than in the cave.
- CO₂ from anthropogenic activities (J_A) — J_A is the production of CO₂ due to human respiration in the cave volume under consideration.
- CO₂ advection (J_{Adv})—this term is the net flow of CO₂ generated by convective movements of the air between two cave volumes.

Other processes, such as the diffusion between cave volumes, biological decomposition within the cave, and hypogenic flows are not included because they are not deemed relevant for the investigated site.

The advection term is given by:

$$J_{Adv} = |Q| \left(C_{in} - C \right) \tag{1}$$

where C and C_{in} are the concentration of carbon dioxide in the "Music hall" and inlet stream respectively while Q is the convective airflow rate.

Based on the above definitions, the "Music hall" system can be described by the following mass balance:

$$V\frac{dC}{dt} = S J_S + J_A + J_{Adv} = S J_S + J_A + |Q| (C_{in} - C)$$
(2)

where S is the plan surface of the "Music hall" (around 2, 500 m²) and V its volume (around 15, 000 m³).

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Under the assumption that J_S , J_A , Q and C_{in} are constant during a single carbon dioxide variation event expression (2) can be integrated to obtain:

$$\frac{C - \frac{S J_S + J_A + |Q|C_{in}}{|Q|}}{C_0 - \frac{S J_S + J_A + |Q|C_{in}}{|Q|}} = \exp(-|Q|t/V)$$
(3)

for $|Q| \neq 0$, where C_0 is the initial carbon dioxide concentration.

If there is no air current through the passage, integration of Eq. 2 gives:

$$C - C_0 = \frac{S J_S + J_A}{V} (t - t_0).$$
(4)

Equations 3 and 4 are applicable only if $C \ll C_{epikarst}$. If this condition is not satisfied then the assumption of constant J_S becomes invalid and its dependency on C and $C_{epikarst}$ should be introduced. For other reasons, if C rises above values where a sensible effect on human physiology occurs, then the assumption of constant J_A may be incorrect.

5.2 Model Regression

The model has been applied under two different conditions in order to split the contribution of natural (J_S) and anthropogenic fluxes (J_A) of carbon dioxide:

- Case 1: natural CO₂ fluctuations with no tourists inside the cave $(J_A = 0)$;
- **Case 1**: short tourist visits where the contribution of natural carbon dioxide input can be considered negligible.

5.2.1 Case 1: Natural CO₂ Fluctuations

A total of 92 relaxation curves and 62 accumulation curves, clearly emerging from the background signal, were identified in the monitoring data. These data have been used to calibrate Eq. 3, written in the form:

$$C = A_1 + (A_2 - A_1) \exp(-A_3 t).$$
(5)

Least-squares regression using an iterative nonlinear algorithm gives values of three optimized parameters, namely:

$$A_1 = \frac{S J_S + J_A + |Q| C_{in}}{|Q|},$$
(6a)

$$A_2 = C_0, (6b)$$

$$A_3 = \frac{Q}{V}.$$
 (6c)

From A_2 and A_3 we obtain directly C_0 and Q. Parameter A_1 contains four physical parameters: J_S , Q, C_{in} and J_A . J_A is taken as zero since we deal with periods with no people inside. Q is known from A_3 , which leaves two independent parameters, J_S and C_{in} to be determined.

A simple steady state mass balance for the whole cave has been constructed under the assumptions that Q and J_S are constants within the cave:

$$C_{in-s.s.} = (S_{m.c.} + S)\frac{J_S}{Q} + C_{atm},$$
(7)

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Fig. 5 Example of model regression



Fig. 6 Estimated ventilation rates

where $S_{m.c.}$ is the surface of the main channel (3, 300 m²), C_{atm} is the external atmospheric concentration of CO₂ (380 ppm) and $C_{in-s.s.}$ is the concentration in the main channel during steady-state conditions. Though obtained under steady-state conditions, the value of $C_{in-s.s.}$ was used as a first approximation to C_{in} . The Eqs. 6a and 7 (with $C_{ins.s.} = C_{in}$) were solved together to obtain J_S and C_{in} respectively. Figure 5 shows the relaxation data and best fit for October 14, 2006.

The optimized values of Q/V ("Music hall" ventilation rate), J_S , and estimated values of C_{in} for all the curves are presented in Figs. 6, 7 and 8 respectively.



Fig. 7 Estimated natural input from soil (J_S)



Fig. 8 Estimated concentrations in the inlet stream (C_{in})

5.2.2 Case 2: Anthropogenic Change of CO₂ Concentration

On 26 October 2006, 100 children visited the cave, staying in the "Music hall" for an estimated 20 min. During 21 January 2007 another experiment was organized and 65 people stayed in the final room of the cave for 30 min. In both cases the rise of CO₂ concentration is clearly visible in Fig. 9. Carbon dioxide increased rapidly during the first few minutes of each visit and at the end the CO₂ is practically confined within the room. J_A has been calculated based on the difference of the carbon dioxide concentration before and after the visits and Eq. 4. Both exchange with the main channel and natural carbon dioxide input have been considered negligible due to the short duration of the visit. The term J_A can be calculated



Fig. 9 Carbon dioxide concentration rise due to anthropogenic contribution

as 2,700 \times 10^{-3} m^3 h^{-1} (26 October 2006) and 1,350 \times 10^{-3} m^3 h^{-1} (21 January 2007) respectively.

6 Discussion

6.1 Ventilation Rate

The calculated values lie in a range from $0.02 h^{-1}$ to $0.54 h^{-1}$ (average = $0.23 h^{-1}$, standard deviation = $0.11 h^{-1}$). Although it probably varies greatly from cave to cave, depending strongly on morphology and cave climate, Faimon et al. (2006) found values of the same magnitude for a cave in the Czech Republic (from $0.03 h^{-1}$ to $0.16 h^{-1}$). The air flow rate estimated for the Srednja Bijambarska Cave ($300-8,100 m^3 h^{-1}$) has not be directly verified. The corresponding wind speeds in the narrowest passage (cross-section of around $2 m^2$) are in the range $0.05-1.10 m s^{-1}$. Although no measurements were performed, during two field visits wind speeds up to $0.1-0.2 m s^{-1}$ were noted.

In addition, Fig. 6 shows that ventilation rates associated with accumulation events are, on average, lower than those calculated from relaxation events. This result was of course expected. It should be noticed that even lower ventilation rates could be present in the examined period but the resulting CO₂ concentration transient curves did not emerge clearly from the background noise and thus were not identified.

6.2 Natural Input from Soil

The natural input of carbon dioxide begins at around $300 \times 10^{-6} \text{ m h}^{-1}$ during the first monitored days in autumn, decreases to an average minimum of roughly $100 \times 10^{-6} \text{ m h}^{-1}$ in winter and then slowly recovers reaching its maximum value around $1,000 \times 10^{-6} \text{ m h}^{-1}$ in



Fig. 10 Relationship between the natural input from the soil (J_S) and the ventilation rate

late August. During September, with the first sustained cold spell, the flux rapidly decreases towards winter values of about $50 \times 10^{-6} \text{ m h}^{-1}$.

In the Císařská cave, values of $20 \times 10^{-6} \text{ m h}^{-1}$ in March and $40 \times 10^{-6} \text{ m h}^{-1}$ in September (corrected for a plan surface of 390 m^2) have been found (Faimon et al. 2006). The data are in fair agreement but values in Srednja Bijambarska Cave show a higher annual variability.

A much higher value of J_S (14,400 × 10⁻⁶ m h⁻¹) has been estimated by Bourges et al. (2001), based on a productive rock surface, a value that is around 12 times greater than the highest values found in Srednja Bijambarska Cave. However, it should be noted that the two results cannot be directly compared since they may refer to different surface definitions (productive rock surface vs. plan surface).

High seasonal fluctuations of carbon dioxide concentration in the soil atmosphere have been reported in the literature (Buyanovsky and Wagner 1983; Amundson and Davidson 1990) and they are often considered directly responsible for cave atmospheric composition changes. However, few authors reported that, if the dripping water derives from a well-mixed epikarst system, its equilibrium p_c can be assumed constant (Fairchild et al. 2000; Spötl et al. 2005).

The seasonal penetration of low p_c cave air into a biphasic air–water compartment upflow from the point where dripping occurs (causing enhanced carbon dioxide degassing) has been proposed to explain part of the chemical and isotopic variability found in speleothems and dripping water, (e.g. see Fairchild and McMillan 2007).

The calculated values of J_S show a positive relationship with the ventilation rate (Fig. 10), probably related to imperfectly mixed conditions in the "Music hall" (situation improved at higher ventilation rates) and/or by the expansion of the area of influence of cave air into the surrounding environment with the possible contribution of CO₂ enhanced degassing. The figure also depicts two different limit situations:

A. During periods when "regime 2" is predominant, the relationship between J_S and the ventilation rate lies at higher values of J_S . This indicates that the surrounding environment is rich in CO₂, and can quickly provide high amounts of carbon dioxide during the first fall in concentration in the cave atmosphere.

B. During periods when "regime 1" is predominant, the surrounding area is already depleted and thus an increase of ventilation is reflected in a lower increase of J_S .

Unfortunately the model output in terms of ventilation rate could not be verified in the field and this uncertainty affects the trustworthiness of values of predicted J_S at different Q. On the other hand the dependency itself shows that spot measurements of carbon dioxide effluxes from a cave maybe misleading if interpreted as background values of CO₂ input to the underground environment. Both limit situations A and B seems to converge for Q close to zero to values of J_S of a few 10^{-6} m h⁻¹. A partial confirmation of this order of magnitude for the background input of carbon dioxide in the cave arrives from the analysis of the rise of concentration during a long summer period using Eq. 4 (under the approximation that Q = 0 for the whole period and J_A is negligible). From 5 July to 26 August the CO₂ concentration increases from 1,500 to 2,100 ppm giving an average value of J_S of 2.9 × 10^{-6} m h⁻¹.

6.3 Concentration in the Inlet Stream

The values of C_{in} , as expected mimic the behaviour of carbon dioxide concentration in the "Music hall" but at lower concentrations closer to the outside air composition.

The values predicted by Eq.5 are compared with three experimental concentrations obtained during the year (Fig.8) and are found to match quite satisfactorily.

6.4 Anthropogenic Input

Based on J_A values obtained by the two "Case 2" experiments, values of $0.45 l_{CO2} \text{ min}^{-1}$ person⁻¹ and $0.35 l_{CO2} \text{ min}^{-1}$ person⁻¹ have been calculated as individual production rates. It should be noted that, while children walked along the normal visitors' path, during the second experiment people stood for the entire time at the same place in the centre of the "Music hall". The dissimilarity of physical activity during the two experiments could explain the difference in the results obtained. A wide range of CO₂ exhalation rate (from 0.2 to $2 l_{CO2} \min^{-1}$ person⁻¹) has previously been documented (Dragovich and Grose 1990; Cigna 1996) depending on age and rate of physical activity. Faimon et al. (2006) found similar values (0.39 ± 0.11 l_{CO2} min^{-1} person^{-1}) for children.

6.5 Model Sensibility to Data Selection

The preliminary selection of relaxation and accumulation curves from the monitoring data was made following the criteria that the absolute difference between initial and final CO₂ concentration is at least double that of the background carbon dioxide concentration oscillations (signal noise). Usually only events with concentration changes higher than 20 ppm have been selected. Curves with a high difference between the initial and final concentrations give the best fitting results with R^2 close to 1 (e.g. on 14 October 2007: $R^2 > 0.99$). On the other hand, curves with a concentration difference close to the background noise level produce poor fitting results. Only curves with $R^2 \ge 0.6$ were retained for further elaboration.

The fact that curves with low slope may stay hidden behind the background noise gives a bias toward high ventilation rates.

The selection of the initial and final point of each curve has also been done manually. The procedure becomes problematic for curves close to the background noise, and the choice of the end point influences the length of the final steady state tail. If too many points belong to the final relaxation stage their relative importance compared to the points on the steep portion will be overestimated during the regression.

These activities introduced some subjectivity in the analysis. However due to the relatively high number of curves processed this problem should be at least statistically unimportant. Estimates of cave geometry (volume, surface) also have a direct influence on the final output.

7 Conclusions

Temporal variations of carbon dioxide concentration (CO₂) in Srednja Bijambarska Cave are controlled by the switching between two ventilation regimes driven by outside temperature changes that may even be diurnal. In agreement with recent studies, the CO₂ spatial profile shows a clear dependence on cave morphology with major increases after narrow passages. However this distribution also depends on the ventilation regime since spatial distribution and time evolution cannot be completely decoupled. The regression of a simple perfectly mixed volume model applied to a cave sector ("Music hall") enabled estimation of ventilation rates between 0.02 h^{-1} and 0.54 h^{-1} (average = 0.23 h^{-1} , standard deviation = 0.11 h^{-1}). The natural input of CO₂ is estimated by the model at around $50 \times 10^{-6} \text{ m h}^{-1}$ during the winter season and up to more than $1,000 \times 10^{-6} \text{ m h}^{-1}$ during the first temperature falls at the end of summer (0.62 and 12.40 µmoles m⁻² s⁻¹ at normal conditions respectively). These values have been found to be related to the cave ventilation rate and dependant on the availability of CO₂ in the surrounding environment. For airflow close to zero the values of J_S seem to converge to a few 10^{-6} m h^{-1} .

The anthropogenic contribution has been calculated from two experiments, giving values of $0.45 l_{CO2} \min^{-1} \text{ person}^{-1}$ and $0.35 l_{CO2} \min^{-1} \text{ person}^{-1}$.

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