First assessment on the air CO₂ dynamic in the show caves of tropical karst, Vietnam

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Abstract: In this study, air, water, and host rock in show caves in a Vietnam's karst region was monitored and analyzed to identify the ventilation regime and track the cave air CO₂ sources. In general, the studied caves are well ventilated. In dynamic – multiple entrance caves, air ventilation is described with the use of U shape model. In static – single entrance cave, air circulation is explained by cold air trap model. Both ventilation models suggest that air is more circulated in winter than in summer. Seasonally, the cave air CO₂ increases from early spring to summer. Value in the deepest part of the single-entrance cave is approximately 1,000 ppmv and 8,000 ppmv in early spring and summer, respectively. In multiple-entrance and wet caves, CO₂ level is fairly constant all over the show section, increasing from 500 ppmv in early spring to 2,000 ppmv in summer. Data of microclimate, CO₂ content, and particularly δ¹³C show that cave air, particularly in single entrance cave, has higher CO₂ concentration during summer due to a stagnation of cave air circulation and an elevated CO₂ input from soil and epikarst. The cave air CO₂ increase is also observed after intense rainfalls. A factor that increase cave air CO₂ in show caves during the festive days could probably be human exhaling but the extent of human factor in these studied cave systems should be further investigated. Cave waters including cave pools and streams mediate CO₂ level in wet caves. Above all, the atmospheric fraction of CO₂ is always dominant (>60%) in all cave sections.

Keywords: Phong Nha – Ke Bang, microclimate, cave air ventilation, soil air CO₂, human exhaling

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INTRODUCTION

Air CO₂ is a key factor in a carbonate karst environment. Carbon dioxide produced in soil and vadose zone by microbial degradation and respiration spreads toward the upper part of the karst and the epikarst, and from there it moves to the subjacent parts of the unsaturated zone, including caves (Faimon et al., 2006; Kowalczyk & Froelich, 2010). CO₂ dissolution gives water its aggressiveness against carbonate rock and participates in the karstification potential. Caves are a result of karstification and they are specific parts of vadose zone where external atmosphere air mixes with vadose zone air (Baldini et al., 2006). Depending on numerous processes and conditions (e.g., temperature, pressure gradient, wind

direction, cave geometry), the cave air CO₂ undergoes variations throughout the year, though normally is more concentrated than the open atmosphere level (Kowalczyk & Froelich, 2010; Fairchild & Baker, 2012; Gregorič et al., 2013; Pflitsch & Piasecki, 2003; Geiger, 1961; Vieten et al., 2016b; Baldini, 2010; Benavente et al., 2010; Bourges et al., 2014; Breecker et al., 2012; Fernández-Cortés et al., 2011, 2015; Matthey et al., 2016, among others).

From a global perspective, CO₂ is one of the most important greenhouse gases and its generation, dispersal, and sequestration on earth surface and crust are subject of different researches. Numerous studies have shown a significant CO₂ reservoir existing in the vadose zone of aquifers and a first approximation estimates that the subterranean CO₂

pool could represents more than half of the total CO₂ content of the atmosphere (Serrano-Ortiz et al. 2010; Fernández-Cortés et al., 2015). Both abiotic and biotic processes that control the CO₂ exchange between atmosphere and vadose zone in karst can vary depending on the ecosystem location, climatic conditions, and particular ventilation regime.

The concentrations of CO₂ in cave air have a close relationship with the deposition of speleothem calcite and the way that chemical proxies for paleoclimate are recorded and interpreted from cave deposits (Dreybrodt, 1988; Baldini, 2010; Banner et al., 2007; Breecker et al., 2012; Cosford et al., 2009; Frisia et al., 2011; Matthey et al., 2010; Spötl et al., 2005). Monitoring of cave environments is necessary to improve understanding and interpretation of speleothem climate proxies (Fairchild et al., 2007; Fairchild & Baker, 2012; James et al., 2015) because variations in speleothem geochemistry are produced through changes in rainfall amount, weather patterns, rainfall source, temperature, vegetation atop the epikarst, and ventilation. Sitespecific cave atmosphere studies help constrain interpretations of regional geochemical records derived from the speleothem analysis (McDermott, 2004, Treble et al., 2005 and Fairchild et al., 2006). It is interesting to note that some high quality records of long term continental paleoclimate obtained from speleothems collected in Asian monsoon region matches well with records of other well-known paleoclimate archives like ice cores and sediment cores (Wang et al., 2001, Hu et al., 2008).

In show caves, measurements of CO₂ concentration are usually done for conservation purposes or, more frequently, for the appropriate management of the visit regime (Bourges et al., 2014). An increase of cave air CO₂ resulted from the visitor exhaling could increase the dissolution of speleothems and the destruction of archaeological cave wall arts (Fernández et al., 1986; Calaforra et al., 2003; Vieten et al., 2016a). Previous studies have found show caves in developing and populous countries like Vietnam are highly vulnerable (Trinh & Garcia-Guinea, 2014; Trần et al., 2014; Trinh et al., accepted). Human impacts have been well studied in Lascaux Cave in France (Coye, 2011) and Altamira Cave in Spain (Sánchez-Moral et al., 1999) and just the CO₂ increase appears to be harmful on long time scale decades-centuries (Vieten et al., 2016a), even more harmful appear to be bacteria and constant illumination (Dupont et al., 2007; Cañveras et al., 2001). Probably especially interesting for touristic cave is the risk of increased condensation corrosion (de Freitas & Schmekel, 2003; Miedema, 2009; Vieten et al., 2016a), where a visitation increased temperature difference can lead to condensation (Tarhule-Lips & Ford, 1998).

To our knowledge, there have been no study that traces the generation and dispersal of CO₂ in show caves in tropical karst of Southeast Asia either for CO₂ sequestration assessment, paleoclimate reconstruction, or conservation/management. Thus, this study is the first effort to evaluate the impact of human visitation, along with natural factors on

spatial and temporal variations of cave air CO₂ in 4 different caves in Phong Nha – Ke Bang National Park (PNKB), Vietnam. We focused particularly on (1) identifying ventilation modes in relation with the cave geometry, (2) assessing the role of tropical climate to the cave air CO₂, (3) evaluating the impact of visitors on cave air CO₂, and (4) depicting the variability of the CO₂ soil/epikarst emission and water degassing in caves.

STUDY SITE

The Phong Nha – Ke Bang National Park (PNKB)

The Phong Nha-Ke Bang National Park (between 17°39'N-105°57'E and 17°21'N-106°24'E) covers an area of 857.54 km² and is a UNESCO World Heritage Site, reflecting its global importance. The park came under UNESCO protection in 2003 because of its extraordinary stratigraphical diversity (from the Precambrian to the present day), the long development of its topography (from the Oligocene to the present day) and the intensively developed tropical karst formations (Fig. 1a,b). Over 300 karst caves have been recorded in the park (Limbirt, 2012). The park has geological and geomorphological diversity and has considerable biodiversity in fauna and flora, and extraordinarily well conserved tropical karst forests. Limestones in the area are sedimentary without marble recrystallization (Thanh et al., 2013) during the Palaeozoic era, about 400 million years ago, one of the oldest major karsts in Asia (Shao et al., 2000). These ancient stratified sedimentary limestones were formed from accumulation of shell, coral, algal, and fecal debris in marine environment. Later, these limestones have experienced several geological changes such as very low metamorphism to transform phytoplankton to kerogen (black color) or local hydrothermalism through fissures placing quartz veins with new hydrothermal minerals. Annual precipitation in the region is about 2,000 – 2,300 mm and evapotranspiration in the region is 1,100 – 1,200 mm (Fig. 2).

The central limestone area is bordered by impermeable strata which collect water on the surface and in the southern part of the park discharge it towards the Chay River lying further north. This inflow of allogenic water is the main factor of the development of the underground caves explored to date.

This study targets three show caves named as Phong Nha, Tien Son, and Thien Duong and a non-show cave named as Hang Chuot (Fig. 1b; Table 1). The first two show caves were open for frequent visits since 1995 and the last one was open later in 2006. They receive thousands of visitors on the daily basis and the number increases yearly (Vietnamtourism, 2016).

Geometry of the studied show caves

The position and vertical profile of the caves are given in Fig. 1. The caves are part of either active or inactive/dead underground streams/rivers. Long history of karstification has made the caves spacious, long, and accessible.

Fig. 1. Map of the study area and sketch of the surveyed caves. (a) map of Vietnam and location of Phong Nha – Ke Bang National park in central Vietnam, (b) topographic map of Phong Nha – Ke Bang National Park and relative positions of the surveyed caves, (c), (d), (e), (f) top down views of surveyed caves, (g), (h), (i), (j) horizontal views of caves. The red lines (passage lines) in (c), (d), (e), (f) are respectively where the cross sections of (g), (h), (i), (j) have been taken. Blue numbers: elevation of the cave floor relative to the cave entrance elevation (m), Red numbers: distance from main entrance (m), Vertical scales: relative elevation, Horizontal Scales: horizontal distance, Solid stars: points of spot surveys and cave air sampling in show sections. Crossed black stars: additional spot surveys and air sampling in non-show section, DM: diurnal monitoring points.

Fig. 2. Monthly temperature, precipitation (Prec), and evapotranspiration (ETP) monitored at station Dong Hoi over the study period: August 2014 - August 2016; arrows indicate the survey times.

Phong Nha Cave

This cave is about 8,300 m long and the section open for regular tours extends about 1,500 m from the entrance. It has long sections of deep water passed by swimming, some sections of wading and walking along sand banks, and nearer to its exit some well decorated dry sections of cave. The first full exploration and survey of the cave was completed in 1992. The entrance for visit is outflow of Son River which flows in the south-north direction (Fig. 1c, g). The other entrance is the Son River inflow which is only accessible by professional cavers. That is the reason it is considered as a wet cave. Like many caves in this area, this cave has been continuously shaped by the local river systems. Inside the cave, galleries are large with some having 100 m width. Specifically in this cave, the air and water surveys and samplings were mostly conducted on small paddling boat traveling along the river running through the cave. Inside the cave, due to the corrosion/dissolution along fractures, river depth varies, reaching more than 18 m deep in some places. Every few years, caves like Phong Nha are inundated during rainy season. Cave wall still shows water mark up to 3 m above the normal level.

Tien Son Cave

The entrance of Tien Son Cave is about 1 km to the west of Phong Nha cave, at an altitude of 135 m amsl (Fig. 1d). This cave is 980 m in length and the visiting section is about 500 m long (Fig. 1h). The cave floor is gradually descending from entrance to the deepest and innermost galleries. The cave ends in a final

calcite choke. The average width and height of Tien Son Cave, the shortest among the 3 studied ones, are 60 and 55 m, respectively. Although Phong Nha and Tien Son caves are in the same mountain, there are no linking grottos between them. The exact cave formation history is uncertain and has to be studied in more detail.

Thien Duong Cave

Total distance of Thien Duong Cave is 31 km, divided into 3 segments as shown in Fig. 1e. The segment targeted of this study is about 5 km long and includes a 1.1 km which is open for visitation (light and pedestrian path are set up in this section). The studied cave segment has 2 entrances at 280 and 140 m amsl. The first one, which is now used for visit, is a crack on the cave ceiling. The second one is a huge sinkhole of about 100 m in diameter (Fig. 1i). Water was found in this cave in different forms from newly drip to deep and large cave pools. In some sections there are water inlets which after heavy rains, a large amount of water can come in via these inlets, quickly flooding the dry passages. Underground flow is active in several sections. Newly formed speleothems were found in many parts as well.

Hang Chuot

This cave is a non-show cave and in this study it is used as a reference for identifying human impact on cave microclimate and cave air CO₂. This is a short cave, only about 200 m in length (Fig. 1f). This cave has 2 distinctive large entrances at both ends (Fig. 1j) to ensure a strong exchange between cave air and exterior. This cave is considered as dry cave as its elevation is above outside ground.

MATERIALS AND METHODS

Our surveys, monitoring, and analyses are categorized as (1) spot surveying, (2) diurnal monitoring, (3) spot air sampling and analysis, and (4) host rock and (5) water sampling and analysis. From August 2014 to August 2016, 5 surveys were conducted in spring and late summer. According to the Nyquist-Shannon's theorem that the sampling rate must be at least twice the maximum frequency present in the signal (the so-called Nyquist rate), this number of surveys over a 2 year span would correctly interpret the cave microclimate conditions if the conditions are dominated by the annual frequency (seasonal oscillation).

Spot surveying

Since 2014, 5 surveys have been conducted in early spring and summer (Table 2). Especially, one survey

Table 1. Cave characteristics.

Cave	Latitude	Longitude	Altitude (m amsl)	Overburden (m)	Show section length (m)	River	Entrances	Height (min-max)	Width (min-max)
Phong Nha	17°34'53"N	106°16'59"E	5	50-250	1,500	Yes	Multiple	2.6-148	1.3-167
Tien Son	17°34'48"N	106°16'52"E	135	20-150	500	No	Single	7-98	10-82
Thien Duong	17°31'45"N	106°13'30"E	280	20-350	1,100	Yes	Multiple	3-72	3-150
Hang Chuot	17°46'37"N	106°04'09"E	190	30-190	NA	No	Multiple	54-71	66-98

taken in April-May 2015 was conducted during the Vietnam national holidays when visitation was later found almost 10 times higher than regular days (Zing, 2015). It should be noted that caves are open for visit every day around the year and there is no visitation limitation setup in all show caves. Thus, the daily visitation increases very much during holidays. In each show cave, 4 spots were checked for microclimate conditions; outside the cave in front of the entrance, within 20 m inside the cave from the entrance, center of the show section, and end of the show section. Additional monitoring and air sampling were taken deep inside Thien Duong Cave, in the non-show section until the next entrance (sink hole), about 5 km from the first entrance (Fig. 1i). Variables of T°C (accuracy: $\pm 0.3^\circ\text{C}$), relative humidity (RH, accuracy: $\pm 0.1\%$), wind speed (accuracy: $\pm 2\%$ rdg., range: 0–30 m s⁻¹), and CO₂

(accuracy: ± 1 ppmv) were monitored with the use of a GrayWolf Toxic Gas TG 501 (USA), a highly accurate and very rapid response sensor stabilizing within 3–4 minutes so that field comparisons are quick. Since all stairs are fenced to prevent visitors from crossing out of the visiting passages, air monitoring was taken few meters far away from the stairs to avoid direct interference from visitors. The Gas TG 501 which combined GrayWolf's advanced hotwire air velocity sensor technology was left stabilized for few minutes and then programmed to record 5 results at 2 minute interval. For the whole monitoring period, only 1 person in charge of microclimate monitoring was within 1 m of the sensor to limit possible interference. Sensor was placed approximately 1 m above cave floor. All microclimate data were recorded between 10–11.30 A.M. and 2.30–4 P.M. during visitation peak hours.

Table 2. Timetable of organized surveys, monitoring, and sampling

Date	Spot survey (1)	Diurnal monitoring (2)	Air sampling (3)	Host rock (4)	Cave water (5)
Aug. 2014	PN, TS, TD			PN, TS, TD	PN, TS, TD
Apr.– May. 2015	PN, TS, TD	TS, TD	PN, TS, TD		PN, TS, TD
Aug. 2015	PN, TS, TD	TS, TD			PN, TS, TD
Mar. 2016	PN, TS, TD	TS, TD	PN, TS, TD		PN, TS, TD
Aug. 2016	PN, TS, TD	TS, TD, HC			PN, TS, TD

Note: PN, TS, TD, and HC are respectively Phong Nha, Tien Son, Thien Duong, and Hang Chuot caves.

Diurnal monitoring

Diurnal monitoring of temperature, humidity and air pCO₂ was performed with the use of a cSense CO₂ + RH/T Monitor w. Data-Logger Kit (CO2Meter, USA). Its CO₂ sensor is designed with non-dispersive infrared waveguide technology and equipped with automatic background calibration preset on for long time drift compensation. Accuracies of CO₂, RH, and T are ± 50 ppmv $\pm 5\%$ rdg, $\pm 3\%$, and $\pm 0.6^\circ\text{C}$, respectively. As shown in Table 2, the system was deployed in Tien Son, Thien Duong, and once in Hang Chuot (a non-show cave used as reference). The system is powered by 2 12V batteries to guarantee the measurement for at least 24 hours. In order to capture the most representative data of cave microclimate, avoiding the mixing zone at the proximity of cave entrance, incidentally affected by visitors, the precise monitoring points were set a bit further from visiting path and not directly on the cave floor. In detail, in Thien Duong, the multi-entrance and show cave, the monitoring unit was deployed near central of show section about 500 m from the entrance, 10 m from the visiting pathway, and 2 m above cave floor. In Tien Son, the single-entrance and show cave, monitoring was deployed at the end of 500 m show section about 20 m from the show path, and 3 m above the ground. In the 200 m non-show cave of Hang Chuot, the unit was placed in between the entrances and 3 m above cave floor. Relative positions of the monitoring points (DM) are indicated in Fig. 1h, i, j.

Spot air sampling and analysis (CO₂ and $\delta^{13}\text{C}$ of CO₂)

Air samples were taken at the spot surveying points in 2 surveys; April-May 2015 and March 2016. All samples were taken from 1 m above the cave floor.

A portable air compressor (AQUANIC s790) was used to pump air at 0.4 l min⁻¹ into 1L Tedlar bags with lock valves designed to ensure the inertness and impermeability of air samples.

Soil air collection was conducted in front of the show caves, precisely at sites located vertically above each cave using a 1 m hollow metal tube (Fernández-Cortés et al., 2015). The tubes were inserted to a depth of 50 cm near the bedrock–soil interface. Soil air was extracted using a microdiaphragm gas pump (KNF Neuberger, Freiburg, Germany) at 3.1 l min⁻¹ at atmospheric pressure. The soil air samples were also pumped into Tedlar bags like cave air samples.

The air samples collected in May 2015 were analyzed using a CRDS analyser model G2201-i (Picarro Inc., USA). The system uses cavity ring down spectroscopy (CRDS), a laser spectroscopic technique highly sensitive for measurement of absolute optical extinction by samples that scatter and absorb light, to identify and quantify $\delta^{13}\text{C}$ of CO₂ and automatically calculates its isotopic value. The analyzer measures the isotopologues of the carbon dioxide (¹²CO₂ and ¹³CO₂) and automatically calculates the $\delta^{13}\text{C}$. The device measurement precisions are 200 ppb and 10 ppb for ¹²CO₂ and ¹³CO₂, respectively. The resulting accuracy is 0.3‰ for $\delta^{13}\text{C}$ after 5 min of analysis. The device was calibrated before each analysis session using synthetic gases with known concentrations. Three in-house standards with certified gas mixtures and known CO₂ concentration (7,000 ppmv, 400 ppmv and zero-CO₂, supplied by PRAXAIR Spain in high-pressure gas cylinders for this study) used to calibrate and adjust the measurement of CO₂ concentration were run regularly at the beginning and at the end of each day/session of analyses to

verify the proper functioning of the Picarro G2101-I analyser. Additionally, some duplicated air samples were analyzed in order to check and adjust our $\delta^{13}\text{C}$ of CO_2 data in function of the NOAA WMO-2004A and WMO-X2007 reference gases. Further details about the methodological and analytical procedures can be found in Fernández-Cortés et al. (2015).

For the samples collected in the March 2016 campaign, CO_2 mole fractions were measured independently in the greenhouse gas laboratory at Royal Holloway University of London (RHUL), UK, with a Picarro G1301 CRDS analyser, calibrated against the NOAA WMO-2004A and WMO-X2007 reference gases. The carbon isotopic ratio ($\delta^{13}\text{C}$ of CO_2) of bag samples was measured in the RHUL lab in triplicate to high precision (± 0.05 ‰) by continuous flow gas chromatography isotope ratio mass spectrometry (CF GC-IRMS) (Fisher et al., 2006).

Cave water sampling and analysis

Water samples for alkalinity, hardness, and $\delta^{13}\text{C}$ of DIC analyses were selectively collected in cave pools/rimestones and underground streams nearby the spot air monitoring points. In Phong Nha, as Son River covers entirely the cave bottom, only stream water samples were taken. In Tien Son, as there is no stream/river running inside the cave, all samples were collected from cave pools. In Thien Duong, waters in both types (cave pools and stream/river) were sampled. As the caves are huge, we could not access to the ceiling to collect newly exposed drip water. Also, no drip water sampler, or any sampling equipment, was allowed to be placed under the dripping spot inside the caves after our expeditions finished. In addition, our pool water sampling was not always at the same pools due to drying up in dry season but we always tried to find the closest pools to the air sampling and monitoring site. Depending on the relative positions of cave pools, sources of water could be from ceiling and cave wall (drip water), from stream during high stand, or even from groundwater (several pools located on the cave floor in Thien Duong have bottom deep below the cave floor and could be connected to groundwater). On the other hand, sampling of stream water was always conducted at the same spots. First, 1-little HDPE bottles were carefully dipped into water bodies to avoid disturbing water bodies and ensure that water near the surface is sampled. Then, sub-samples for different analysis were extracted from these 1-little bottles.

The sub-samples subjected to isotope analysis were pretreated *in situ*. All inorganic carbonate species were precipitated from the water at high pH and the wet precipitate is shipped to the laboratory. In detail, 300 ml of cave water was added with first 5 ml of SrSO_4 solution and then few drops of concentrated NaOH. The sample bottles were filled to the top, tightened with cap, and left stabilized for 3 hours. The wet precipitate was then carefully decanted and transferred to smaller 25 ml HDPE screw cap bottle prior transferred to laboratory for $\delta^{13}\text{C}$ analysis.

In situ monitoring of the water physico-chemical parameters (e.g., Temperature, pH, Conductivity) was

performed with the use of a Hydrolab Sonde 5a (USA). The accuracies of temperature, pH, and conductivity are $\pm 0.01^\circ\text{C}$, ± 0.2 , and $\pm 1\%$ of reading ($\pm 0.001 \mu\text{S/cm}$), respectively.

Immediately after arrival to the laboratory in cold box after maximum 3 days, water alkalinity was measured on filtered samples and determined by the single-point titration method using methyl orange as indicator (Trinh et al., 2016). Water hardness was determined according to the EDTA titration method (Trinh et al., 2009).

The partial pressure of gaseous CO_2 that would be at equilibrium with aqueous carbonates in water ($p\text{CO}_{2,\text{water}}$) is calculated as:

$$p\text{CO}_{2,\text{water}} = \frac{\text{Alk} \cdot [\text{H}^+]}{K_{\text{CO}} \cdot K_{\text{C1}} \cdot 10^6} \quad (1)$$

Where $p\text{CO}_{2,\text{water}}$ is in ppmv, the alkalinity (Alk) corresponds to the “normal” measurement of bicarbonate alkalinity expressed in $\mu\text{eq/l}$ units ($\text{Alk} = \text{Alk}_{\text{C}}$), and $[\text{H}^+]$ is hydrogen concentration in water ($\mu\text{eq/l} = 10^{(6-\text{pH})}$). The K_{CO} and K_{C1} values are equilibrium coefficients of bicarbonate and carbonate species in water and their values were taken from Stumm and Morgan (1996) as follow:

$$K_{\text{CO}} = \frac{[\text{H}_2\text{CO}_3^0]}{p\text{CO}_2} = \exp\left(-60.2409 + 93.4517 \frac{100}{T} + 23.3585 \cdot \ln\left(\frac{T}{100}\right)\right) \quad (2)$$

$$K_{\text{C1}} = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3^0]} = \exp\left(3.17537 - \frac{2329.1378}{T} - 1.597015 \cdot \ln(T)\right) \quad (3)$$

with T is Kelvin temperature.

Saturation index of CaCO_3 (SI_{CaCO_3}) is calculated as (Neal et al., 1998)

$$SI_{\text{CaCO}_3} = \log_{10}\left(\frac{[\text{Ca}^{2+}] \cdot [\text{HCO}_3^-] \cdot 10^{-1.85}}{[\text{H}^+]}\right) \quad (4)$$

If $SI_{\text{CaCO}_3} > 0$, the aqueous solution is CaCO_3 supersaturated and prone to CaCO_3 precipitation. If $SI_{\text{CaCO}_3} < 0$, the solution is CaCO_3 undersaturated and no CaCO_3 precipitation occurs.

Host rock sampling and analysis

The host rock samples were taken by breaking tips of rocks near the cave entrance.

For the C isotope analysis of host rock and carbonate species in cave water, powder samples were weighed by microbalance and introduced into a combustion module coupled to a Picarro CRDS system at Center for Energy, Environmental and Technological Research (CIEMAT), Spain (Robredo et al., 2011). Briefly, the C present in the sample is transformed into CO_2 by flash combustion in a Costech module and then introduced using N_2 as carrier gas into a Picarro isotopic analyzer model G1121-i. The equipment was calibrated with reference materials certificated for $\delta^{13}\text{C}$ in the range

+2 to -26‰_{VPDB}. Analytical precision was 0.11‰ for CaCO₃ standard samples namely NBS 18, NBT 19, and IAEA-CO-8 (n=10) and 0.21‰ in triplicate samples.

The Micro-Raman spectra of samples were carried out in a Thermo-Fischer DXR Raman Microscope (West Palm Beach, FL 33407, USA). The system has Olympus BX-RLA2 Microscope and a CCD (1024x256 pixels) detector, motorized XY stage, auto-focus and microscope objectives Olympus UIS2 series. A light source at 532 nm of a frequency doubled Nd:YVO4 DPSS solid laser (maximum power 30mW) was used for the sample excitation. We used the 20X objective, the laser source at 532 nm at 6 mW in laser mode power at 100%. The average spectral resolution in the Raman shift ranging from 100 to 3,600 cm⁻¹ was 4 cm⁻¹, i.e., grating 900 lines/mm and 2 μm spot sizes. The system was operated under OMNIC 1.0 software fitting routinely conditions such as pinhole aperture of 25 μm, bleaching time 30 s and four exposures average timed 10 s each.

RESULTS

Characteristics of cave waters and host rock

Water monitoring and analyses show a large variation in water quality (Table 3). For instances, specific conductivity in water was between 50 and 280 mS cm⁻¹ (results not shown). pH varied between 7.8 and 8.6, showing the alkaline characteristics of water usually found in karst region. Water hardness ranged between 0.1 and 2.0 mmol L⁻¹. Total alkalinity, exhibiting total inorganic carbonate in water, varied from 0.2 to 4 mmol L⁻¹.

Seasonally, hardness and alkalinity fluctuated more during summer-rainy season than during spring-dry period (Fig. 3a). A high 1:1 correlation between hardness (CaCO₃) and alkalinity (HCO₃⁻), especially during spring surveys and in stream water, implies karstification was main process producing dissolved Ca and CO₂ in water (Fig. 3a). Apart from that, some cave pool samples collected in Thien Duong in summer surveys showed a different trend of hardness-alkalinity relationship from the limestone dissolution trend (Fig. 3a). Also in Thien Duong where both types of water exist, the analytical results show a more similarity between pool water and stream water in spring/dry period than during summer/rainy period (Table 3). For the same type of water, there was a similar trend in both summer and spring samples: water in Thien Duong seems more diluted than in Phong Nha and in Tien Son. The only exception (opposition) is about hardness in cave pools in summer that the mean value in Thien Duong was higher than in Tien Son. However, this exception might not be representative since the number of samples in Thien Duong is only 3 and all 3 samples were from the same cave pool.

Saturation index of CaCO₃ in water was calculated from hardness, alkalinity, and pH according to formula [2]. The positive mean saturation index (SI_{CaCO3}) indicates that majority of water samples were CaCO₃ supersaturated. Like water hardness and alkalinity, SI varied more in summer than in spring and more in cave pools than in stream waters. Seasonality, in

cave pools, SI was lower in summer than in spring. In stream waters, SI was not different between seasons. In summer, SI was lower in cave pools than in stream waters. In spring, the difference between cave pools and streams was less obvious than in summer.

Partial pressure of CO₂ in water (pCO_{2,water}) was calculated from alkalinity, pH, and water temperature with formula [1]. Thus, water having alkalinity in the range of 2 – 4 mmol L⁻¹ at 25°C and pH=8 would have a pCO_{2,water} between 550 and 1,100 ppmv. In general, pCO₂ was lower in summer than in spring and varied stronger in cave pools than in stream waters. Particularly, in some cave pools, pCO₂ was calculated as smaller than 400 ppmv (the outside air pCO₂).

The carbon isotope ratio of water CO₂ (δ¹³C of DIC) varied from -11.8‰ to -5.7‰. It was found that water collected from small pool splashed with water dropped directly from ceiling and muddy pool have lower δ¹³C of DIC than large cave pool water and underground flow water. In general, water contacted recently with soil and epikarst appears to have higher alkalinity and lower δ¹³C of DIC than water experienced more contact with atmosphere (Fig. 3b).

Fig. 3. Crossplots of (a) Ca vs HCO₃ and (b) δ¹³C of DIC vs log(pCO₂) water in water collected from different water bodies (pool, river), in different caves (Tien Son (TS), Thien Duong (TD), Phong Nha (PN)), and in different seasons (summer (sum.), spring (spr.)).

Our Raman spectroscopical analyses were performed on (1) host rock to confirm that the material is dominantly calcite and (2) grains collected in the internal cave sands to show quartz (SiO₂), anatase (TiO₂), florencite (CeAl₃(PO₄)₂(OH)₆) and tumchaite (Na₂(Zr,Sn)Si₄O₁₁·2(H₂O)) which are minerals typically formed by hydrothermal alteration of dolomite-calcite rocks. Such mineralizations are more frequently

Table 3. Cave water quality (N is number of samples) CP: Cave pool water, SR: Stream and river water.

Parameter	Sample type	pH			Alkalinity (mmol L ⁻¹)			Hardness (mmol L ⁻¹)			SI _{CaCO3}			pCO _{2,water} (ppmv)			δ ¹³ C _{DIC} (‰)		
		TS	TD	PN	TS	TD	PN	TS	TD	PN	TS	TD	PN	TS	TD	PN	TS	TD	PN
Cave	N	9	3	9	9	3	9	9	3	9	9	3	9	9	3	9	3	1	1
	Min	7.9	7.9	7.8	0.2	1.0	2.3	1.1	1.5	1.1	0.4	0.2	0.5	86	313	190	275	-11.8	
	Mean	8.0	8.0	8.2	1.9	1.2	3.0	2.4	0.9	1.7	1.0	0.4	1.0	516	331	635	607	-9.1	-10.2
	Max	8.1	8.0	8.6	2.7	1.3	3.4	3.4	1.4	1.9	1.6	0.7	1.2	767	344	1,100	781	-5.7	-6.0
Spring	N	4	4	6	4	4	6	4	4	6	4	4	6	4	4	6	4	3	3
	Min	7.9	8.1	7.9	2.6	1.6	2.5	2.4	1.3	0.8	1.1	0.6	0.5	668	138	273	204	-10.8	-11.1
	Mean	8.0	8.3	8.1	3.6	2.5	3.2	2.5	1.5	1.0	1.3	0.7	0.9	936	538	810	611	-8.7	-9.9
	Max	8.0	8.6	8.4	4.0	2.9	3.6	2.6	2.0	1.5	1.4	1.0	1.0	1,090	644	986	699	-6.2	-9.3

observed in ancient limestones and dolostones. Carbon isotopic analysis of limestone host rocks shows a narrow range in δ¹³C compositions; between 0.52 and 0.72‰. All results are in good agreement with the regional limestone characteristics formed during the Palaeozoic era (Shao et al., 2000).

Cave atmosphere conditions (T°C, humidity, wind speed, CO₂, and δ¹³C of CO₂)

In all surveys spanning from early spring (March) to late summer (August), temperature inside the caves was always lower than outside atmospheric temperature (Fig. 4T). Only in March 2016 cave air temperature was approximately close to the night time temperature of outside air (around 20°C) monitored at station Dong Hoi (17°28'28"N, 106°36'15"E), the closest meteorological station in the area. In the Phong Nha Cave where entrance is as large as the interior gallery and in the same elevation with cave floor, temperature was more resemble with the outside temperature than in other caves (21°C in spring and 25 - 56°C in summer). Temperature deep inside Tien Son, the single-entrance, and dry cave and Thien Duong, a multiple-entrance cave with high above ground entrances, did not fluctuate much between different surveys (20 - 22°C), attesting the thermic stability of cave atmosphere.

Depending on the entrance size, relative humidity could slightly fluctuate/oscillate near the entrance, but it was always stable and close to the saturation level deep inside the caves (Fig. 4H). Averagely, RH deep inside the caves was lowest in Tien Son – the dry cave (94%) and highest in Thien Duong – a wet cave (99%). Still, these values are much higher than outside value (66%). Seasonally, the cave air RH was higher in the summer surveys than in the spring surveys. Spatially, from entrance to the interior, RH varied more gradually in spring than in summer, implying a better exchange of RH between cave interior and outside atmosphere. It is interesting to note that water, abundant in wet caves, could add more humid to cave air when RH drops far below saturation level. Without underground flow to buffer humidity, a dry cave would probably have lower and more abrupt humidity profile than a wet cave when air circulation with exterior is strong.

Wind speed pattern detected in the single entrance cave was different from the one found in the multiple entrance caves (Fig. 4W). It should be stated that entrance is considered as size compatible to the cave interior to guarantee that air could flow under the difference of pressure. Small cracks of few cm² in size and penetrating through a host rock layer of 10s m in thickness are not considered as entrances of a cave of hundreds m² in cross-section and thousands m in length. Thus, it is clear that the air circulation in Thien Duong and Phong Nha was detectable and fairly steady all over the show sections thanks to the large and multi-entrance and the underground river. On the other hand, in Tien Son (a single-entrance cave with no underground flow) air circulation in the inner section was not detectable in all surveys (Fig. 4bW). In Thien Duong and Phong Nha, it is also important to note that, air flow detected in spring is generally

Fig. 4. The cave microclimate in 5 surveys (Aug. 2014, Apr. 2015, Aug. 2015, Mar. 2016, Aug. 2016), (a) Phong Nha Cave, (b) Tien Son Cave, and (c) Thien Duong Cave.

stronger than in summer. We particularly observed during our surveys that in Thien Duong Cave, wind blew steadily from tourism operation entrance into the cave and in Phong Nha, the wind direction was mainly from inside to outside.

The cave air CO₂ concentrations are generally higher than background atmospheric value (Fig. 4P). Cave air CO₂ exhibits a seasonal difference in all caves. High CO₂ concentrations occurred during the warm summer periods, and low concentrations were found in spring time. Especially in Tien Son, the single-entrance one, CO₂ accumulated in the deepest section (Fig. 1h), reaching closely to 1%. In detail, CO₂ concentration in the innermost gallery ranged from 570 in spring (March 2016) up to 8,000 ppmv in summer (August 2016). Carbon dioxide was also highest in Tien Son among the surveyed caves. For the same times, in Thien Duong Cave, it ranged from 470 to 1,190 ppmv. Atmospheric CO₂ measured at 0.5 m above the open ground outside the caves were 360 and 630 ppmv, respectively. Soil air CO₂ taken in April-May 2015 and March 2016 campaigns provided a value of 3,400 and 1,600 ppmv, respectively. In addition, CO₂ detected in non-show section of Thien Duong is shown in Fig. 5. Generally, values found in non-show section are relatively lower than in show section.

Fig. 5. Spatial variation of cave air CO₂ in Thien Duong Cave shows that CO₂ tends to increase in show section than in non-show section (gray area shows visiting section).

Based on the data of temperature, RH, and cave air CO₂ content, we have averagely estimated the virtual temperature (Tv) of cave air and compared it to the exterior air one. Formulation of the virtual temperature calculation is well represented in Sánchez-Cañete et al. (2013). At T°C = 20°C, RH = 98%, and pCO₂ in the range of 0.2 – 1%, Tv in cave is about 1.2 – 2.2°C higher than the measured temperature. For outside air (T°C = 25 – 30°C, RH = 66% and pCO₂ = 400 ppmv), the difference is between 2.4 and 3.4°C. Taking into account the fact that in all our surveys, the measured outside temperature was always higher than inside one, the difference of outside-inside Tv would not change the sign. In general, the air composition of the studied caves barely has any influence on the air density and that is logic since the caves are highly ventilated and, consequently, the CO₂ concentrations and RH are close

to background atmosphere. The air density differences are mainly controlled by temperature.

Analytical results of $\delta^{13}\text{C}$ from the 2 spring surveys are shown in Fig. 4D. In general, from outside into the cave, $\delta^{13}\text{C}$ decreased gradually; from -11‰ near entrance to -26‰ in lower and deeper sections. Excluding the soil air samples, the isotope fraction in cave air was more widespread and lower during the 2015 survey (between -25.7 and -15.2‰) than during the 2016 one (between -14.3 and -11.4‰). Comparison among the caves shows that Tien Son Cave has the largest range of $\delta^{13}\text{C}$ value and Phong Nha has the smallest range of $\delta^{13}\text{C}$. It is interesting to note that during the April-May 2015 survey, the isotope fraction in the innermost section of Tien Son Cave was -25.7‰, which is lower than soil air value picked up during the 2016 survey (-21‰ and -22‰). The carbon isotope fraction in open air outside the caves, less than 1 m above ground, varied from -18.7 to -10.8‰. More importantly, there was an anti-correlation between the CO₂ content and $\delta^{13}\text{C}$ of CO₂. Correlation coefficient between $\delta^{13}\text{C}$ of CO₂ and the inversed CO₂ was ≥ 0.99 for all subsets of samples (samples of the same cave and the same survey) (Table 4).

Keeling plot and $\delta^{13}\text{C}$ of CO₂ in soil and atmosphere

The CO₂ concentration in cave air results from the mixing of background atmospheric CO₂ with CO₂ produced from soil, water, cave biota, and possibly human. The mixing processes (advection and diffusion) between 2 (or more) end-members can be interpreted with the use of Keeling plot method (Pataki et al., 2003). Table 4 represents y-intercept value of Keeling plot for outside air and each cave of different campaigns ranging from -23.7 to -29.1‰. Keeling plot drawn from the 2 survey results shows 2 distinctive patterns. In the April-May 2015 survey, regression lines (both slope and intercept) of cave air samples were quite close to one another and to the outside air (Fig. 6). Especially, intercept of Thien Duong is more negative than outside air (Table 4). In the March 2016 survey, on the other hand, there are discrepancies of slope and intercept of samples collected from different caves and all intercept values are higher than the outside air one. The highest intercept value is for air in Tien Son (Table 4).

In order to estimate the $\delta^{13}\text{C}$ of CO₂ of the soil and atmosphere end members, we rely on Keeling plot of the outside air samples. As shown in Fig. 6, our air samples collected outside of the caves, within 50 cm above the ground and completely under the forest canopy, possessed varying values in both concentration and isotope fraction. Theoretically, compared with the cave air samples, those outside air samples are expectedly less affected by diffusion process as well as very unlikely contain human breath CO₂. Linear regression for those outside air samples illustrates an advective mixing of 2 end members; soil production flux and atmospheric air. In fact, a very high correlation coefficient ($R^2=1.00$, Table 4) found between CO₂ content and its $\delta^{13}\text{C}$ value supports for this 2 end member advective mixing claim. There is no other source (another end member) or process (e.g.,

diffusion) involved in this outside air CO₂ isotopic – content variation. The $1/\text{CO}_2$ value for ‘pure’ CO₂ is 10^{-6} but this value is so small that for practical purposes we can regard the point as lying on the X-axis itself, where $1/\text{CO}_2 = 0$ (Mattey et al., 2016). Thus, extrapolation down to the X-axis (intercept) gives the $\delta^{13}\text{C}$ of CO₂ of the soil end member. The regressed intercept of -28.6 (Table 4) implies that the C3 type plants dominate the region (Vogel, 1993). To the upper end, considering that atmospheric CO₂ content is 400 ppmv, the $\delta^{13}\text{C}$ of the atmospheric CO₂ calculated from this regression equation is -7.7‰, well agreed with data recorded at 2 NOAA’s meteorological observatory stations (Mauna Loa Observatory and Christmas Island) (NOAA, 2017) located in Pacific Ocean at 20°N and 2°N latitudes (noted that PNKB is at 17°N).

Fig. 6. Keeling plots of $1/\text{CO}_2$ versus $\delta^{13}\text{C}$ for outside air (Out.), and cave air in Phong Nha (PN), Thien Duong (TD), and Tien Son (TS). Numbers 15 and 16 denote the April-May 2015 and March 2016 surveys, respectively. Assuming soil air (atmosphere air) has $p\text{CO}_2 = 13,500$ ppmv (400 ppmv), the % distribution of atmosphere-soil CO₂ along the advective mixing line (solid black line) is roughly constructed. Broken curved black arrows start at mixtures of atmospheric air with soil production flux (the composition of the overall flux of CO₂ from roots and soil organic matter into the soil gas), labeled as % of pure additional CO₂ and show the effects of Rayleigh fractionation with a kinetic fractionation of 4.4‰ due to upwards diffusion of CO₂ to open atmosphere (Camarda et al., 2007).

Diurnal oscillation of cave air conditions (T°C, RH, and CO₂)

In general, the monitoring results represent a diurnal oscillation of CO₂ and temperature and a saturated humidity in the show caves. For all results, CO₂ increased from morning, around 7 A.M. which is also the time caves are open for visit, reached maximum level around 3 P.M. and then gradually decreased to the minimum level at around 3 A.M (Fig. 7a). Margin of difference between day and night of CO₂ is 100 – 400 ppmv in Thien Duong and 100 – 150 ppmv in Tien Son. Interestingly, comparing between

the show caves and the non-show cave, CO₂ was higher during daytime than during nighttime in the formers but inversely higher during nighttime than during daytime in the latter.

Diurnal variation of temperature in the innermost section of Tien Son Cave was about 0.1 – 0.2°C (Fig. 7b). Interestingly, contradict to the outside atmosphere, temperature appeared to be a bit higher during night time than in day time. In a single entrance cave like Tien Son, some study has concluded that cave air temperature has a lag time to outside temperature (Fairchild & Baker, 2012). It should be stated that the monitoring was conducted in March, a period having nocturnal temperature close to cave air temperature. In Thien Duong, the multi-entrance cave, temperature was more oscillating than in Tien Son (about 0.4°C) and, different from Tien Son, low and high values were found in night and day times, respectively (Fig. 7b). Compared to outside atmosphere where temperature between night and day was from 7 to 10°C difference (Fig. 2), the diurnal temperature oscillation in both caves was much smaller. More importantly, the outside minus inside temperature was always positive, implying a higher cave air density than outside atmosphere. Between the single-entrance and multiple-entrance caves, the daily variation imprints more in the latter than the former one. Temperature in the non-show cave oscillated approximately 1°C between day (high) and night (low) which is more than in the show caves. Such stronger oscillation could be interpreted as stronger exchange between cave air and exterior atmosphere where daily temperature fluctuation was about 5 to 10°C between night and day. This non-show multiple-entrance cave is characterized with 2 large entrances at 2 end of the 200 m cave length (Fig. 1j).

There is not much to discuss about humidity in the show caves since all monitoring logs show a constantly saturated humidity (Fig. 7c). Only in Hang Chuot, RH showed a diurnal pattern - low (high) during the day (night) time, mimicking the external atmospheric condition (Fig. 7c). We suspect that the constantly saturated RH could be due to equipment problem that some RH sensor when deployed to very high humidity medium may drift and loss of measurement accuracy. Comparison with the spot air sampling data, we conclude that at RH above 95% like in deep sections of the show caves, RH sensor in our monitoring equipment did not work very well.

DISCUSSION

Ventilation in the studied caves

Historically, caves were classified into two groups according to their ventilation: (i) static caves (single-

Table 4. Keeling plots in different caves.

Date	Outside		Thien Duong		Tien Son		Phong Nha	
	Intercept	R ²	Intercept	R ²	Intercept	R ²	Intercept	R ²
Apr.-May 2015	-28.6	1.00	-29.1	1.00	-28.3	0.99	-27.1	0.99
Mar. 2016			-25.3	0.99	-23.7	1.00	-26.5	0.99

Fig. 7. Continuous monitoring of (a) cave air CO₂, (b) temperature, and (c) humidity (RH) in Tien Son Cave on 6-7th August 2015 (max – min outside T.: 33 – 26°C), Thien Duong Cave on 15-16th March 2016 (max – min outside T.: 28-20°C), and Hang Chuot Cave on 9-10th August 2016 (max – min outside T.: 34-29°C).

entrance caves); and (ii) dynamic caves (multiple-entrance caves) (Bögli, 1978). Understanding the sorted caves as models of thermally induced airflows may help estimate air flow between exterior and interior. The dynamic cave model (system with two and more entrances at different altitudes) ventilates during the whole season by a so-called chimney effect. The airflows are zero only at $T_{\text{ext}} = T_{\text{cave}}$ (where T_{ext} is external air temperature and T_{cave} is cave air temperature [°]). Based on the signs of differences $T_{\text{ext}} - T_{\text{cave}} > 0$ or $T_{\text{ext}} - T_{\text{cave}} < 0$, cave air flows from the upper entrance towards the lower entrance or vice versa. In contrast, the static cave model ventilates predominantly during one season when either $T_{\text{ext}} < T_{\text{cave}}$ or $T_{\text{ext}} > T_{\text{cave}}$, depending on whether the cave space is located below the entrance (cold air trap) or above the entrance (warm air trap), respectively (Vieten et al., 2016b and citations within).

Essentially, it could be concluded from monitoring results that the mechanics of air circulation in the single-entrance cave (Tien Son) is different from the one in the multiple-entrance caves (Thien Duong and Phong Nha). In the single cave, air circulation depends on the air-density difference between cave air and exterior, similar to the static cave model mentioned in Faimon et al. (2012). In multiple-entrance cave, ventilation is a function of the differences in air density (and hence pressure) inside and outside the cave, agreeing to the U-shape model described in Faimon and Lang (2013).

Cold air trap model in the single-entrance cave

In detail, the Tien Son cave's entrance is high above the first chamber cave floor and the cave floor elevation drops steadily from the entrance to a 26.6 m lower level near the end of the 500 m show section (Fig. 1d). With that geometry and as demonstrated by monitoring results, cave air ventilation is comparatively in accordance with the cold air trap type circulation introduced in Faimon et al. (2012) in which air flows between the cave interior and the external atmosphere are controlled by the air-density gradient, determined by temperature changes between the interior and the exterior. During winter time when outside temperature is lower than cave air temperature, exterior air density is denser than interior one, convection takes place to drive hot and less dense air out of the cave which is replaced by cold and denser outside air. During summer time, air inside the caves maintains a lower temperature and higher density than exterior, this cold air mass is practically trapped inside the cave. Advective flow is diminished. The cold air trap model applied to the single-entrance Tien Son Cave leads to a vision that time for warm cave air blowing out of the cave (cave air is warmer than outside) was shorter than time for fresh cave air escaping to the atmosphere (cave air is fresher than outside). This vision is likely true since (1) in our visits spanning from March to August, cave air temperature was always higher than outside one and (2) September is as hot as July-August in the area (Fig. 2). Thus, the cold air period in caves should be from March (or earlier) to sometime after August. It

is well agreed with remark from local people that air inside the cave is usually fresher than outside.

U-shape model in the multiple-entrance caves

According to the U-shape model, a multiple-entrance cave like Thien Duong and Phong Nha can be simplified as a system of multiple columns connecting to each other at the lowest point of the cave. Each column is measured from the entrance to the lowest point of the cave (or water level in wet cave like Phong Nha). The airflow driving forces, i.e., pressure differences, result from the differences in weights of the individual columns in the system.

During summer when atmospheric temperature is high, air mass in the cave has higher density creating higher pressure at the same levels than atmosphere and the pressure difference causes air flow from column with the highest pressure to the lower one, and then out to atmosphere. During winter, conversely, the air mass in the cave has lower pressure than atmosphere and the air flow is from the lowest pressure column to the higher one, and subsequently out to the atmosphere. According to Faimon & Lang (2013), airflows are weaker in the summer season in comparison with ones in the winter season under the same driving forces and that cold air tends to be conserved in the cave. In other words, a multiple entrance cave ventilates more intensively in cold seasons in comparison with ventilation in warm seasons. It is consistent with our observation that air circulation in the early spring survey (March 2016) was, in general, stronger than the summer campaigns in Phong Nha and Thien Duong Caves (Fig. 4W). The explanation for such air circulation intensity seasonality is that, as quoted from Faimon & Lang (2013), during winter, external cold air entering the cave by the lower entrance cools the air of shorter column and increases the weight of already heavier shorter column at this moment. This process creates positive feedback between external temperature and the driving force, which amplifies the differences between lower column and higher column weights and, consecutively, increase cave airflow. During summer, warm and light external air penetrating the cave from the upper entrance lightens the heavier longer column at this moment to create negative feedback between the external temperature and the airflow driving forces, which decreases the cave airflows. In our study, we found (1) a steady flow from upper entrance to the lower entrance and a constantly lower than outside temperature inside the caves during summer and (2) a stagnation of air circulation and a close to outside temperature inside the caves during spring. Those features are fully depicted in Faimon & Lang (2013).

Either U-shape or cold air trap mode, ventilation should be stronger in winter/colder time and that makes the cold period longer than the hot period inside the caves. Some caves in US, Spain, and Japan were reported to experience fastest ventilation in winter (Wilkening & Watkins, 1976, Fernández et al., 1986, Tanahara et al., 1997, Buecher, 1999, Dueñas et al., 1999, and Banner et al., 2007). As

a consequence, it is possible that caves need less time to release all heat they accumulate during hot weather into cold atmosphere outside than time to absorb heat. The phenomenon can be transmitted into the cave air temperature oscillation as the period/season of cave air colder than outside atmosphere is longer than the season of cave air hotter than outside atmosphere. That is in agreement with our observation in PNKB since the caves were cold not only in summer and autumn season but also in spring time. Carbon dioxide would mutually decrease to near atmospheric level during the cave exhaling period and then accumulate again during the stagnation time

Signature of different CO₂ sources with the use of the $\delta^{13}\text{C}$ – CO₂ relationship

It should be restated that the twice per year surveys conducted in this preliminary study could interpret the CO₂ pattern if this pattern is dominantly annually fluctuated. On the other hand, there could be a misinterpretation if higher frequency factor(s) (e.g., rainy events) dominates the cave CO₂ variation. As shown in Fig. 4, 6, and 8, cave air CO₂ exhibits a seasonal difference in all caves, similar to cave studies in Spain (Fernández-Cortés et al., 2009), USA (Banner et al., 2007), Austria (Spötl et al., 2005), Ireland (Baldini et al., 2008), Poland (Przylibski, 1999), and Japan (Tanahara et al., 1997), among others. Compared to other studies elsewhere in temperate or less humid regions, the diurnal oscillation margins of CO₂ as well as T°C and RH recorded inside the show caves (Fig. 7) are either similar (Breitenbach et al., 2015) or smaller (Baldini et al., 2008; Kowalczyk & Froelich, 2010; Garcia-Anton et al., 2013). Theoretically, CO₂ input into a show cave includes (1) natural contributions associated with direct input from soils/epikarst and vadose ground, microbial decay of organic matter in cave sediments, endogenous such as volcanism or magmatism, cave water degassing, respiration of animals living in the caves, and (2) anthropogenic contribution stemming from visitor exhaling. Based on our observations, variation in the cave air CO₂ concentrations in PNKB is balanced between the contributions from soil/epikarst, cave water, and visitor exhaling and the exterior atmosphere. The only exception is perhaps the dry cave where water plays a minor role. In this sub-section, the significance and variability of the 4 sources contributing to the cave CO₂ mass balance are discussed.

Atmospheric input

To better assess the mixing process existing inside a cave, stable carbon isotopes appear to be a useful variable. An increasing number of authors use the Keeling plot to express cave air as a mix between several end-members, mostly between external atmosphere with low CO₂ and an higher $\delta^{13}\text{C}$ of CO₂ value as opposed to a “light end-member” with high CO₂ and a low $\delta^{13}\text{C}$ of CO₂ value (Spötl et al., 2005; Kowalczyk & Froelich, 2010; Matthey et al., 2010; Frisia et al., 2011; Riechelmann et al., 2011; Tremaine et al., 2011). The light end-member

source should be located close to the roots of C3 type vegetation, which is the most common type growing in a tropical evergreen forest region (Pataki et al., 2003). Close to the vegetation roots, CO₂ is low in ¹³C isotope with $\delta^{13}\text{C}$ of CO₂ ranging from -30 to -24‰ (Vogel, 1993). Due to a different diffusion coefficient for ¹²C and ¹³C, soil air $\delta^{13}\text{C}$ near the earth surface could be increased by about 4 to 5‰ (Dorr & Munich, 1986; Cerling et al., 1991; Davidson, 1995) compared to root respired and decomposed CO₂. As highlighted in the result section, the $\delta^{13}\text{C}$ range in our soil air samples (-26 and -21‰) and the extrapolated soil end member (-28.6‰) (Table 4, and Fig. 6) confirm the dominance of the C3 type plants in PNKB.

Keeling plot shows clearly that air circulation is strong in multiple-entrance caves to smooth CO₂ level all over the cave passage. Data points obtained from each sampling campaign are graphically congregated (Fig. 6). The most homogenous cave is Phong Nha where cave entrance is huge and at the same elevation with active underground river flow. In the single-entrance cave, Tien Son, CO₂ near the entrance is different from the innermost section, indicating a weaker air circulation there. The plot also shows that atmospheric composition of cave air CO₂ ranges between 60 and 99%, mostly in the range of 95 and 99% (Fig. 6). That reflects well a conclusion presented in the precedent sections that all studied caves are well ventilated. Even in the innermost section of Tien Son Cave (the most confined sites among our sampling sites), the atmosphere fraction was generally higher than 95%. Other CO₂ sources in this dry cave are emitted from soil/epikarst and exhaled from visitors. They are discussed in next sub-sections.

Between 2 surveys, the ranges of CO₂ and of its $\delta^{13}\text{C}$ indicate that atmospheric fraction in cave air during March was higher than during April-May. The isotope fraction (CO₂ level) was more positive (less concentrated) during March than during April-May. Such decrease of atmospheric air fraction in cave air toward summer time reflects a limit in cave air circulation during summer. This reflection is in line with our precedent discussion on the mode of air ventilation in the caves.

Cave water degassing

As shown in the result section (Fig. 3), there is a strong variation of water quality and CO₂ content and that is not surprising because water in caves of PNKB stemmed from different sources such as rainwater directly drop through cracks on ceiling and sinkholes, river water (underground flow), or drip water seeping through surface soil and epikarst. When inside the caves, they were found in both mobile and still states. Some (cave pools and rimestones) has high retention and some (underground flow) just quickly moves through. Since cave waters stem from different sources (e.g., rain or river) and experience different flow paths (e.g., through soil, epikarst, or river), their properties (e.g., total alkalinity and $\delta^{13}\text{C}$ of CO₂) were different. For instance, the hardness-alkalinity trends in Fig. 3a indicate that while most water samples

have infiltrated through or a longtime in contact with limestone (relative equality between alkalinity and hardness), 5 samples have their chemical compositions stemmed from different sources. Noticeably, these different chemical composition samples were picked up in rainy season. Different water sources may also explain for a lower than outside air pCO₂ of water pCO₂ in some cave pools. Further studies focusing on the regional hydrology and groundwater chemistry are still needed to identify and confirm the water sources in those cave pools.

Since we did not actually sample drip water, in this sub-section, we only discuss the CO₂ exchange between large water bodies (cave pools and underground streams) and cave atmosphere. More importantly, we consider that in large and well ventilated caves like in PNKB, the role of still water masses (e.g., cave pools or dripping) sporadically distributed inside dry cave cannot play a major role in mediating cave air CO₂. Only stream/river running through the wet caves would be a significant source of buffering cave air CO₂.

Cave water CO₂ degassing rates are essentially dependent upon how larger water pCO₂ than cave air pCO₂ is. Large pCO₂ difference between cave water and cave air will result in faster degassing and higher calcite deposition rates. Commonly, CO₂ is lost from cave water bodies to the gaseous phase (cave air) because the water carries in solution biogenic CO₂ evolved in the soil zone where the concentration is up to two orders of magnitude higher than in the free atmosphere (Dulinski & Rozanski, 1990; Kaufmann, 2003). Apparently, it is not the case in PNKB where large water bodies, collected mostly from wet caves, have the same order of magnitude of cave air CO₂ (Table 3 and Fig. 3, 4). In other words, the cave air CO₂ was more or less in equilibrium with the water CO₂, lessening the aggregate flux of CO₂ from water to cave air. A plausible explanation for this equilibrium is that caves are long, high, and large. Most sampled waters are exposed to the cave atmosphere long enough to get equilibrated with the cave air CO₂. Since water represents in every corner of the wet caves, it can buffer (absorb or degas) large portion of CO₂ and, indeed, we observed no sharp change of CO₂ in both cave water and cave air.

Theoretically, the degassing reaction increases isotopically heavy carbon dioxide in DIC and releases isotopically light carbon dioxide to the cave air (Frisia et al., 2011). The CO₂ degassing can be evaluated from the stable carbon isotope difference in total inorganic carbon ($\delta^{13}\text{C}$ of DIC) between undegassed water entering the cave and water that has equilibrated with cave air. Indeed, as commented in the result section, we found that relatively old water (large cave pools and streams) has heavier $\delta^{13}\text{C}$ of DIC than water in small cave pools actively receiving drip water (shorter time exposing to the cave atmosphere) (Fig. 3b).

As a whole, based on the CO₂ distribution, unsaturated RH, and $\delta^{13}\text{C}$ of DIC between old and new cave waters, it is possible that the water-air CO₂

exchange might take place previously and the cave air CO₂ in wet caves had a fraction derived from water.

Soil and epikarst CO₂ input

There are 3 main mechanics defining the soil air CO₂ input in cave; (1) the CO₂ production in soil and epikarst, (2) the air transport in soil column, and (3) the permeability of surface soil. To assess the soil CO₂ emission strength, we looked into the impact of temperature and rainfall on the CO₂ production and transport in soil and epikarst. In tropical climate, three mechanisms (Mec.) are in turn dependent on temperature and rainfall.

Mec. 1: Soil CO₂ production is derived from respiration of both autotrophs and heterotrophs. A wide consensus exists that soil biota respiration is controlled by temperature and moisture (see Davidson et al., 1998; or Fang & Moncrieff, 2001 and references therein). Usually, soil CO₂ production reaches the lowest value in late winter and the highest value in summer (Frisia et al., 2011). The process is also lower when soil is dry than when soil is wet (Serrano-Ortiz et al., 2010). Soil moisture supports heterotrophic respiration and enhances CO₂ production as long as soil is not saturated with water (Moyano et al., 2013).

Mec. 2: Gas transport in soil occurs by both advection and diffusion. Because diffusion is much slower than advection, the CO₂ emission from soil/epikarst to cave air should be strong when advection dominates and weak when diffusion prevails. Temperature changes cause advective movements of gas in or out of the soil (Mattey et al., 2016). While advection is a bi-directional process, it does not cause fractionation of the soil CO₂. The other principal transport process is diffusion and this always acts to transports CO₂ from high to low concentration and causes the CO₂ in the pore space to have more positive $\delta^{13}\text{C}$. Fractionation by diffusion ensures that the CO₂ in the pore space is always increased in $\delta^{13}\text{C}$ relative to the respiration fluxes from decomposition and root respiration (Cerling, 1984). The kinetic fractionation during diffusion of CO₂ from depth to the soil surface is likely to vary depending on the relative contributions of diffusion and advective movement of gas to the overall flux of CO₂ from the soil (Camarda et al., 2007). In the Keeling plot, the relative contribution of diffusion over advection is shown as the deviation of sample points from mixing line of autogenic soil gas and atmospheric value toward higher $\delta^{13}\text{C}$. Linear regression of the CO₂ data experienced from diffusive movement would result in a higher (more positive) intercept value than the one dominated by advection (Mattey et al., 2016).

Mec. 3: In monsoon climate, particularly in coastal region like PNKB, rainfall is another factor that should be taken into account. Indeed, there was a theory that during and after rain, the pores and fissures near the surface that connect to the external atmosphere are blocked by the more abundant water. Carbon dioxide produced from humification and mineralization is trapped and concentrated in soil and epikarst. As the pores and fissures that connect to the cave wall are less wet than surface soil, the blocked CO₂ will go to cave air instead of to atmosphere (Serrano-Ortiz et al., 2010).

Looking at the CO_2 and $\delta^{13}\text{C}$ of exterior air shown in Fig. 4P and 4D, we conclude that during summer time (August), the CO_2 flux emitted from soil surface, in general, is stronger than during spring time (March, April-May). An explanation could be that high temperature increases degradation of OM and respiration of organisms (Mec. 1) and advection dominates in soil column (Mec. 2).

Keeling plot (Fig. 6) shows a more deviation of data points from mixing line in March 2016 than in April-May 2015 for all 3 caves. Based on the Mec 2, one can easily interpret that in March, temperature in soil and epikarst does not vary much. Advection is weak, leaving diffusion as the main process of soil air CO_2 movement. Shown in Keeling plot, the March data are deviated from the mixing line. In April-May, summer starts, temperature in soil column varies, and advection prevails. Regression of the April-May data provides a similar slope and intercept as the outside air data. Generalization of this diffusion-advection competition is that soil air transport is weak in spring time and strong in summer time.

Based on the diurnal variation (Fig. 7), the isotopic- CO_2 values in soil air samples (Fig. 6), as well as spatial variation of cave air CO_2 especially in deeper section of the single entrance cave (Fig. 4bP), we estimate that soil air CO_2 level near the surface fluctuates seasonally, from 10^3 s in cold season to 10^4 s in hot season. In detail, in deeper section of Tien Son Cave, diurnal monitoring and point survey show CO_2 level up to nearly 10^4 ppmv (Fig. 4bP, 6). The soil air CO_2 in soil and epikarst is expected to be concentrated more than that. In fact, stable isotope data proves that the maximum soil air CO_2 content is around 10^4 ppmv. Matthey et al. (2016) reviewed that in the C3 type plant domination region, the endogenous soil gas is produced with a $\delta^{13}\text{C}$ of -28 to -26‰. If we assume that this range is also valid in PNKB, the corresponding soil air CO_2 content calculated by using the outside air regression equation (the 2 end member advective dominated mixing model) is 3,200 - 13,500 ppmv. Considering the maximum value of 13,500 ppmv, this value is reasonably about 50% higher than the maximum value detected in inner section of Tien Son in summer (Fig. 4bP). Thus, the 10^4 s ppmv is a plausible value that we would find in soil in PNKB in summer time. At the other end, in spring (March precisely), direct analysis of soil air CO_2 reveals a range of 1,500 - 3,000 ppmv (Fig. 6), even lower than the cave air CO_2 inside single entrance cave in August (Fig. 4bP). We go further to suspect that, not only in spring but also in winter, soil air CO_2 near the earth surface would not be as high as in summer. The reasons are (1) microbial activities diminish in low temperature and dry condition (Mec. 1) and (2) strong air circulation in caves (discussed in precedent sub-section) would evade soil air CO_2 reaching to the soil-air interface faster in winter than in summer. Thus, the soil air CO_2 reaches the minimum level at some time in winter-spring, probably around 10^3 ppmv. In fact, our estimated range conforms to numerous direct

measurements in karst soils elsewhere (between 10^3 and 10^4 ppmv) (Bourges et al., 2001; Spötl et al., 2005; Matthey et al., 2016).

Mec. 3 is proper to decode the positive correlation between rainfall and cave air CO_2 in the deepest part of the single entrance cave (Fig. 8). In fact, innermost section of Tien Son is, among other caves and sections, most stable in term of temperature, air pressure, and air circulation (calmest). Tien Son is also the least visited among the show caves. The effect of rainfall to the cave air CO_2 level would, therefore, be more easily assessed with the use of data collected in this section than in other caves/sections.

Fig. 8. Cave air CO_2 in the innermost section of Tien Son Cave, showing a correlation with weekly rainfall (or soil humidity) prior to the survey dates. Weekly rainfall data were selected based on the thickness of overburden layer, the cave size, and the karst limestone filtration rate (Shevnin et al., 2006).

Combination of all discussion about the soil air CO_2 seasonality, we draw a picture that the soil air CO_2 flux to the cave air during rainy summer is highest among seasons.

Human exhaling

Basically, since the caves are large and well ventilated, it is not easy to assess impact of human (respiration) on the cave air CO_2 . Still, our limited data show (1) diurnally, CO_2 increased during the visiting hours (Fig. 7a), (2) spatially, CO_2 was more concentrated in show section than in non-show section (Fig. 5), and (3) isotopically, there was a depleted tendency of $\delta^{13}\text{C}$ of cave air CO_2 during holidays when visitation is excessive (Zing, 2015) as compare to outside air where human impact is trivial (Fig. 6).

About the first sign of temporal/diurnal CO_2 oscillation, not only CO_2 was higher during visiting hours (day time) than non-visiting hours (night time) in the show caves, there was also a contrasting pattern of CO_2 in non-show/reference cave (Fig. 7a) – lower CO_2 during day time than during night time. Probably, the CO_2 pattern in the non-show cave inherits the outside atmospheric CO_2 oscillation that the CO_2 decrease during the day was due to photosynthesis in the jungle outside of the cave. Of course, a natural phenomenon such as a less dense air concentrated with CO_2 rising from the lower section of the cave to the monitoring

point could be the sole reason for this increased CO₂ in the show section during the daytime. Further investigations including annual-basis monitoring and air circulation mapping are necessary to assure whether human have significantly contributed to the CO₂ enrichment in show section during visiting time.

About the second sign, the spot surveys have shown a general trend of higher CO₂ in cave air in show section than in non-show section in Thien Duong (Fig. 5), the only show cave that we have additional monitoring points beyond the show section.

About the third sign, it is all well-known that there is a similarity in carbon isotope ratio between human diet and human exhaled CO₂ and as discussed above human diet in the region would consist mainly of C3 type plants, the vegetation has $\delta^{13}\text{C}$ in the range of -30 to -26‰ (Mattey et al., 2016). Some other study on human breath found a similarity with those of car exhaust-air mixtures, i.e., $-22.3 \pm 0.2\text{‰}$ (Affek & Eiler, 2006). Therefore, a mixture of CO₂ added with human exhaled CO₂ represented in Keeling plot would produce a more negative intercept value than the one not added with human factor. Based on that hypothesis, we compare the samples picked up during high visitation (April-May survey) and the samples least impacted by human (outside air samples) and, as predicted; cave air during high visitation has very negative intercept. Particularly, air in Thien Duong has a more negative intercept than outside air (Fig. 6, Table 4). Among several factors that may lead to the same problem: very negative intercept, human factor appears to be the most realistic reason.

CONCLUSION

The show caves in PNKB are found well connected with the exterior atmosphere thanks to their large or multiple entrances.

Depending on the cave geometry, there are 2 different models of air circulation in the show caves in PNKB; cold air trap model and U-shape model. Either model would increase ventilation during winter when outside temperature is lower than inside the cave.

Stable C isotopes and Keeling plot were used to assess the soil CO₂ emission seasonality, pinpoint human exhaling CO₂, and allocate the soil and atmospheric CO₂ fractions in cave air. In summer, intensified CO₂ production and advective flow domination in soil column generate stronger soil air CO₂ emission than in other seasons.

Seasonality of cave air circulation and soil air CO₂ emission leads to an impression that cave air CO₂ is higher in summer than in winter. In winter-spring time, cave air CO₂ was in the same order of magnitude with the atmospheric level (less than 1,000 ppmv). In summer, CO₂ could reach as high as 10⁴ ppmv in deep section of the single entrance cave after heavy rain.

Human input is detected during our visits which is reflected via both CO₂ content itself and $\delta^{13}\text{C}$ of CO₂. The impact from visitors on cave air CO₂ should be addressed in near future via long term and intensive monitoring and analyses.

Although water presents in many parts of the multiple-entrance and wet caves, it is not easy to assess its role in mediating the cave air CO₂ because of the water quality and origin complexity and the cave air circulation. Nevertheless, as cave air CO₂ is less concentrated and air is more circulated in the multiple-entrance and wet caves than in the single-entrance and dry cave, degassing is expectedly faster which concomitantly results in faster CaCO₃ precipitation (speleothem growth potential) in the former caves than in the latter. In fact, we found that stalagmites in the former caves have faster growth rate than in the latter one (results not shown).

It is hypothesized based on our sparse surveys that intense rainfall could result in a cave air CO₂ enrichment. Still, more frequent cave visits, especially after rain events, should be taken to clarify this rainfall-cave CO₂ relationship.

There is a need to conduct surveys in winter and particularly analysis of $\delta^{13}\text{C}$ of CO₂ to affirmatively assemble ventilation regime of the PNKB's caves. Regrettably, lack of ability to perform stable isotope analysis in Vietnam and difficulty in handling and mailing of air samples to our research partners in UK and Spain led to the fact that only 2 sets of cave air samples taken in spring 2015 and 2016 were analyzed for $\delta^{13}\text{C}$.

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