

# PARTIAL PRESSURES OF CO<sub>2</sub> IN EPIKARSTIC ZONE DEDUCED FROM HYDROGEOCHEMISTRY OF PERMANENT DRIPS, THE MORAVIAN KARST, CZECH REPUBLIC

## DELNI TLAK CO<sub>2</sub> V EPIKRAŠKI CONI, KOT GA RAZKRIVAJO HIDROKEMIČNE RAZISKAVE STALNIH VODNIH CURKOV

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### Abstract

UDC 551.444:550.4(437.32)

*Jiří Faimon, Monika Ličbínská, Petr Zajíček & Ondra Sracek: Partial pressures of CO<sub>2</sub> in epikarstic zone deduced from hydrogeochemistry of permanent drips, the Moravian Karst, Czech Republic*

Permanent drips from straw stalactites of selected caves of the Moravian Karst were studied during one-year period. A hypothetical partial pressure of CO<sub>2</sub> that has participated in limestone dissolution,  $P_{\text{CO}_2(\text{H})} = 10^{-1.53 \pm 0.04}$ , was calculated from the dripwater chemistry. The value significantly exceeds the partial pressures generally measured in relevant shallow karst soils,  $P_{\text{CO}_2(\text{soil})} = 10^{-2.72 \pm 0.02}$ . This finding may have important implications for karst/cave conservation and paleoenvironmental reconstructions.

**Keywords:** cave, carbon dioxide, dripwater, hydrogeochemistry, hypothetical partial pressure, karst processes, karstification model.

### Izveček

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*Jiří Faimon, Monika Ličbínská, Petr Zajíček & Ondra Sracek: Delni tlak CO<sub>2</sub> v epikraški coni, kot ga razkrivajo hidrokemične raziskave stalnih vodnih curkov*

V obdobju enega leta smo analizirali preniklo vodo izpod stalaktitnih cevčic v izbranih jamah Moravskega krasa. Iz analiz sklepamo, da je hipotetični delni tlak CO<sub>2</sub>, pri katerem poteka raztapljanje apnenca  $P_{\text{CO}_2(\text{H})} = 10^{-1.53 \pm 0.04}$ . Ta vrednost znatno presega vrednosti meritev delnega tlaka CO<sub>2</sub> v kraški prsteh  $P_{\text{CO}_2(\text{soil})} = 10^{-2.72 \pm 0.02}$ . Dobljeni rezultati so potencialno pomembni za zaščito jam in krasa ter rekonstrukcijo paleoklime.

**Ključne besede:** jama, ogljikov dioksid, prenikle vode, hidrogeokemija, hipotetični delni tlak, kraški procesi, model zakrasovanja.

## INTRODUCTION

Currently, scientific effort focuses on karst processes for two main reasons: (1) karst systems require better conservation because they are widely impacted by anthropogenic activities (Fernández *et al.* 1986; Dragovich & Grose 1990; Pulido-Bosch *et al.* 1997; Baker & Genty 1998; Hoyos *et al.* 1998; Balák *et al.* 1999; Sánchez-Moral *et al.* 1999; Song *et al.* 2000, Carrasco *et al.* 2002; Faimon

*et al.* 2004b, 2006; Beach *et al.* 2008; Russell & MacLean 2008) and (2) terrestrial speleothems are increasingly used as archives of paleoclimate data (see McDermott 2004, or Fairchild *et al.* 2006, for a review). Basic geochemical interactions in carbonate karst are summarized in box model in Fig. 1. It comprises five elementary processes:

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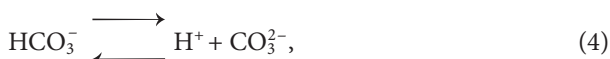
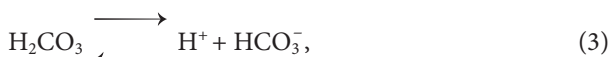
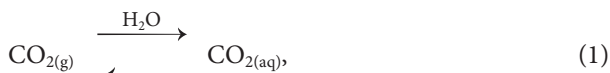
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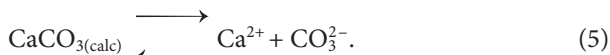
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Received/Prejeto: 14.8.2011



and



Details on the processes (Eq. 1–5) can be found elsewhere (e.g., Plummer & Busenberg 1982; Dreybrodt 1988; Stumm & Morgan 1996). All the processes in solution appear to be at equilibrium due to high rate of hydrolytical/dissociation reactions (Stumm & Morgan 1996, pp. 192–194), even though, the conversion of  $\text{CO}_{2(\text{aq})}$  into aqueous carbonate species could be somewhat slower (Dreybrodt *et al.* 1996, 1997). In contrast, partial disequilibrium is frequently observed at the both AS-boundary (atmosphere–solution boundary) and SC-boundary (solution–calcite boundary) because of relatively slow dissolution/degassing of gaseous  $\text{CO}_2$  and calcite dissolution/precipitation. Disequilibrium extent is quantified by saturation index,  $\text{SI}_{(\text{calc})}$ , in the case of the SC-boundary and by difference between the partial pressure in atmosphere,  $P_{\text{CO}_{2(\text{g})}}$ , and the partial pressure related to the activity of aqueous carbonate species,  $P_{\text{CO}_{2(\text{w})}}$ , in the case of the AS-boundary. Generally, total equilibrium is conditioned by partial equilibria of all elementary processes (Eq. 1–5). This means that all fluxes (depicted by arrows in the Eq. 1–5) must be balanced by relevant counter-fluxes. Total equilibrium can be attained relatively quickly (in days or tens of days) at various levels in a karst profile (soils, epikarst, vadose zone), but it can be disturbed by changing conditions. Changes in solution composition caused by water mixing or change of  $\text{CO}_2$  partial pressure along water flow path are the most important factors. Whereas the problem of water mixing was originally discussed in Bögli (1964, 1980), the issue of  $\text{CO}_2$  partial pressure changes along the flow path of the water is addressed in this article. As a karst profile is not accessible easily, caves represent a cross-section into vadose zone and cave dripwaters carry a record of preceding karst processes. The karst waters entering a cave are mostly saturated at higher  $\text{CO}_2$  partial pressure (typical for karst  $\text{CO}_2$  sources) in comparison with instantaneous partial pressure of  $\text{CO}_2$  in a cave. As a response, dripwater degasses (the process Eq. 1 is running from right to left),  $\text{CO}_{2(\text{aq})}$  activity decreases, and all additional processes (Eq. 2–5) reach a new

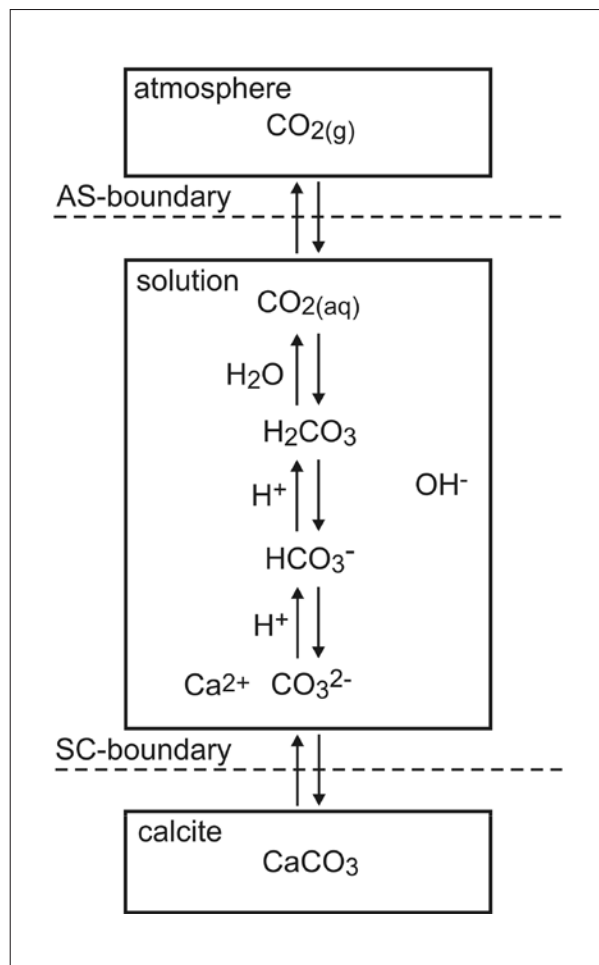


Fig. 1: Box model of basic interactions in carbonate karst.

equilibrium (Holland *et al.* 1964). As a result, pH and  $\text{CO}_3^{2-}$  activity increase and water becomes supersaturated with respect to calcite. Eventually, the excess of calcium and carbonate ions is expelled from the solution as calcite (speleothem growth) (see – e.g., Dreybrodt 1988, for a review). In this article, we demonstrate that there is a possibility to reconstruct the original partial  $\text{CO}_2$  pressure by geochemical modeling. It is believed that biogenic  $\text{CO}_2$  produced in karst soils is a main source of karst  $\text{CO}_2$ . It is derived mainly from (1) autotrophic and (2) heterotrophic respiration (see – Kuzyakov & Larionova 2005; Kuzyakov 2006 – for review). The  $\text{CO}_2$  concentrations show high seasonality with highest values in summer and lower values in autumn/winter (Uchida *et al.* 1997; Moncrieff & Fang 1999; Pilegaard *et al.* 2001; Faimon *et al.* 2004b, 2010, 2012). Little is known about the epikarstic sources of  $\text{CO}_2$ . Up to now, it has rather been matter of hypotheses and speculations (Atkinson 1977; Fairchild *et al.* 2000, 2006; Spötl *et al.* 2005; Faimon *et al.* 2010, 2012). However, the recent results of Benavente *et al.* (2010) who measured up to 6 vol. % of

CO<sub>2</sub> in karst vadose zone indicate that epikarstic CO<sub>2</sub> sources could be significant. The aim of the present work is (1) to specify partial pressure of CO<sub>2</sub> participating in

dripwater chemistry formation, (2) to try distinguishing individual CO<sub>2</sub> sources, and (3) to evaluate the role of seasonal variations.

## RESEARCH SITE AND METHODOLOGY

### SITE CHARACTERIZATION

The Moravian Karst (see – e.g., Absolon 1970; Balák *et al.* 1999; Otava & Balák 2002) is the largest karst area in the Bohemian Massif. It is situated north of Brno (49°13' to 49°25' N, 16°38' to 16°47' E) as a part of the Drahaný Highlands. Altitude varies between 244 m and 613 m; average value is 447.5 m. Karst rocks cover an area of 94 km<sup>2</sup> forming a belt 3–5 km wide and 25 km long. Total rock thickness is estimated to be 500–1,000 m. Besides some Jurassic sandstones/limestones and Cretaceous sediments, the Moravian Karst is formed mainly by Middle and Upper Devonian limestones. They are divided into two formations, the Macocha Fmt. (Vavřinec Lmst., Josefov Lmst., Lažánky Lmst., Vilémovice Lmst.) and the Líšeň Fmt. (Křtiny Lmst., Hády-Říčka Lmst.). The largest cave system is the Amatérská Cave (over 15 km of corridors). At present, four caves are open to the public, the Punkevní Caves, the Sloupsko-Šošůvské Caves, the Kateřinská Cave, and the Balcarka Cave. The whole karst area is geologically very stable and any endogenous carbon dioxide emanations were not reported.

The study was performed in the northern part of the Moravian Karst, in the Punkevní Cave, the Balcarka Cave, and the Amatérská Cave (Fig. 2). The parent limestones (Vilémovice Lmst.) are composed of calcite as a predominant component. Dripwaters are of Ca-HCO<sub>3</sub> type. Overlying vegetation comprises a mix of dispersed deciduous woodland (beech dominates), conifer woodland (spruce dominates), grasses with a thin brown

rendzina soil cover and a part of vegetation is composed of agriculture plants, e.g. wheat, oilseed rape, and mustard plant. Mean annual rainfall in the study area is about 700 mm and mean annual temperature is about 10°C.

### SAMPLING AND ANALYTICS

Totally 88 dripwater samples were studied during one-year-period study (2002–2003). From 11 drips, 4 drip rates were relatively slow (28.1±6.6 ml/hour), 3 drip rates were quick (1070.6±427.4 ml/hour), and 4 drip rates were moderate (194.4±48.4 ml/hour) (the confidence intervals  $\alpha=0.05$ ). The samples of dripwater were collected from speleothems into polyethylene vessels of volume 50–100 ml. Time of sampling varied in the range of tens minutes to two hours. Immediately in the cave environment, pH (WTW pH 330i, WTW pH-electrode SetTix 22), alkalinity (microtitration by 0.05 mol l<sup>-1</sup> HCl (evaluated as a Gran plot, Stumm & Morgan 1996, pp. 179–186, or Appelo & Postma 2005, pp. 183–186), and aqueous calcium (complexometric microtitration by 0.01 mol l<sup>-1</sup> EDTA, 10% KOH, calcein as inner indicator) were determined. The waters were then analyzed in the laboratory for K, Mg, Na (AAS), NH<sub>4</sub><sup>+</sup>, NO<sub>2</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, NO<sub>3</sub><sup>-</sup> (spectrophotometry), SO<sub>4</sub><sup>2-</sup> and Cl (microtitration). The estimated analytical errors were below 5%. Cave CO<sub>2</sub> concentrations were measured in situ by 2-channel IR-detector FT A600-CO2H linked with ALMEMO 2290-4 V5, Ahlborn, Germany (measuring range: 0 to 10,000 ppmv; accuracy: ± 50 ppmv + 2 vol. % of measured value in the range of 0 to 5000 ppmv; resolution: 1 ppmv or 0.0001 vol %). Data on shallow soil CO<sub>2</sub> concentrations were taken from Faimon *et al.* (2010, 2012).

### DATA PROCESSING

The speciation, saturation indices, and hypothetical P<sub>CO<sub>2</sub></sub> values were computed by the PHREEQC code (Parkhurst & Appello 1999). Statistical analysis was performed in the STATISTICA code (StatSoft, Inc., www.statsoft.cz).

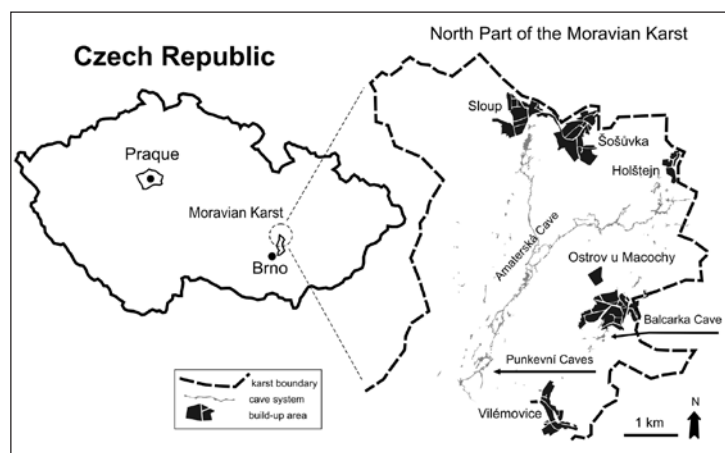


Fig. 2: Sketch map of the Moravian Karst and the caves of interest.

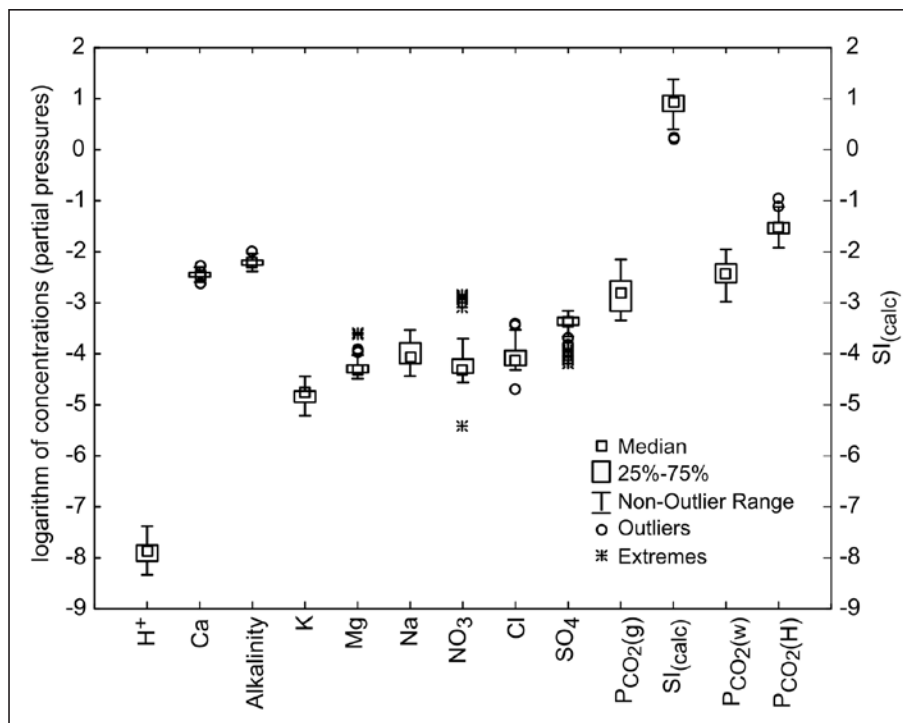


Fig. 3: Dripwater composition, monitored cave  $P_{\text{CO}_2(\text{g})}$  saturation indices, and calculated  $P_{\text{CO}_2(\text{w})}$  and  $P_{\text{CO}_2(\text{H})}$  (88 samples).

## RESULTS

### DRIPWATER COMPOSITION

The hydrochemistry of 88 dripwater samples is summarized in the box-plot in Fig. 3. The pH values varied in the range from 7.38 to 8.33 (7.88 median;  $7.90 \pm 0.05$  confidence interval). The calcium concentration varied in the range  $(2.42\text{--}5.52) \times 10^{-3} \text{ mol L}^{-1}$  with  $3.58 \times 10^{-3} \text{ mol L}^{-1}$  median and  $(3.61 \pm 0.14) \times 10^{-3} \text{ mol L}^{-1}$  confidence interval. Alkalinity varied in the range  $(0.41\text{--}1.05) \times 10^{-2} \text{ eq L}^{-1}$  ( $6.30 \times 10^{-3} \text{ eq L}^{-1}$  medians,  $(6.26 \pm 0.27) \times 10^{-3} \text{ eq L}^{-1}$  confidence interval). The concentrations of K, Mg, and Na were in  $(1.53 \pm 0.11) \times 10^{-5}$ ,  $(7.60 \pm 1.40) \times 10^{-5}$ , and  $(1.18 \pm 0.15) \times 10^{-4} \text{ mol L}^{-1}$  confidence intervals, respectively. The concentrations of  $\text{NO}_3^-$ ,  $\text{Cl}^-$ , and  $\text{SO}_4^{2-}$  were in  $(1.63 \pm 0.72) \times 10^{-4}$ ,  $(8.92 \pm 1.60) \times 10^{-5}$ , and  $(4.07 \pm 0.32) \times 10^{-4} \text{ mol L}^{-1}$  confidence intervals, respectively. The given composition roughly falls into the range reported for dripwaters by McDonald *et al.* (2007), Jiménez-Sánchez *et al.* (2008), or Baker *et al.* (2000). On the other hand, dripwaters collected in the study are somewhat more mineralized than dripwaters reported by, e.g., Covelli *et al.* (1998), Vocal *et al.* (1999), Musgrove & Banner (2004), Spötl *et al.* (2005), or Cai *et al.* (2011). Partial pressures of

$\text{CO}_2$  in cave atmosphere varied in the range  $10^{-3.35}\text{--}10^{-2.15}$  ( $10^{-2.81}$  median,  $10^{-2.83 \pm 0.07}$  confidence interval), which is consistent with the values reported by Ek & Gewelt (1985), Spötl *et al.* (2005), Baldini *et al.* (2006) or Faimon *et al.* (2010, 2012). All confidence interval are for  $\alpha=0.05$  (see Davies 2002).

### SATURATION INDICES, $SI_{(\text{calc})}$ AND $P_{\text{CO}_2(\text{w})}$

Saturation index with respect to calcite,  $SI_{(\text{calcite})} = \log(Q/K_c)$  (where  $Q = a_{\text{Ca}^{2+}} a_{\text{CO}_3^{2-}}$  and  $K_c$  is calcite solubility product), and partial pressure of gaseous  $\text{CO}_2$  that would be at equilibrium with aqueous  $\text{CO}_2$ ,  $P_{\text{CO}_2(\text{w})}$ , were calculated using PHREEQC code. The  $SI_{(\text{calcite})}$  values varied in the range 0.22–1.38 (0.92 median,  $0.89 \pm 0.05$  confidence interval) (see Fig. 3). These values somewhat exceed those presented by Covelli *et al.* (1998), Tooth & Fairchild (2003), or Spötl *et al.* (2005). The  $P_{\text{CO}_2(\text{w})}$  values were in the range  $10^{-2.98}\text{--}10^{-1.95}$  ( $10^{-2.43}$  median,  $10^{-2.44 \pm 0.05}$  confidence interval) (see Fig. 3), which is consistent with Faimon *et al.* (2006, 2012). Note that the values significantly exceeded the  $P_{\text{CO}_2(\text{g})}$  monitored in cave air. All confidence interval are calculated for  $\alpha=0.05$ .

## DATA ANALYSIS

Correlations of all variables (concentrations of aqueous species, saturation indices, and partial CO<sub>2</sub> pressures) in form of a nonparametric Spearman's correlation coefficient,  $\rho$ , are given in the matrix in Tab. 1. The statistically significant correlations at  $\alpha=0.05$  (see Davies 2002) are highlighted ( $\rho > 0.22$ ). The couples of variables Ca/logP<sub>CO<sub>2</sub>(H)</sub>, alk/logP<sub>CO<sub>2</sub>(H)</sub>, Mg/Cl, and logP<sub>CO<sub>2</sub>(g)</sub>/logP<sub>CO<sub>2</sub>(w)</sub> show strong positive correlations ( $\rho \geq 0.60$ ). In contrast, strong correlations of the couples pH/logP<sub>CO<sub>2</sub>(w)</sub>, pH/logP<sub>CO<sub>2</sub>(g)</sub>, and SI<sub>(calc)</sub>/logP<sub>CO<sub>2</sub>(w)</sub> are negative.

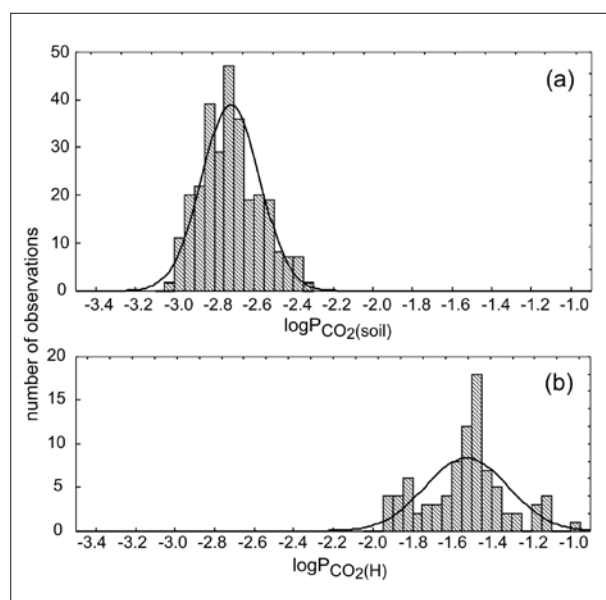
Weaker correlations ( $0.40 \leq \rho < 0.60$ ) were found for the couples Ca/alk, alk/Mg, alk/logP<sub>CO<sub>2</sub>(w)</sub>, Mg/Na, Mg/NO<sub>3</sub>, Mg/SO<sub>4</sub>, Mg/logP<sub>CO<sub>2</sub>(H)</sub>, Na/NO<sub>3</sub>, Na/Cl, NO<sub>3</sub>/Cl, Cl/SO<sub>4</sub>, logP<sub>CO<sub>2</sub>(w)</sub>/logP<sub>CO<sub>2</sub>(H)</sub> (positive) and K/Na, K/NO<sub>3</sub>, SI<sub>(calc)</sub>/logP<sub>CO<sub>2</sub>(g)</sub> (negative).

Very weak correlations ( $0.22 < \rho < 0.40$ ) were found for the couples Ca/K, Ca/Mg, Ca/SO<sub>4</sub>, Ca/SI<sub>(calc)</sub>, Ca/logP<sub>CO<sub>2</sub>(w)</sub>, alk/SO<sub>4</sub>, alk/SI<sub>(calc)</sub>, alk/logP<sub>CO<sub>2</sub>(g)</sub>, K/SI<sub>(calc)</sub>, K/logP<sub>CO<sub>2</sub>(H)</sub>, Mg/logP<sub>CO<sub>2</sub>(g)</sub>, Mg/logP<sub>CO<sub>2</sub>(w)</sub>, Na/SO<sub>4</sub>, Cl/logP<sub>CO<sub>2</sub>(w)</sub>, SO<sub>4</sub>/logP<sub>CO<sub>2</sub>(H)</sub>, SI<sub>(calc)</sub>/logP<sub>CO<sub>2</sub>(H)</sub>, logP<sub>CO<sub>2</sub>(g)</sub>/logP<sub>CO<sub>2</sub>(H)</sub> (positive), and pH/Cl, K/Cl (negative).

Tab. 1: Spearman Rank Order Correlations. Statistically significant correlations ( $\alpha=0.05$ ) are highlighted.

	pH	Ca	alk	K	Mg	Na	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	SI <sub>(calc)</sub>	logP <sub>CO<sub>2</sub>(g)</sub>	logP <sub>CO<sub>2</sub>(w)</sub>	logP <sub>CO<sub>2</sub>(H)</sub>
pH	1.00												
Ca	-0.20	1.00											
alk	-0.16	<b>0.56</b>	1.00										
K	0.09	<b>0.23</b>	0.15	1.00									
Mg	-0.19	<b>0.36</b>	<b>0.49</b>	-0.21	1.00								
Na	-0.15	-0.09	0.02	<b>-0.57</b>	<b>0.58</b>	1.00							
NO <sub>3</sub> <sup>-</sup>	-0.12	-0.14	-0.13	<b>-0.45</b>	<b>0.43</b>	<b>0.51</b>	1.00						
Cl <sup>-</sup>	<b>-0.25</b>	0.17	0.12	<b>-0.25</b>	<b>0.61</b>	<b>0.54</b>	<b>0.56</b>	1.00					
SO <sub>4</sub> <sup>2-</sup>	-0.03	<b>0.31</b>	<b>0.30</b>	0.01	<b>0.43</b>	<b>0.32</b>	0.14	<b>0.48</b>	1.00				
SI <sub>(calc)</sub>	<b>0.83</b>	<b>0.28</b>	<b>0.30</b>	<b>0.23</b>	0.07	-0.15	-0.19	-0.12	0.17	1.00			
logP <sub>CO<sub>2</sub>(g)</sub>	<b>-0.61</b>	0.10	<b>0.39</b>	0.10	<b>0.30</b>	0.14	0.08	0.18	0.05	<b>-0.41</b>	1.00		
logP <sub>CO<sub>2</sub>(w)</sub>	<b>-0.95</b>	<b>0.35</b>	<b>0.43</b>	-0.02	<b>0.32</b>	0.14	0.08	<b>0.28</b>	0.14	<b>-0.66</b>	<b>0.67</b>	1.00	
logP <sub>CO<sub>2</sub>(H)</sub>	-0.18	<b>0.77</b>	<b>0.94</b>	<b>0.22</b>	<b>0.49</b>	-0.02	-0.16	0.14	<b>0.30</b>	<b>0.32</b>	<b>0.33</b>	<b>0.43</b>	1.00

alk – alkalinity

CALCULATION OF P<sub>CO<sub>2</sub>(H)</sub>

The calculation focuses on the determination of a hypothetical partial CO<sub>2</sub> pressure, P<sub>CO<sub>2</sub>(H)</sub>, that has participated in both limestone dissolution and development of resulting water chemistry. The P<sub>CO<sub>2</sub>(H)</sub> was found as the partial CO<sub>2</sub> pressure, at which degassed dripwater of a given composition would return to the equilibrium with calcite. By PHREEQC code, P<sub>CO<sub>2</sub>(H)</sub> were determined by “adjusting” pH so that solution was at equilibrium with calcite, see the input file in Appendix.

Fig. 4: Frequency diagrams of partial pressures of CO<sub>2</sub> in (a) shallow karst soils (286 samples) (Faimon et al. 2010, 2012) and (b) hypothetical epikarst CO<sub>2</sub> source (88 samples).

Alternatively, the  $\log P_{\text{CO}_2(\text{H})}$  may be estimated from the equation

$$\log P_{\text{CO}_2(\text{H})} = \log P_{\text{CO}_2(\text{W})} + \text{SI}_{(\text{calcite})} \quad (6)$$

that is result of combining the expressions for equilibrium constants of the processes given by eqns. 1–5 with the simplified electric charge balance,  $2[\text{Ca}^{2+}] \equiv [\text{HCO}_3^-]$ . Eqn. (6) is valid close to calcite-water- $\text{CO}_2$  equilibrium. With  $\text{SI}_{(\text{calcite})}$  increasing up to  $\sim 1.5$ , the  $\log P_{\text{CO}_2(\text{H})}$  relative error increases exponentially up to  $\sim 10\%$ .

## DISCUSSION

### INTERPRETATION OF CORRELATIONS

The strong positive correlations of  $\text{Ca}/\log P_{\text{CO}_2(\text{H})}$  and  $\text{alk}/\log P_{\text{CO}_2(\text{H})}$  reflect stoichiometry of limestone dissolution (see Eq. 1–5). Note that  $\log P_{\text{CO}_2(\text{H})}$  must fit the dominant aqueous species that control its calculation. The dissolution stoichiometry is also mirrored by the weaker positive correlations of  $\text{Ca}/\text{alk}$ ,  $\text{alk}/\text{Mg}$ ,  $\text{Mg}/\log P_{\text{CO}_2(\text{H})}$  and  $\text{Ca}/\text{Mg}$ . Some positive correlations ( $\text{Ca}/\text{SI}_{(\text{calc})}$ ,  $\text{alk}/\text{SI}_{(\text{calc})}$ ,  $\text{Ca}/\log P_{\text{CO}_2(\text{W})}$ ,  $\text{Mg}/\log P_{\text{CO}_2(\text{W})}$ ,  $\text{SI}_{(\text{calc})}/\log P_{\text{CO}_2(\text{H})}$ ,  $\log P_{\text{CO}_2(\text{W})}/\log P_{\text{CO}_2(\text{H})}$ ) indicate dependence of variables on the extent of water mineralization. The positive correlations of  $\text{pH}/\text{SI}_{(\text{calc})}$ ,  $\log P_{\text{CO}_2(\text{g})}/\log P_{\text{CO}_2(\text{W})}$ ,  $\text{alk}/\log P_{\text{CO}_2(\text{W})}$ ,  $\text{alk}/\log P_{\text{CO}_2(\text{g})}$ , together with negative correlations of  $\text{pH}/\log P_{\text{CO}_2(\text{W})}$ ,  $\text{pH}/\log P_{\text{CO}_2(\text{g})}$ ,  $\text{SI}_{(\text{calc})}/\log P_{\text{CO}_2(\text{W})}$  or  $\text{SI}_{(\text{calc})}/\log P_{\text{CO}_2(\text{g})}$ , reflect dripwater degassing. The weak positive correlation  $\log P_{\text{CO}_2(\text{g})}/\log P_{\text{CO}_2(\text{H})}$  indicates interrelationship between source  $\text{CO}_2$  and cave  $\text{CO}_2$ . The positive correlations of variables such as  $\text{Na}/\text{Mg}$ ,  $\text{Na}/\text{NO}_3$ ,  $\text{NO}_3/\text{Cl}$ ,  $\text{Na}/\text{Cl}$ ,  $\text{Cl}/\text{SO}_4$ ,  $\text{Na}/\text{SO}_4$ ,  $\text{Mg}/\text{Cl}$ ,  $\text{Mg}/\text{NO}_3$  and  $\text{Mg}/\text{SO}_4$  are probably consequence of rain water stoichiometry and/or agriculture activities. The reasons for other weak correlations as  $\text{Ca}/\text{K}$ ,  $\text{Ca}/\text{SO}_4$ ,  $\text{SO}_4/\log P_{\text{CO}_2(\text{H})}$ ,  $\text{alk}/\text{SO}_4$ ,  $\text{K}/\text{SI}_{(\text{calc})}$ ,  $\text{K}/\log P_{\text{CO}_2(\text{H})}$ ,  $\text{Mg}/\log P_{\text{CO}_2(\text{g})}$ ,  $\text{Cl}/\log P_{\text{CO}_2(\text{W})}$  (positive) and  $\text{K}/\text{Na}$ ,  $\text{pH}/\text{Cl}$ ,  $\text{K}/\text{Cl}$ ,  $\text{K}/\text{NO}_3$  (negative) are less comprehensible.

### SATURATION INDICES

The dripwater data have been plotted as the graph of pH vs. Ca concentration (Fig. 5). As can be seen, all the experimental points are above the equilibrium line. They are roughly arranged into a horizontal line that corresponds to degassing process. Extrapolation of the line to the left towards the equilibrium line shows the composition corresponding to  $P_{\text{CO}_2(\text{H})}$  value. The summer and winter data are partly separated, but they both show the similar  $P_{\text{CO}_2(\text{H})}$  values. The shift of the winter data to the

The found  $P_{\text{CO}_2(\text{H})}$  values ranged from  $10^{-1.92}$  to  $10^{-0.96}$  ( $10^{-1.51}$  median,  $10^{-1.53 \pm 0.04}$  ( $\alpha=0.05$ )) (see Fig. 3). Distribution of the calculated  $P_{\text{CO}_2(\text{H})}$  is given in the frequency diagram in Fig. 4 and is compared with  $P_{\text{CO}_2(\text{soil})}$  values found in shallow karst soils by Faimon *et al.* (2010, 2012). Note that the  $\log P_{\text{CO}_2(\text{soil})}$  and  $\log P_{\text{CO}_2(\text{H})}$  show very different modes,  $-2.75$  and  $-1.45$ , respectively. Seasonal variation of  $P_{\text{CO}_2(\text{H})}$  are small; the summer values,  $10^{-1.48 \pm 0.06}$  (May to September), only slightly exceeded the winter values,  $10^{-1.59 \pm 0.05}$  ( $\alpha=0.05$ ) (October to March).

right (to higher supersaturation) mirrors higher degassing because of increasing difference between (1) the initial  $P_{\text{CO}_2(\text{g})}$  participating on dripwater formation (corresponding to  $P_{\text{CO}_2(\text{H})}$ ) and (2) the cave air  $P_{\text{CO}_2(\text{g})}$  reduced by stronger winter ventilation. Besides, this seasonality indicates that the studied dripwaters were degassed as far as in cave environment.

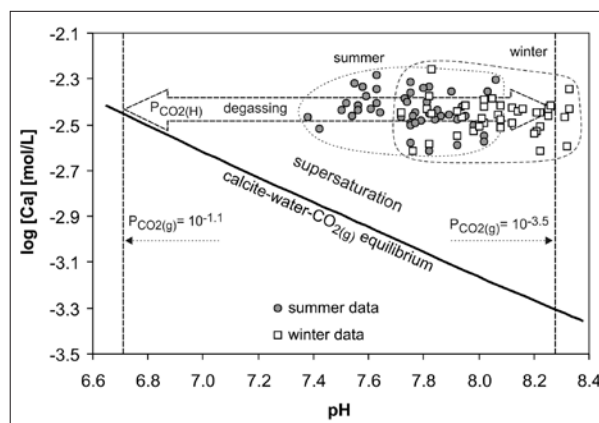


Fig. 5: The plot of Ca concentration against pH. The bold line indicates total equilibrium in pure calcite-water- $\text{CO}_2(\text{g})$  system. The intersections of perpendicular dashed lines with the equilibrium line denote equilibrium composition at different  $P_{\text{CO}_2(\text{g})}$   $10^{-1.1}$  (left) and  $10^{-3.5}$  (right). Evolution in horizontal direction corresponds to water degassing.

### $P_{\text{CO}_2(\text{H})}$ AND KARSTIFICATION MECHANISMS

Principally, two different karstification models can be distinguished: (1) *closed system model (CSM)*, where the concentrations of aqueous carbonate species are not replenished from surrounding environment and (2) *open system model (OSM)*, where the water dissolving limestone is in contact with the source of gaseous  $\text{CO}_2$ . The

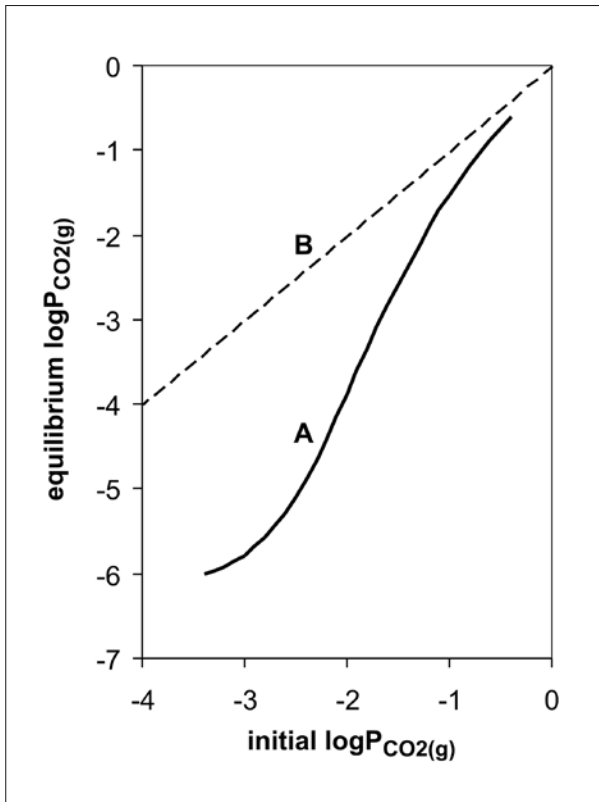


Fig. 6: Dependence of equilibrium  $P_{\text{CO}_2(\text{g})}$  on initial  $P_{\text{CO}_2(\text{g})}$  under CSM conditions (A) and OSM conditions (B).

real karstification process is probably a compromise between both models.

#### $P_{\text{CO}_2(\text{H})}$ IN CLOSED SYSTEM

Based on the CSM, the seepage water is initially saturated by CO<sub>2</sub> at given  $P_{\text{CO}_2(\text{g})}$  and equilibrates with calcite in the zone that is without a contact with original gaseous CO<sub>2</sub>. Such situation could be conceivable, e.g., if the movement of seepage water were faster than CO<sub>2</sub> diffusion from solution/atmosphere boundary and calcite dissolution. In this case, a certain portion of CO<sub>2(aq)</sub> is “consumed” by dissolution and equilibrium  $P_{\text{CO}_2(\text{g})}$  (corresponding to  $P_{\text{CO}_2(\text{w})}$  and also to calculated  $P_{\text{CO}_2(\text{H})}$ ) is lower than the initial one. It is documented in Fig. 6 by deviation of the curve (A) representing the CSM from the curve (B) valid for the OSM. As follows from Fig. 6, the deviation is smaller when the initial  $P_{\text{CO}_2(\text{g})}$  is higher. In case that water does not achieve equilibrium with calcite, the deviation is proportionally smaller. To summarize, actual initial  $P_{\text{CO}_2(\text{g})}$  participating on dripwater chemistry under the CSM conditions could even be higher than that calculated as  $P_{\text{CO}_2(\text{H})}$ .

Another theoretical possibility to disturb  $P_{\text{CO}_2(\text{H})}$  under closed system conditions is an addition of acidi-

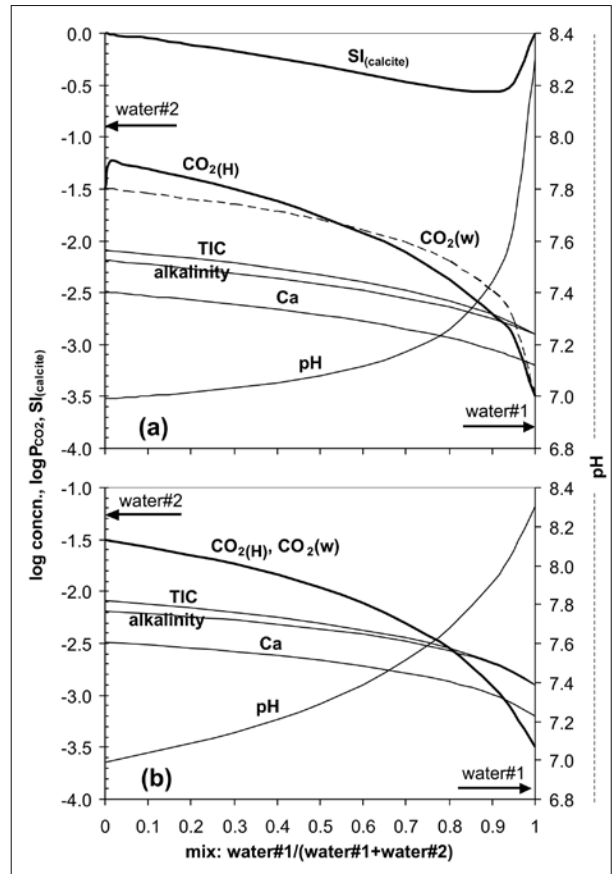


Fig. 7: Mixing model – evolution of hydrogeochemical variables during mixing of two waters of different hydrochemistry. (A) Non-reactive mixing model of the water#1 and water#2. (B) Reactive mixing model; mix of the waters#1 and water#2 subsequently equilibrated with calcite ( $SI_{\text{calc}}=0$ ).

ty from an external source to the initially saturated water. As result,  $P_{\text{CO}_2(\text{H})}$  shifts to higher value than that, at which the water has actually been saturated. In fact, it is hardly conceivable idea under real karst conditions.

#### $P_{\text{CO}_2(\text{H})}$ IN OPEN SYSTEM

Under the OSM conditions, seepage water is saturated by both CO<sub>2</sub> and calcite to equilibrium at constant  $P_{\text{CO}_2}$ . Therefore, the initial and equilibrium  $P_{\text{CO}_2}$  are the same (see the curve A in Fig. 6). It should be noted that constant  $P_{\text{CO}_2}$  requires an extensive CO<sub>2</sub> reservoir with strong input fluxes. As the seepage water can equilibrate with both CO<sub>2(\text{g})</sub> and calcite already at the base of soil profile or in epikarst, we believe that real karst conditions are generally shifted closer to OSM. The relatively high values of  $p_{\text{CO}_2(\text{H})}$  calculated from our data set are consistent with this idea. In case that water does not achieve equilibrium with calcite under OSM conditions, the hypothetical partial pressure  $P_{\text{CO}_2(\text{H})}$  is simply  $P_{\text{CO}_2(\text{w})}$ . In case of pre-

precipitation calcite along transport path, the calculated  $P_{\text{CO}_2(\text{H})}$  would be lower than that actual initial  $P_{\text{CO}_2(\text{g})}$ .

A problem of both former models is potential mixing of waters in vadose zone. In Fig. 7, mixing model is given for two different initial waters: the water #1 which has been saturated with respect to calcite at  $P_{\text{CO}_2(\text{g})} \sim 10^{-3.5}$  (see  $SI_{(\text{calcite})} = 0$ , and  $P_{\text{CO}_2(\text{w})} = 10^{-3.5}$ ) and the water #2 which has been saturated with respect to calcite at  $P_{\text{CO}_2(\text{g})} \sim 10^{-1.5}$  (see  $SI_{(\text{calcite})} = 0$ , and  $P_{\text{CO}_2(\text{w})} = 10^{-1.5}$ ). The first mixing model is non-reactive; it includes simple mixing without any other processes (Fig. 7a). The resulting mix (calculated as  $\text{water\#1}/(\text{water\#1} + \text{water\#2})$ ) is unsaturated with respect to calcite,  $SI_{(\text{calcite})} < 0$ , despite equilibrium of both initial waters. It is consistent with the assumptions of Bögli (1964, 1980), Gabrovšek & Dreybrodt (2000), Dreybrodt *et al.* (2010), or Qian & Peiyue (2011). The  $P_{\text{CO}_2(\text{H})}$  values deduced from such mix can be somewhat overrated with respect to the actual  $P_{\text{CO}_2}$  values controlling calcite saturation of the initial waters. The reason is in the interpretation of the  $SI_{(\text{calc})}$  decrement as a consequence of  $P_{\text{CO}_2(\text{H})}$  enhancement. It indicates that the non-reactive mixing model produces a positive error for water unsaturated with respect to calcite. It should be noted that it is not the case of the studied dripwaters. The second model is reactive; water mixing is followed by subsequent calcite dissolution up to saturation, which probably better corresponds to real conditions. The calculated  $P_{\text{CO}_2(\text{H})}$  (equivalent to  $P_{\text{CO}_2(\text{w})}$ ) is always between the initial  $P_{\text{CO}_2(\text{w})}$  values for water#1 and water #2 (see Fig. 7b). It means that the calculated  $P_{\text{CO}_2(\text{H})}$  is located between the lowest and the highest  $P_{\text{CO}_2(\text{g})}$  values, with which the waters were in contact.

#### IMPLICATIONS

The reconstruction of initial  $P_{\text{CO}_2(\text{g})}$  from dripwater chemistry is not trivial. The calculated  $P_{\text{CO}_2(\text{H})}$  values can be

influenced to some extent by karstification mechanism (closed vs. open system) and by various processes (water mixing, precipitation, acidification). However, most of these possibilities lead to  $P_{\text{CO}_2(\text{H})}$  values lower than that initial  $P_{\text{CO}_2(\text{g})}$  actually participating on dripwater chemistry. If water interacts with limestone under open conditions with respect to  $\text{CO}_2(\text{g})$  (as probably in this study),  $P_{\text{CO}_2(\text{H})}$  may be a good estimator of initial  $P_{\text{CO}_2(\text{g})}$ . In all cases,  $P_{\text{CO}_2(\text{H})}$  could be understood as an important dripwater parameter that allows a better estimation of the conditions of limestone dissolution and dripwater formation.

The values derived from dripwater hydrochemistry,  $P_{\text{CO}_2(\text{H})} \sim 10^{-1.53 \pm 0.04}$ , and the partial pressures in relevant karst soils,  $P_{\text{CO}_2(\text{soil})} \sim 10^{-2.72 \pm 0.02}$ , show a clear inconsistency, predicted already by Bourges *et al.* 2001 or Faimon *et al.* 2010, 2012. As the percolating waters were in a contact with  $\text{CO}_2$  of higher partial pressure than those in soils, it can be deduced that the  $\text{CO}_2$  source is situated deeper in karst profile. We believe that this  $\text{CO}_2$  is a product of decomposition of organic matter flushed and buried together with limestone weathering products in karrens of deeper epikarstic zone. Such  $\text{CO}_2$  source located deeper below ground surface in epikarst zone is consistent with the idea of Atkinson (1977) about “ground air  $\text{CO}_2$ ” and also with the results of direct measurements in epikarst zone by Benavente *et al.* (2010). The small difference between summer and winter  $P_{\text{CO}_2(\text{H})}$  values indicates that the source could be less dependent on external conditions than generally expected. The  $\text{CO}_2$  production could be also less sensitive to short-term climatic changes, which is important information for the researchers dealing with paleoenvironmental reconstruction. In addition, such  $\text{CO}_2$  source could also be less vulnerable by processes in shallow karst soils such as, e.g., changes of vegetation cover or agriculture activities.

#### CONCLUSIONS

Hydrochemistry of permanent drips in selected caves of the Moravian Karst was studied. All dripwaters show supersaturation with respect to calcite. Correlations of analyzed variables indicate that it is a result of  $\text{CO}_2$  degassing from dripwater. Based on a simplified model, a hypothetical partial pressure of the  $\text{CO}_2$  that had participated in dripwater chemistry formation was calculated. The resulting values,  $P_{\text{CO}_2(\text{H})} = 10^{-1.53 \pm 0.04}$ , exceed substantially

those directly measured in shallow karst soils. These findings question the widely accepted idea that shallow soils are a dominant source of karst  $\text{CO}_2$ . As an alternative source, it offers  $\text{CO}_2$  produced in deeper epikarstic zone. In such case, water hydrogeochemistry would not necessarily reflect short-term climatic changes and processes in soils. This conclusion may play a role in paleoclimatic reconstructions and karst protection.



## ACKNOWLEDGMENTS

The authors wish to thank Wolfgang Dreybrodt and Simone Milanolo for their comments that helped to im-

prove the article. The study was supported by the fund GA205/03/1128 of the Grant Agency of Czech Republic.

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