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KARST SOILS: DEPENDENCE OF CO_2 CONCENTRATIONS ON PORE DIMENSION

ODVISNOST KONCENTRACIJE CO_2 OD VELIKOSTI POR V KRAŠKIH PRSTEH

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Abstract UDC 631.41:551.435.8(437.32)
Martin Blecha & Jiří Faimon: Karst soils: Dependence of CO_2 concentrations on pore dimension
CO_2 concentrations were studied in the selected soils of the Moravian Karst, Czech Republic. The direct measurement in the air of drill-holes has indicated that the concentrations depend inversely on a pore dimension. The simplified relation between the drill-hole diameter and CO_2 concentration, $c^0_{CO2}=\frac{c_{CO2}-bD}{1+aD}$, was proposed, where c^0_{CO2} is the CO_2 concentration extrapolated to the zero drill-hole diameter in ppmv, c_{CO2} is directly measured CO_2 concentration in ppmv, and D is drill-hole diameter in cm. a and b are parameters in cm^{-1} and ppmv cm^{-1}, respectively. For the karst soils formed at grass field and deciduous forest, the values of a and b parameters were determined as −0.146±0.012 (standard error) cm^{-1} and 262.0±56.3 ppmv cm^{-1}, respectively. The dependence between c_{CO2} and D was less obvious for the heavy clay soils of coniferous forest. To understand the dependence better, a conceptual model was created taking into account the concentration gradients and mass fluxes.
Keywords: CO_2 concentration, drill-hole diameter, karst soil, model.

Izvleček UDK 631.41:551.435.8(437.32)
Martin Blecha & Jiří Faimon: Odvisnost koncentracije CO_2 od velikosti por v kraških prsteh
Raziskovali smo koncentracijo CO_2 v izbranih prsteh na Moravskem krasu v Češki republiki. Neposredne meritve v vrtinah so pokazale, da odvisnost koncentracije CO_2 od premera vrtin zadovoljivo opiše enačba $c^0_{CO2}=\frac{c_{CO2}-bD}{1+aD}$, kjer je D [cm] premer vrtine v cm, c_{CO2} je vrednost meritve, c^0_{CO2} [ppmv] je ekstrapolirana koncentracija CO_2 za $D = 0$, a [cm^{-1}] in b [ppmv/cm] pa sta regresijska parametra. Za prsti na kraških travnikih smo dobili vrednosti parametrov a = −0,146±0,012 cm^{-1} in b = 262,0±56,3 ppmv·$cm.^{-1}$. Odvisnost med c_{CO2} in D je manj značilna v glinenih prsteh iglastih gozdov. Merjene odvisnosti smo pojasnili z modelom, ki upošteva gradiente koncentracij in masne tokove.
Ključne besede: koncentracije CO_2, premer vrtin, kraška prst, modeliranje.

INTRODUCTION

Carbon dioxide is the key component in carbonate karst that affects (i) limestone dissolution (e.g. Stumm & Morgan 1996), (ii) calcite/aragonite speleothem growth (e.g. Dreybrodt 1988), or speleothem corrosion (Sarbu & Lascu 1997). Researchers believe that karst/cave CO_2 is derived from karst soils (e.g. Ford & Williams 2007). The soil CO_2 is produced by the respiration of (1) autotrophs and (2) heterotrophs (Kuzyakov & Larionova

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2005; Kuzyakov 2006). CO_2 production may depend on temperature/moisture, soil profile depth, organic matter content, total rainfall, photosynthesis/solar radiation, and various anthropogenic factors such as soil tillage, or artificial change in vegetation cover. The role of abiotic sources is also considered (e.g., Serrano-Ortiz et al. 2010). Soil CO_2 is generally an important part of the global carbon cycle (e.g., Schlesinger & Andrews 2000).

The CO_2 concentrations in karst soil air are typically measured in a range from 0.1 to 1.0 vol. % (Yoshimura *et al.* 2001; Li *et al.* 2002; Spötl *et al.* 2005; Kawai *et al.* 2006; Faimon & Ličbinská 2010; Sanchez-Cañete *et al.* 2011; Faimon *et al.* 2012a). Some indices, e.g., karst water chemistry, enhanced CO_2 levels in certain caves, limited total soil pore volumes, CO_2 fluxes into external atmosphere, etc., question the soil capability for filling cave volume up to given concentrations. This indicates some more productive CO_2 sources participating on karst CO_2. The idea of an "underground CO_2" was already proposed by Atkinson (1977). For the karst environment, an epikarstic source is sometimes hypothesized (Fairchild *et al.* 2000; Spötl *et al.* 2005; Faimon *et al.* 2012a; Cuesva *et al.* 2011, Peyraube *et al.* 2012, 2013). The hypothesis is supported by evident discrepancy between (1) CO_2 concentrations directly measured in karst soils and (2) CO_2 concentrations reconstructed from dripwater hydrogeochemistry (see, Faimon *et al.* 2012b). Recently, Benavente *et al.* (2010) confirmed the existence of the enhanced CO_2 concentrations deeply in subsoil by an in-situ measurement. Even thought we agree with the idea of the epikarstic source, we have primarily concentrated on karst soils and its efficiency to fill enlarged pores by CO_2. The purpose of this study is to demonstrate how the diameter of drill-hole in soil profile can influence CO_2 concentrations.

METHODS

RESEARCH LOCATION

The study was performed in the Moravian Karst, the largest karst area in the Bohemian Massif (Czech Republic). It represents a belt of Middle and Upper Devonian limestones, 3–6 km wide and 25 km long (corresponding to 94 km^2 area). Typical soils consist of Rendzic Lep-

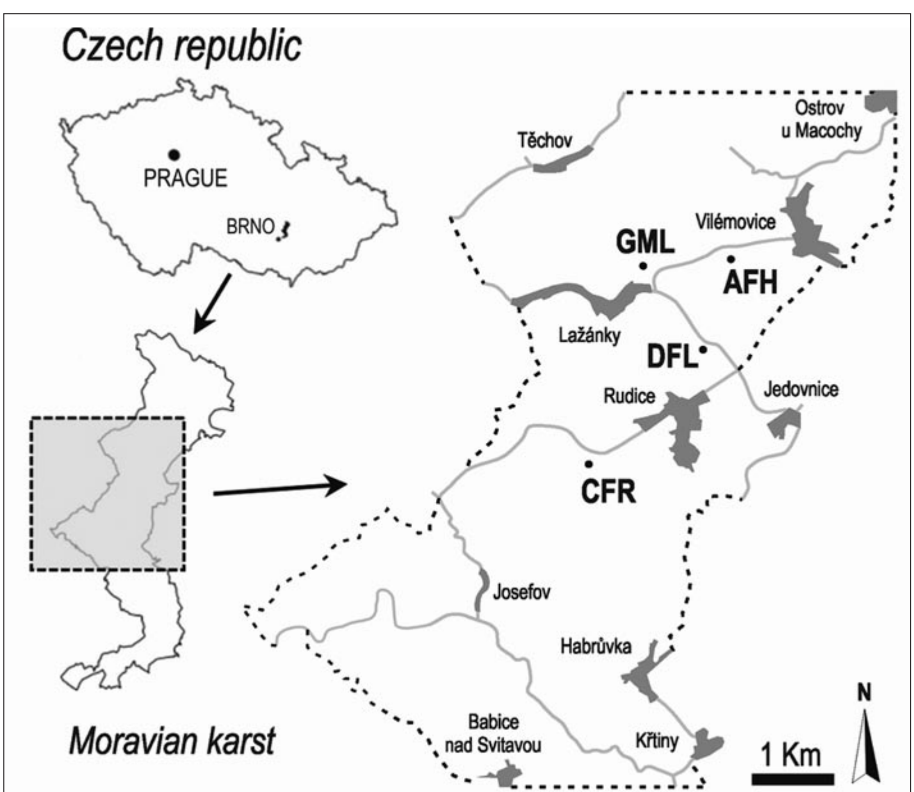

Fig. 1: Research location with monitoring sites.

Tab. 1: The soils and sampling sites.

Site	*coordinates*	*envir.*	*vegetation cover*	*pedogenic substrate*	*soil type*	*b. dens. g/cm3*	*por.*	*org. mat. wt. %*	*abbrevn.*
Harbechy Plateau	49°21´34´´N 16°43´49´´E	agricult. field	after harvest (wheat)	loam loesses	Haplic Luvisol	1.049	0.60	5.40	AFH
Lažánky I	49°21´24´´N 16°42´55´´E	meadow	grassy	devonian limestone	Rendzic Leptosols	0.702	0.72	13.22	GML
Lažánky II	49°20´47´´N 16°43´50´´E	forest	deciduous	loam loesses	Haplic Luvisol	0.880	0.65	8.88	DFL
Rudice	49°19´53´´N 16°42´34´´E	forest	coniferous	loam loesses	Stagnosols	1.086	0.57	8.51	CFR

envir. – environment; b. dens. – bulk density; por. – porosity; org. mat. – organic matter

tosols, Haplic Luvisols, and Albeluvisols. The research sites were located at the meadow and deciduous forests at Lažánky (Blansko), the agricultural field near the sinkhole Společňák at Vilémovice (Harbechy Plateau), and the coniferous forest at Rudice, see Fig. 1. The details on these sites/soils are illustrated in Tab. 1.

MONITORING

At every research location, shallow holes, 25 cm deep, and 7.0, 5.0, 2.7, and 2.0 cm in diameter were manually drilled into soils by using hand augers. These drill-holes were arranged into a line as follows: The 7-cm-hole was in the middle and further holes with decreasing diameters were on both sides. The drill-hole spacing was 20 cm each from other. The walls of drill-holes were reinforced by a plastic net. The top of the drill-hole was sealed by a plastic cap.

The CO_2 levels, temperature, and relative humidity in drill-hole air were repeatedly measured throughout two periods. The 1st period lasted from August 27 until September 13, 2012. The second began on May 5 and ended on May 17, 2013. The results were recorded between 3–6 P.M. The hand-held sensor FYA600–CO2H (Ahlborn, Germany) (±50 ppmv +2% of the values in the range < 5000 ppmv; ±100 ppmv +3% of the values in the range of 5000–10000 ppmv) working on principle of two-channel infrared absorption spectrometer (NDIR technology) was used to measure the CO_2 concentration. Since the sensor is cylindrical, 18 mm in diameter, it was placed directly into the drill-hole air at a depth of about of 11–12 cm. The sensor FHA646E1 (Ahlborn, Germany) was used to measure the temperature and relatively humidity (±0.4 °C in the range from –20 to 0 °C and ±0.1 °C in the range from 0 to +70 °C, and ±2% RH in the range from 0 to 100% RH at 25 °C). The sensors were plugged into the drill-hole by a rubber selvage to prevent CO_2 from escaping. The data were recorded after the stabilization of measured value. All the data were gathered by the data logger ALMEMO 2590 4S (Ahlborn, Germany).

RESULTS

The temperature of the external atmosphere varied between 15 and 25 °C except for September 13, 2012, being dropped to 11°C. In all the drill-holes, the temperature ranged from 9 to 19 °C and developed in conformity with the external atmosphere. The relative humidity of the air in the holes ranged from 92 to 100%. The CO_2 concentrations varied based on both time and drill-hole diameter. The CFR site was the only location where the CO_2 concentrations did not show any trend (Fig. 2). The enhanced concentrations of CO_2 (between 2382 and 7716 ppmv) were systematically measured in the drill-holes with the smallest diameter. In contrast, the lowest concentrations were found in the drill-holes with the biggest diameter (between 568 and 3192 ppmv). Absolute minimum in concentrations (568 ppmv) was observed in the 7-cm drill-hole at the AFH site on September 13, 2012. The highest maximum of carbon dioxide concentration, 7716 ppmv, was measured in the 2-cm drill-holes at the DFL site on May 9, 2013.

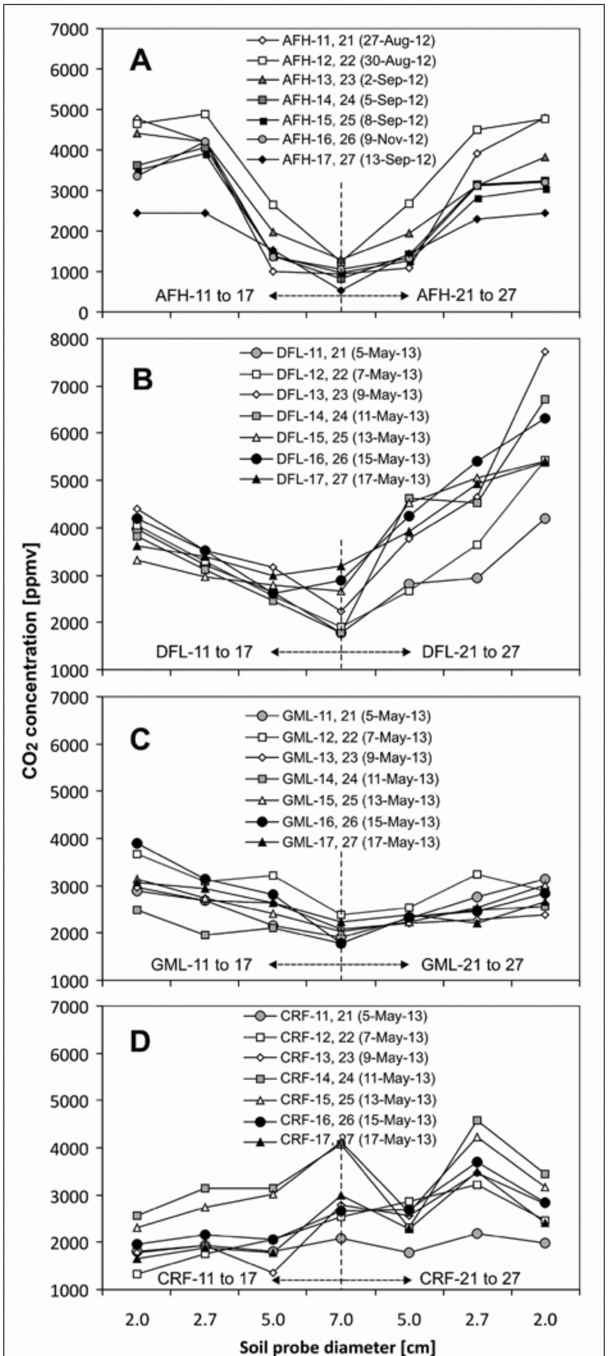

Fig. 2: CO_2 concentrations measured in the soil drill-holes of various diameters at the sites AFH (A), DFL(B), GML(C), and CRF (D). The drill-holes were 25 cm deep. The distance between the individual holes was 20 cm.

DATA ANALYSIS

CO_2 CONCENTRATIONS VS. DRILL-HOLE DIAMETER

The results of the correlation analysis of the variables, drill-hole diameter and measured CO_2 concentrations, are shown in Tab. 2. The strong negative correlations predominate for the AFH site (the correlations that are significant at $\alpha = 0.05$ appear in nine cases; the correlations significant at $\alpha = 0.10$ appear in additional four cases). The negative correlation for the DFL and GML sites are only slightly less convincing (at each site, the correlations significant at $\alpha = 0.05$ are visible in seven cases; the correlations significant at $\alpha = 0.10$ appear in additional three cases). In contrast, the correlations for the CRF site seemed to be inconclusive. They are paradoxically positive: the correlation significant at $\alpha = 0.05$ appear in two cases; the correlations significant at $\alpha = 0.10$ appear in one case).

TEMPERATURE EFFECT

The correlations between the logarithm of CO_2 concentration and reciprocal temperature in Kelvins were tested, based on the assumption that CO_2 concentrations correspond with CO_2 production and that the production obeys the Arrhenius equation. However, both the variables, $\ln(c_{CO2})$ and $1/T$, correlate only sporadically, which is demonstrated in Tab. 3. Two negative correlations significant at $\alpha = 0.05$ were found for the AFH and GML sites. Only one significant negative correlation was found for the DFL soil. Paradoxically, just positive correlations predominate in case of the CFR site.

REGRESSION ANALYSIS

The data on CO_2 concentrations and diameters were regressed by the equation

$$c_{CO2} = s\,D + c^0_{(CO2),} \tag{1}$$

where c_{CO2} is the measured CO_2 concentration, *s* is the slope of dependence, *D* is the diameter [cm] and $c^0_{(CO2)}$ is the CO_2 concentration extrapolated to a zero *D*. The discovered linear dependence parameters (eq. 1) are shown in Tab. 4. For all the parameters, standard error and p-values are given. The dependence slope *s* ranged between −910.7 and −49.7 ppmv cm^{-1} for all the AFH, GML, and DFL sites; the higher the *s* value, the stronger the dependence of CO_2 concentration on the diameter D. The significance of the s-parameter is consistent with the results of the correlation analysis. The y-intercept, $c^0_{(CO2)}$, ranged from 2466 to 8395 ppmv for all of the AFH, GML, and DFL sites and changed with the slope *s*. All these $c^0_{(CO2)}$ parameters are significant at $\alpha = 0.05$. For the CRF sites, the s-parameters are paradoxically positive with high uncertainty in most cases. The significant values for CRF-12 and CRF-15 are the

Tab. 2: Pearson's correlations between soil c_{CO2} and drill-hole diameter.

AFH-11	AFH-12	AFH-13	AFH-14	AFH-15	AFH-16	AFH-17
–0.94	**–0.98**	**–0.98**	*–0.95*	*–0.94*	*–0.90*	**–0.99**
AFH-21	AFH-22	AFH-23	AFH-24	AFH-25	AFH-26	AFH-27
–0.94	**–1.00**	**–0.98**	**–0.98**	**–0.97**	**–0.96**	**–1.00**
DFL-11	DFL-12	DFL-13	DFL-14	DFL-15	DFL-16	DFL-17
–0.98	**–0.98**	**–0.95**	**–0.98**	*–0.90*	–0.83	–0.76
DFL-21	DFL-22	DFL-23	DFL-24	DFL-25	DFL-26	DFL-27
–0.90	*–0.92*	–0.90	–0.90	**–0.96**	**–0.99**	**–1.00**
GML-11	GML-12	GML-13	GML-14	GML-15	GML-16	GML-17
–0.99	–0.87	*–0.93*	–0.75	**–0.97**	**–0.96**	**–0.99**
GML-21	GML-22	GML-23	GML-24	GML-25	GML-26	GML-27
–0.98	–0.85	**–0.98**	*–0.95*	*–0.92*	**–0.95**	–0.55
CFR-11	CFR-12	CFR-13	CFR-14	CFR-15	CFR-16	CFR-17
0.64	**0.97**	0.55	*0.91*	**0.96**	0.82	0.85
CFR-21	CFR-22	CFR-23	CFR-24	CFR-25	CFR-26	CFR-27
–0.19	–0.26	–0.48	–0.12	0.14	–0.56	–0.01

The correlations highligted are significant at $\alpha = 0.05$
The correlation by italic are significant at $\alpha = 0.10$

only exception. The $c^0_{(CO2)}$ parameters are more significant.

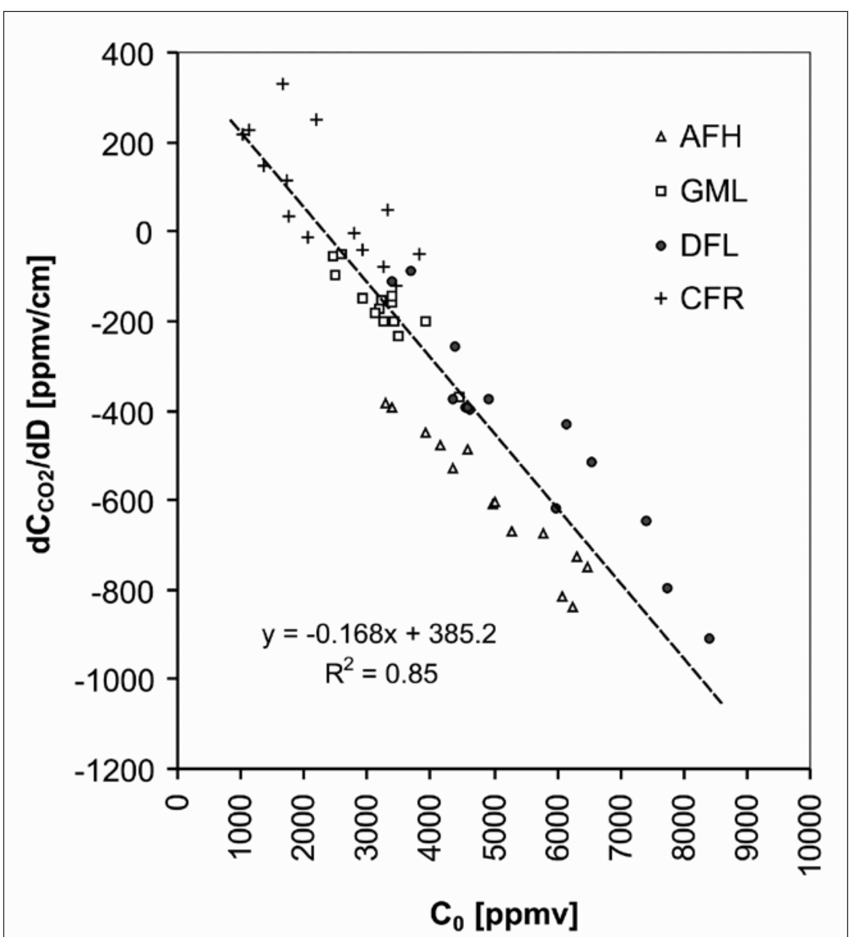

Fig. 3: Relation between the slopes and zero diameter concentrations.

The slopes $s = dc_{CO2}/dD$ follow the equation

$$\frac{dc_{CO2}}{dD} = a\, c^0_{CO2} + b, \qquad (2)$$

where *a, b* are the parameters and the other symbols have their standard meaning.

The parameters were found through regression analysis. They are listed in Tab. 5 by the monitoring sites.

For the individual sites, *a*-parameter varied between –0.13 and –0.16 cm^{-1}, and *b*-parameter ranged from 88 to 422 ppmv cm^{-1}. For the total combined data of all the sites, $a = -0.178$ cm^{-1} and $b = 421.2$ ppmv cm^{-1} (see Fig. 3). For the meadow and deciduous forest soils without the CFR soil, $a = -0.158$ cm^{-1} and $b = 310.6$ ppmv cm^{-1}.

Tab. 4: The regression parameters of the dependence $c_{CO2} = s D + c_{0(CO2)}$.

		s-parameter			$c_{(CO2)}$ parameter			whole model	
site	**date**	**s**	**std. err.** [(a)]	**p**	$c_{0(CO2)}$	**std. err.**	**p**	R^2	**p**
AFH-11 [(b)]	27-Aug-12	*–840.1*	218.5	0.061	**6229.9**	1008.8	0.025	0.88	0.061
AFH-12	30-Aug-12	**–747.2**	101.5	0.018	**6470.8**	468.7	0.005	**0.96**	**0.018**
AFH-13	2-Sep-12	**–674.2**	98.3	0.021	**5793.6**	453.8	0.006	**0.96**	**0.021**
AFH-14	5-Sep-12	*–669.5*	161.6	0.054	**5266.6**	746.0	0.019	0.90	0.054
AFH-15	8-Sep-12	*–609.3*	159.1	0.062	**4987.9**	734.6	0.021	0.88	0.062
AFH-16	9-Nov-12	–602.7	209.7	0.103	**5008.7**	968.3	0.035	0.81	0.103
AFH-17	13-Sep-12	**–394.6**	45.3	0.013	**3386.3**	209.2	0.004	**0.97**	**0.013**
AFH-21	27-Aug-12	*–815.3*	201.0	0.056	**6090.3**	928.1	0.022	0.89	0.056
AFH-22	30-Aug-12	**–724.1**	32.5	0.002	**6311.3**	150.1	0.001	**1.00**	**0.002**
AFH-23	2-Sep-12	**–489.0**	66.4	0.018	**4581.7**	306.7	0.004	**0.96**	**0.018**
AFH-24	5-Sep-12	**–528.5**	75.0	0.020	**4360.4**	346.2	0.006	**0.96**	**0.020**
AFH-25	8-Sep-12	**–449.8**	82.5	0.032	**3910.0**	381.0	0.009	**0.94**	**0.032**
AFH-26	9-Nov-12	**–478.6**	99.5	0.041	**4169.1**	459.3	0.012	**0.92**	**0.041**
AFH-27	13-Sep-12	**–383.1**	24.5	0.004	**3276.4**	113.0	0.001	**0.99**	**0.004**
GML11	5-May-13	**–199.0**	21.0	0.011	**3246.0**	96.9	0.001	**0.98**	**0.011**
GML12	7-May-13	–202.0	81.3	0.131	**3931.9**	375.6	0.009	0.76	0.131
GML13	9-May-13	*–152.2*	41.8	0.068	**3230.3**	193.1	0.004	0.87	0.068
GML14	11-May-13	–98.0	60.4	0.246	**2493.4**	278.7	0.012	0.57	0.246
GML15	13-May-13	**–200.1**	35.8	0.031	**3418.6**	165.5	0.002	0.94	**0.031**
GML16	15-May-13	**–367.8**	75.4	0.040	**4448.4**	348.0	0.006	**0.92**	**0.040**
GML17	17-May-13	**–159.1**	12.3	0.006	**3381.4**	56.9	0.000	**0.99**	**0.006**
GML21	5-May-13	**–232.5**	30.6	0.017	**3503.1**	141.3	0.002	**0.97**	**0.017**
GML22	7-May-13	–145.3	63.7	0.150	**3373.5**	294.2	0.008	0.72	0.150
GML23	9-May-13	**–54.7**	7.5	0.018	**2466.0**	34.4	0.000	**0.96**	**0.018**
GML24	11-May-13	*–148.3*	35.2	0.052	**2907.7**	162.6	0.003	0.90	0.052
GML25	13-May-13	*–174.5*	51.3	0.077	**3188.2**	236.7	0.005	0.85	0.077
GML26	15-May-13	**–180.1**	40.6	0.047	**3113.2**	187.6	0.004	**0.91**	**0.047**
GML27	17-May-13	–49.7	53.2	0.449	**2586.8**	245.6	0.009	0.30	0.449
DFL-11	5-May-13	**–394.3**	61.9	0.024	**4545.0**	285.8	0.004	**0.95**	**0.024**
DFL-12	7-May-13	**–397.1**	62.8	0.024	**4613.1**	290.1	0.004	**0.95**	**0.024**
DFL-13	9-May-13	**–374.2**	85.2	0.048	**4900.4**	393.2	0.006	**0.91**	**0.048**
DFL-14	11-May-13	**–374.1**	57.1	0.022	**4360.8**	263.5	0.004	**0.96**	**0.022**
DFL-15	13-May-13	*–112.2*	37.9	0.098	**3402.1**	175.0	0.003	0.81	0.098
DFL-16	15-May-13	–257.2	121.1	0.168	**4377.1**	559.0	0.016	0.69	0.168
DFL-17	17-May-13	–89.2	54.6	0.244	**3672.9**	252.2	0.005	0.57	0.244
DFL-21	5-May-13	*–392.9*	134.3	0.100	**4572.4**	620.2	0.018	0.81	0.100
DFL-22	7-May-13	*–617.9*	183.1	0.078	**5992.1**	845.6	0.019	0.85	0.078
DFL-23	9-May-13	*–910.7*	312.4	0.100	**8394.6**	1442.5	0.028	0.81	0.100
DFL-24	11-May-13	–796.7	276.0	0.102	**7737.3**	1274.4	0.026	0.81	0.102
DFL-25	13-May-13	**–512.7**	112.4	0.045	**6552.3**	519.0	0.006	**0.91**	**0.045**
DFL-26	15-May-13	**–646.0**	56.1	0.007	**7406.7**	259.2	0.001	**0.99**	**0.007**
DFL-27	17-May-13	**–429.1**	25.4	0.003	**6144.4**	117.3	0.000	**0.99**	**0.003**
CRF-11	5-May-13	36.0	30.2	0.356	**1757.4**	139.7	0.006	0.41	0.356
CRF-12	7-May-13	**216.3**	35.1	0.025	**1018.1**	162.0	0.024	**0.95**	**0.025**
CRF-13	9-May-13	144.5	153.8	0.447	1359.6	710.3	0.196	0.31	0.447
CRF-14	11-May-13	*250.4*	79.9	0.089	**2195.1**	369.1	0.027	0.83	0.089
CRF-15	13-May-13	**328.3**	69.6	0.042	**1675.5**	321.6	0.035	**0.92**	**0.042**
CRF-16	15-May-13	112.9	56.4	0.183	**1736.6**	260.2	0.022	0.67	0.183
CRF-17	17-May-13	228.6	102.3	0.155	1125.2	472.3	0.140	0.71	0.155
CRF-21	5-May-13	–14.1	52.6	0.814	**2063.1**	242.8	0.014	0.03	0.814
CRF-22	7-May-13	–39.5	104.8	0.743	**2937.6**	484.0	0.026	0.07	0.743
CRF-23	9-May-13	–80.7	105.3	0.524	**3240.0**	486.3	0.022	0.23	0.524
CRF-24	11-May-13	–52.2	301.5	0.878	3826.5	1392.1	0.111	0.01	0.878
CRF-25	13-May-13	48.8	235.9	0.855	*3332.3*	1089.4	0.092	0.02	0.855
CRF-26	15-May-13	–118.8	124.2	0.440	**3464.8**	573.5	0.026	0.31	0.440
CRF-27	17-May-13	–3.1	174.0	0.987	*2806.8*	803.6	0.073	0.00	0.987

(a) standard error

(b) the first number means direction form central drill-hole; the second number corresponds to date

The highlighted parameters are statistically significant at α = 0.05

The parameters by italic are significant at α = 0.10

Tab. 5: The model a, b parameters.

	parameters						whole model	
	a	*std. err.* [(a)]	*p*	*b*	*std. err.*	*p*	R^2	*p*
AFH	**–0.134**	0.011	0.000	66.7	55.1	0.250	**0.93**	**0.000**
GML	**–0.133**	0.017	0.000	**262.9**	55.2	0.000	**0.84**	**0.000**
DFL	**–0.140**	0.014	0.000	**317.8**	80.0	0.002	**0.89**	**0.000**
CRF	**–0.114**	0.028	0.001	**341.4**	69.3	0.000	**0.58**	**0.001**
as w CRF[(b)]	**–0.146**	0.012	0.001	**262.0**	56.3	0.000	**0.80**	**0.000**
AS[(c)]	**–0.168**	0.010	0.000	**385.2**	42.3	0.000	**0.85**	**0.000**

The highlighted parameters are statistically significant at α = 0.05
(a) standard error
(b) all soils without CRF
(c) all soil

MATHEMATICAL MODEL

Inserting the differences $\Delta c_{CO2} = (c_{CO2} - c^0_{CO2})$ for the differentials dc_{CO2} and $\Delta D = D$ for dD, and consecutive rewriting transform the eqn. (2) into

$$c^0_{CO2} = \frac{c_{CO2} - bD}{1 + aD}. \qquad (3)$$

From a mathematical point of view, the expression (Eq. 3) is defined if $D \neq -\frac{1}{a}$. Because the diameter D must be positive, it should lie between the intervals $\frac{c_{CO2}}{b} \leq D < -\frac{1}{a}$ and $\frac{c_{CO2}}{b} \geq D > -\frac{1}{a}$.

DISCUSSION

The measured CO_2 concentrations agree with the values given by other researchers studying the karst soils. Under using the same monitoring methods, Faimon and Ličbinská (2010) and Faimon *et al.* (2012a) found the CO_2 concentration of about 2000–3000 ppmv in the Moravian Karst (Czech republic) for similar soils and 5-cm drill-hole diameters at 20 °C (May). Other researchers used methods based on the sampling of soil the atmosphere and their subsequent analysis in-situ or in the laboratory. Such concentrations vary from 500 to 9000 ppmv based on local conditions (Spötl *et al.* 2005; Kawai *et al.* 2006; Yoshimura *et al.* 2001; Li *et al.* 2002; Sanchez-Cañete *et al.* 2011).

Variations of CO_2 concentrations in individual drill-hole during monitoring periods are most likely controlled by external conditions. The effect of the light intensity on photosynthesis and, consecutively, on the respiration of autotrophs seems to be the most significant (Kuzyakov & Larionova 2005; Kuzyakov 2006). The temperature seems to have a rather small effect, as indicated by the weak correlations in Tab. 3. The impact of an external wind on total CO_2 efflux may be also important (Pérez-Priego *et al.* 2013). All the external influences have been eliminated in the mathematical model, Eq. (3).

The *a, b* parameters of the model somewhat differ among various soil samples (see Tab. 5). As the soil porosity (controlling CO_2 efflux) seems to be similar in all the soils (Tab. 1), CO_2 production may have a dominant effect. However, it is worth mentioning that the reached CO_2 concentrations do not follow the organic matter content in the soils (compare Tab. 1 and Fig. 2).

The analysis of the mathematical model (Eq. 3) showed that the difference between corrected and measured concentrations, $\Delta c = c^0_{CO_2} - c_{CO_2}$, increases with the value of *a*-parameter, whereas *b*-parameter decreases this effect. As it follows from Fig. 4, the *a*-parameter gives the slope and *b*-parameter gives the intercept of the dependence $c^0_{CO_2} = f(c_{CO_2})$. When compared the measured and corrected concentrations, the measured CO_2 concentrations in 2-cm drill-holes are affected by the systematical negative errors ranging from 22 to 31%. This error increases up to 575% in case of 7-cm drill-hole. Therefore, concentrations directly measured in drill-holes generally require correction, e.g., based on our mathematical model.

The conceptual model of the mechanism of attaining CO_2 concentration in soil drill-hole was derived in order to understand better the pore dimension effect (Fig. 5). The CO_2 production, along with the CO_2 effluxes from bulk soil into (1) the external atmosphere and (2) drill-hole free air, create the concentration gradients in both vertical and horizontal directions. In these directions, gaseous CO_2 migrates by diffusion under the different CO_2 diffusion coefficients in (1) bulk soil and (2) free air of the drill-hole. The vertical gradients in the soils should exceed the vertical gradient in the free air of the drill-hole. Therefore, the horizontal gradients between soils and air in the drill-hole/pore have diminished upwards and may turn their sign near the surface. This leads to CO_2 escaping horizontally through the drill-hole walls into the atmosphere. Because the diffusional flux depends on the diffusional area, CO_2 loss increases with the higher drill-hole diameters.

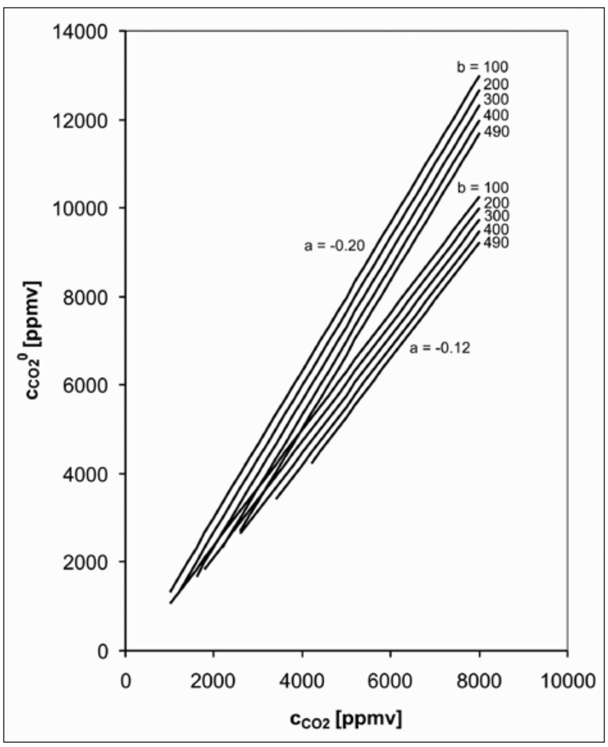

Fig. 4: Nomogram of the function $c_{CO2}{}^{0} = f(c_{CO2})$ for diameter D = 2 cm and different a, b parameters. See text for details.

As the conceptual model shows, CO_2 production, concentration gradients, and diffusional fluxes are fundamental for reaching steady state CO_2 concentrations in the given soil pore space. The input flux is responsible for the soil capacity to attain given concentration. However, soil permeability affects the output fluxes, which is important for establishing steady states. Because the soil capacity is limited for to preserving primordial concentrations in enlarged soil pores, it seems to be insufficient to reach the concentrations generally measured or deduced for the vadose zone (e.g., cave). Thus, these results

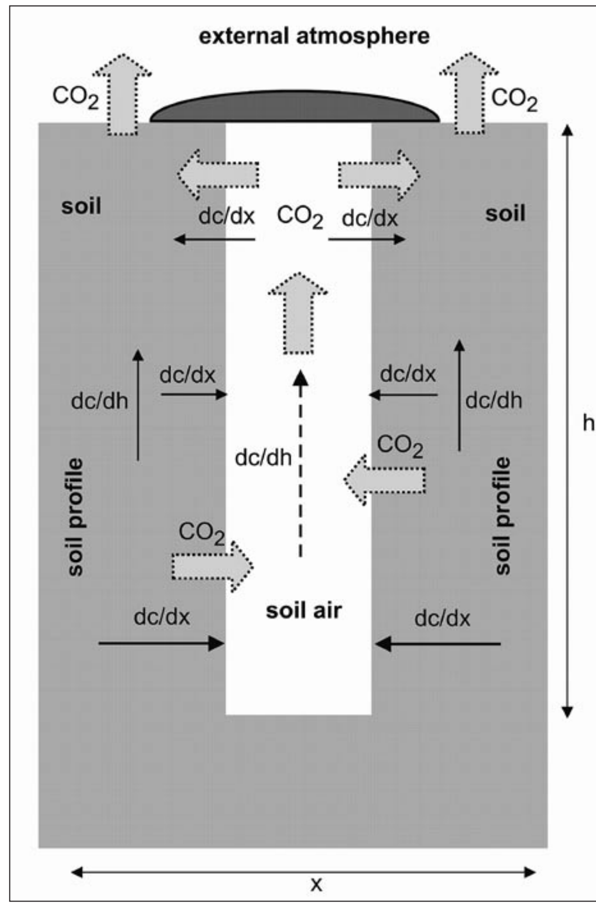

Fig. 5: Conceptual model of CO_2 concentration gradients and fluxes in soil profile.

re-open the hypothesis about an additional source of karst/cave CO_2 lying deeper in the epikarst.

CONCLUSIONS

Soil CO_2 was studied in the Moravian Karst (Czech Republic). It was proved that the CO_2 concentrations in common karst soils (developed at field, meadow, and deciduous forest) depend negatively on drill-hole diameter and, thus, on the dimension of pores in the soil profile. In contrast, this dependence was just unconvincing in case of the loamy soils of deciduous forest.

The work generally indicated a low capability of shallow karst soils to fill bigger pores in soil profile by CO_2. This re-opens the question how such limited source could be sufficient to fill up more voluminous and well-vented caves, as it is generally believed. The work supports the idea of a deeper-laying epikarstic source of gaseous CO_2 that is involved in the basic karst processes.

The results represent a preliminary study that maps the former problems. Further studies are necessary to explain better both the sources and behavior of karst CO_2. From a technical point of view, this work simply shows a systematical negative error in determination of soil CO_2 concentrations by a direct measuring in drill-holes and offers the possibility of calibration. The findings of this research may be of interest to karsologists, speleologists, and environmentalists.

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