

# Isotopic composition of carbon in atmospheric air; use of a diffusion model at the water/atmosphere interface in Velenje Basin

## Izotopska sestava ogljika v atmosferskem zraku in difuzijski model na fazni meji voda/atmosfera v Velenjskem bazenu

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*Ključne besede:* atmosferski ogljikov dioksid, ogljikovi izotopi, fazna meja zrak/voda, difuzijski model, Velenjski bazen, termoelektrarna, antropogeni vpliv

### Abstract

CO<sub>2</sub> concentrations (partial pressure of CO<sub>2</sub>, pCO<sub>2</sub>), and isotope compositions of carbon dioxide in air ( $\delta^{13}\text{C}_{\text{CO}_2}$ ), temperature (T) and relative humidity (H) have been measured in the atmosphere in the Velenje Basin. Samples were collected monthly in the calendar year 2011 from 9 locations in the area where the largest thermal power plant in Slovenia with the greatest emission of CO<sub>2</sub> to the atmosphere (around 4M t/year) is located. Values of pCO<sub>2</sub> ranged from 239 to 460 ppm with an average value of 294 ppm, which is below the average atmospheric CO<sub>2</sub> pressure (360 ppm).  $\delta^{13}\text{C}_{\text{CO}_2}$  ranged from -18.0 to -6.4 ‰, with an average value of -11.7 ‰. These values are similar to those measured in Wrocław, Poland. We performed the comparison of  $\delta^{13}\text{C}_{\text{CO}_2}$  values in atmospheric air with Wrocław since researchers used similar approach to trace  $\delta^{13}\text{C}_{\text{CO}_2}$  around anthropogenic sources. The isotopic composition of dissolved inorganic carbon ( $\delta^{13}\text{C}_{\text{DIC}}$ ) in rivers and lakes from the Velenje basin changes seasonally from -13.5 to -7.1‰. The values of  $\delta^{13}\text{C}_{\text{DIC}}$  indicate the occurrence of biogeochemical processes in the surface waters, with dissolution of carbonates and degradation of organic matter being the most important. A concentration and diffusion model was used to calculate the time of equilibration between dissolved inorganic carbon in natural sources (rivers) and atmospheric CO<sub>2</sub>.

### Izvleček

Ta študija opisuje rezultate analize koncentracij CO<sub>2</sub> v zraku (parcialni tlak CO<sub>2</sub>, pCO<sub>2</sub>) in izotopske sestave ogljika v atmosferskem zraku ( $\delta^{13}\text{C}_{\text{CO}_2}$ ), temperature (T) in relativne vlažnosti (H) v atmosferi iz Velenjskega bazena. Vzorce smo vzorčili mesečno na 9 lokacijah v koledarskem letu 2011 na območju Velenjskega bazena, kjer je locirana največja termoelektrarna v Sloveniji, ki predstavlja največjega proizvajalca emisij CO<sub>2</sub> v atmosfero (okoli 4 Mt/leto). Koncentracije pCO<sub>2</sub> v zraku se v času te študije spreminjajo od 239 do 460 ppm. Merjene povprečne koncentracije pCO<sub>2</sub> v naši študiji znašajo 294 ppm in so pod povprečnim atmosferskim tlakom CO<sub>2</sub>, ki znaša 360 ppm. Merjena  $\delta^{13}\text{C}_{\text{CO}_2}$  se spreminja od -18,0 do -6,4 ‰ s povprečno vrednostjo  $\delta^{13}\text{C}_{\text{CO}_2}$  -11,7 ‰. Vrednosti atmosferskega CO<sub>2</sub> in  $\delta^{13}\text{C}_{\text{CO}_2}$  so v času te raziskave podobne vrednostim objavljenim za Wrocław, Poljska. Naredili smo primerjavo z  $\delta^{13}\text{C}_{\text{CO}_2}$  vrednostmi v atmosferskem zraku z Wrocławom, ker so raziskovalci uporabili podoben pristop sledenja  $\delta^{13}\text{C}_{\text{CO}_2}$  vrednosti okrog antropogenih virov. Izotopska sestava raztopljenega anorganskega ogljika ( $\delta^{13}\text{C}_{\text{DIC}}$ ) v rekah in jezerih Velenjskega bazena se je v letu 2011 sezonsko spreminjala od -13,5 do -7,1 ‰. Vrednosti  $\delta^{13}\text{C}_{\text{DIC}}$  odražajo biogeokemijske procese v površinskih vodah, med katerimi sta najpomembnejša raztapljanje karbonatov in razgradnja organske snovi. Izdelali smo tudi koncentracijski in izotopski difuzijski model za izračun časa uravnoteženja med atmosferskim CO<sub>2</sub> in raztopljenim CO<sub>2</sub> na rečnih točkah.

### Introduction

Investigation of the fate of atmospheric CO<sub>2</sub> is central to efforts to measure and predict global anthropogenic changes and to assess the impact of fossil fuel usage on environmental quality (EEA, 1998, 2003). Analyses of the concentration and anisotropic composition

of atmospheric CO<sub>2</sub> have been carried out to assess their anthropogenic impact (KUC et al., 2003; LONGINELLI & SELMO, 2005; PATAKI et al., 2005; ZIMNOCH et al., 2004). In the atmospheric boundary layer, the concentration and carbon isotope composition of atmospheric CO<sub>2</sub> ( $\delta^{13}\text{C}_{\text{CO}_2}$ ) is determined by the mixing of tropospheric air with locally derived air that is affected by

anthropogenic and/or biogenic  $\text{CO}_2$  sources and sinks (ZIMNOCH et al., 2004). Biogenic  $\text{CO}_2$  originates from plant respiration and from heterogenic soil microbes which convert soil organic matter to  $\text{CO}_2$ . Because  $^{12}\text{C}$  is taken up preferentially by plants during photosynthesis, soils are lower in  $^{13}\text{C}$  than the atmosphere (BOWLING et al., 2008). Where C3 vegetation (e.g. Filipendulion (with dominant and characteristic species *Filipendula ulmaria* (L.) Maxim.) and Bidention (species from genera *Bidens* L., *Rorippa* Scop., *Chenopodium* L., *Polygonum* L.,...), *Fagus sylvatica* L., *Picea abies* (L.) Karst., *Abies alba* P. Mill.) dominates, as is the case for the studied area, soil organic matter and  $\text{CO}_2$  respired by vegetation exhibit  $\delta^{13}\text{C}$  values between  $-28$  and  $-20$  ‰ (SZARAN, 2002). Values of  $\delta^{13}\text{C}_{\text{CO}_2}$  derived from burning fossil fuels (anthropogenic sources) range from  $-40.5$  (natural gas burning fumes) to  $-24.6$  ‰ (coal burning fumes) (WIDORY & JAVOY, 2003). Combustion of coal produces almost twice as much carbon dioxide per unit of energy as does the combustion of natural gas, while the amount from the combustion of crude oil falls in between (Energy Information Administration, Emissions of Greenhouse Gases in the United States 1985-1990 (DOE/EIA-0573)). In the vegetative season the anthropogenic input is minimized and the biological input is dominant (LONGINELLI & SEMO, 2005). Values of  $\delta^{13}\text{C}_{\text{CO}_2}$  and  $\text{pCO}_2$  in the atmosphere have also been used to determine pollution levels in the atmosphere (ZWOŹDZIAK et al., 2010).

Concentrations of dissolved inorganic carbon, DIC, and its isotopic composition ( $\delta^{13}\text{C}_{\text{DIC}}$ ) in freshwater environments have been widely investigated (AMIOTTE-SUCHET et al., 1999; ATEKWANA & KRISHNAMURTHY, 1998; MARFIA et al., 2004; KANDUČ et al., 2007) and groundwater/surface water interactions, with evaluation of

biogeochemical processes, have been reported for Velenje Basin (KANDUČ et al., 2010, KANDUČ et al., 2014).

Here we report measurements of  $\text{pCO}_2$  (partial pressure) and  $\delta^{13}\text{C}_{\text{CO}_2}$  in the vicinity of the Šoštanj thermal plant which is the biggest emitter of  $\text{CO}_2$  to the atmosphere in Slovenia. Thus, around 4 Mt of  $\text{CO}_2$  are emitted (EMEP/EEA, 2013) into the atmosphere per year. The aim of this study was 1) to measure monthly air concentrations of  $\text{pCO}_2$  and to measure  $\delta^{13}\text{C}_{\text{CO}_2}$  in air to determine the influence of the combustion of lignite on  $\text{pCO}_2$  concentrations and to define the origin of the  $\text{CO}_2$  in the air masses in Velenje Basin, 2) to compare  $\text{pCO}_2$  concentrations and  $\delta^{13}\text{C}$  in air with published data (Wroclaw between 1<sup>st</sup> January and 31<sup>st</sup> December 2008) and 3) using the concentration and isotope diffusion model to calculate the time of equilibration of  $\text{CO}_2$  needed to equilibrate concentrations of  $\text{pCO}_2$  and  $\delta^{13}\text{C}_{\text{DIC}}$  values between air/water interface.

## Materials and methods

Partial pressure of  $\text{CO}_2$  ( $\text{pCO}_2$ ) in the atmosphere was measured above surface water at 9 locations (Figure 1) in Velenje Basin, using an IAQ-CALC Indoor Air Quality Meter, Model 7545, Thrust Science Innovation (TSI) with an accuracy of  $\pm 3$  % of reading or  $\pm 50$  ppm. Air samples for measurement of the carbon isotope composition in carbon dioxide in air ( $\delta^{13}\text{C}_{\text{CO}_2}$ ) were sampled as follows: a Labco ampoule (4 ampoules per location) was opened in the windward direction to let it fill with air. After filling (about 2 minutes), the ampoule was immediately closed and transported to the laboratory for prompt analysis of carbon isotope composition ( $\delta^{13}\text{C}_{\text{CO}_2}$ ). Air for  $\delta^{13}\text{C}_{\text{CO}_2}$  analysis was sampled 2 m above surface water. At the same locations, relative humidity (H), and

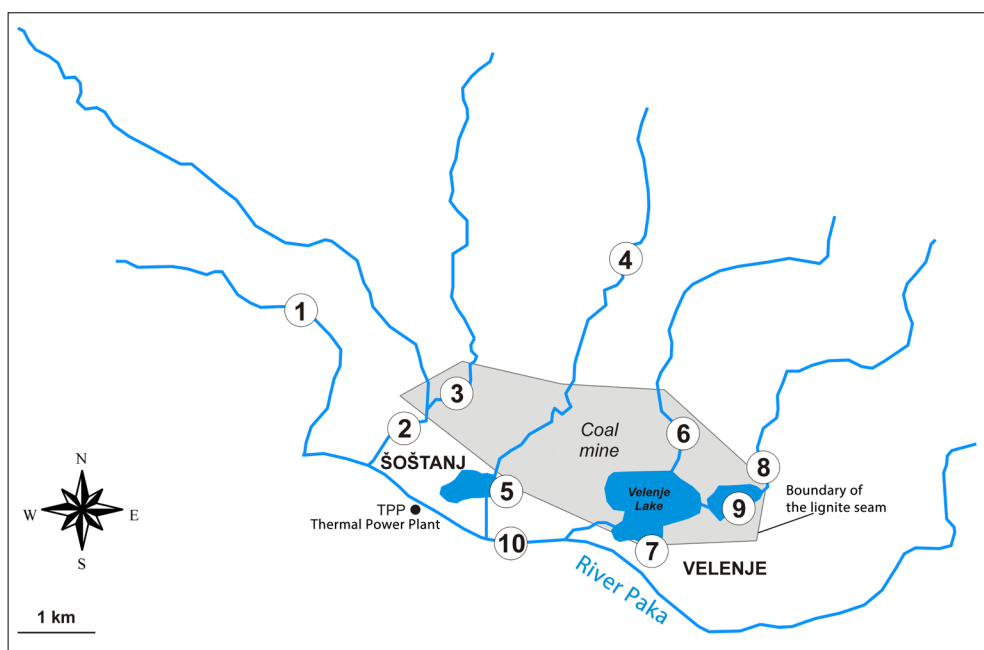


Figure 1. Sampling locations (10 locations) from Velenje Basin area (river locations: 1, 2, 3, 4, 6 and 8, lake locations: 5, 7, 9).

temperature (T), in the air were measured monthly during the year 2011.  $\delta^{13}\text{C}_{\text{CO}_2}$  in air was measured with a Europa Scientific 20-20 continuous flow IRMS ANCA-TG preparation module with an estimated precision of  $\pm 0.3$  ‰. Working standards calibrated to VPDB (Vienna Pee Dee Belemnite) were used during measurements with a defined value of  $-3.2$  ‰ for  $\text{CO}_2$ . Since  $\text{CO}_2$  concentrations in air are very low, working standards were diluted to air  $\text{CO}_2$  concentrations to optimize peak area. At the same locations surface water samples (additionally at location 3, which was not sampled for  $\delta^{13}\text{C}_{\text{CO}_2}$  air measurements) were collected seasonally for  $\delta^{13}\text{C}_{\text{DIC}}$  measurements (Table 1, Figure 1).

Surface waters (lakes and rivers) were measured at 10 locations for alkalinity and  $\delta^{13}\text{C}_{\text{DIC}}$  (Figure 1). Discharge data were obtained from the Slovenian Environment Agency for the gauging stations: Paka at Šoštanj, Gaberke at Velunja and Lepena at Škale (INTERNET). Total alkalinity of surface waters was measured according to Gran (GIESKES, 1974). The stable isotope content of dissolved inorganic carbon ( $\delta^{13}\text{C}_{\text{DIC}}$ ) in surface waters (lakes and rivers) was determined on an IsoPrime GV isotope ratio mass spectrometer coupled with a MultiflowBio preparation module.

Phosphoric acid (100%) was added (100-200  $\mu\text{l}$ ) to a septum tube and then purged with pure He. A water sample (1 ml) was then injected into the tube and  $\text{CO}_2$  measured directly from the headspace. Two standard solutions of  $\text{Na}_2\text{CO}_3$  (Carlo Erba and Scientific Fisher), with known  $\delta^{13}\text{C}_{\text{DIC}}$  values of  $-10.8 \pm 0.2$  ‰ and  $-4.8 \pm 0.2$  ‰, were used to calibrate  $\delta^{13}\text{C}_{\text{DIC}}$  measurements (SPÖTL 2005; KANDUČ et al., 2007). When sampling surface waters,  $\text{pCO}_2$  immediately above the surface water was measured in an open system and in a closed system.  $\text{pCO}_2$  was measured in a closed system above water as follows. A cardboard box with a surface area of  $36 \text{ cm}^2$  and a probe for  $\text{pCO}_2$  measurements (IAQ-CALC Indoor Air Quality Meter, Model 7545, Thrust Science Innovation (TSI)) was placed through a hole in a cardboard box and, after 10 minutes (GÖRKA et al., 2011) of equilibration between water and air phase,  $\text{pCO}_2$  (partial pressure of  $\text{CO}_2$ ) was read.

## Results and discussion

Atmospheric data: relative humidity (H), temperature (T),  $\delta^{13}\text{C}_{\text{CO}_2}$  and  $\text{pCO}_2$  in calendar year 2011 with notes on weather conditions are presented in Table 1. Locations from 1-10 are labeled in Figure 1.

Table 1. Sampling locations with sampling dates, air temperature (T), relative humidity (H), and values of  $\text{pCO}_2$ ,  $\delta^{13}\text{C}_{\text{CO}_2}$  together with notes on weather conditions.

No.	Location	Date	T (°C)	H (%)	$\text{pCO}_2$ (ppm)	$\delta^{13}\text{C}_{\text{CO}_2}$ (‰)	NOTES
1	Toplica, 8h20	28.1.2011	10.5	52.8	350	-14.0	sunny
1	Toplica, 8h30	30.3.2011	21.0	26.6	305	-11.9	sunny
1	Toplica, 8h25	19.4.2011	20.8	22.7	290	-11.2	sunny
1	Toplica, 8h22	19.5.2011	26.4	36.1	272	-12.3	sunny
1	Toplica, 8h23	16.6.2011	31.1	41.0	250	-10.6	sunny
1	Toplica, 8h26	18.7.2011	21.2	78.0	285	-13.9	showers
1	Toplica, 8h27	26.8.2011	29.1	46.3	297	-12.7	sunny
1	Toplica, 8h28	15.9.2011	26.3	33.9	266	-12.0	sunny
1	Toplica, 8h35	29.9.2011	18.2	56.3	294	-12.4	sunny
1	Toplica, 8h38	10.10.2011	14.5	45.4	295	-8.1	sunny, after snow
2	Pečovnica, 8h40	28.1.2011	6.5	59.8	360	-10.9	sunny
2	Pečovnica, 8h50	30.3.2011	22.0	30.7	316	-12.5	sunny
2	Pečovnica, 8h45	19.4.2011	20.9	36.3	306	-9.3	sunny
2	Pečovnica, 8h42	19.5.2011	25.6	39.0	272	-12.9	sunny
2	Pečovnica, 8h43	16.6.2011	31.4	38.2	270	-11.0	sunny
2	Pečovnica, 8h46	18.7.2011	21.0	75.9	296	-13.1	showers
2	Pečovnica, 8h47	26.8.2011	31.0	38.5	303	-11.6	sunny
2	Pečovnica, 8h48	15.9.2011	22.4	37.6	255	-10.9	sunny
2	Pečovnica, 8h40	29.9.2011	17.5	55.1	303	-11.3	sunny
2	Pečovnica, 8h55	10.10.2011	12.6	45.3	297	-9.9	sunny, after snow
2	Pečovnica, 8h58	11.11.2011	9.0	53.0	309	-13.0	sunny
4	Velunja, 9h00	28.1.2011	8.8	55.4	333	-12.1	sunny
4	Velunja, 9h10	10.3.2011	17.4	32.4	316	-12.5	sunny
4	Velunja, 9h05	30.3.2011	21.6	31.3	294	-12.1	sunny
4	Velunja, 9h02	19.4.2011	21.4	21.5	300	-10.1	sunny
4	Velunja, 9h03	19.5.2011	25.7	36.6	272	-11.9	sunny

4 Velunja, 9h03	19.5.2011	25.7	36.6	272	-11.9	sunny
4 Velunja, 9h06	16.6.2011	35.0	37.4	239	-13.0	sunny
4 Velunja, 9h07	18.7.2011	21.1	76.0	294	-13.5	showers
4 Velunja, 9h08	26.8.2011	29.1	45.0	275	-11.3	sunny
4 Velunja, 9h10	15.9.2011	25.9	28.3	247	-11.5	sunny
4 Velunja, 9h15	29.9.2011	18.9	46.0	280	-9.5	sunny
4 Velunja, 9h20	11.11.2011	8.0	55.0	270	-11.1	sunny
5 Šoštanjško jezero, 9h20	28.1.2011	9.1	54.0	330	-10.4	sunny
5 Šoštanjško jezero, 9h30	10.3.2011	13.6	27.2	330	-11.5	sunny
5 Šoštanjško jezero, 9h25	30.3.2011	21.5	31.2	312	-11.9	sunny
5 Šoštanjško jezero, 9h22	19.4.2011	19.6	23.0	292	-11.3	sunny
5 Šoštanjško jezero, 9h23	19.5.2011	28.5	27.0	270	-10.5	sunny
5 Šoštanjško jezero, 9h26	16.6.2011	29.0	47.8	255	-11.0	sunny
5 Šoštanjško jezero,9h27	18.7.2011	21.3	77.1	303	-12.0	showers
5 Šoštanjško jezero, 9h28	26.8.2011	28.4	38.0	280	-11.3	sunny
5 Šoštanjško jezero, 9h30	15.9.2011	30.8	27.9	269	-10.2	sunny
5 Šoštanjško jezero, 9h35	29.9.2011	19.9	51.7	320	-10.8	sunny
5 Šoštanjško jezero, 9h40	10.10.2011	8.3	65.9	290	-15.6	sunny, after snow
5 Šoštanjško jezero, 9h45	11.11.2011	7.7	53.9	311	-12.3	sunny
6 Ljubela, 9h40	28.1.2011	8.6	51.8	320	-11.9	sunny
6 Ljubela, 9h50	10.3.2011	16.5	21.0	314	-12.0	sunny
6 Ljubela, 9h45	30.3.2011	20.0	30.0	299	-13.0	sunny
6 Ljubela, 9h42	19.4.2011	19.2	30.3	289	-9.5	sunny
6 Ljubela, 9h 43	19.5.2011	23.5	38.2	270	-10.5	sunny
6 Ljubela, 9h46	16.6.2011	29.4	31.4	242	-10.5	sunny
6 Ljubela, 9h47	18.7.2011	20.7	72.4	290	-11.8	showers
6 Ljubela, 9h48	26.8.2011				-12.0	sunny
6 Ljubela, 9h 50	15.9.2011	27.6	34.5	252	-12.0	sunny
6 Ljubela, 9h 55	29.9.2011	21.3	47.3	283	-12.3	sunny
6 Ljubela, 10h00	10.10.2011	8.2	66.3	280	-7.7	sunny, after snow
6 Ljubela, 10h05	11.11.2011	9.9	54.0	250	-11.1	sunny
7 Velenjsko jezero, 10h00	28.1.2011	9.2	54.5	328	-9.4	sunny
7 Velenjsko jezero,10h10	10.3.2011	15.3	20.2	316	-11.1	sunny
7 Velenjsko jezero, 10h05	30.3.2011	22.3	31.5	299	-12.8	sunny
7 Velenjsko jezero, 10h12	19.4.2011	19.2	31.9	295	-11.7	sunny
7 Velenjsko jezero, 10h13	19.5.2011	26.6	36.5	271	-10.5	sunny
7 Velenjsko jezero, 10h16	16.6.2011	35.0	37.4	239	-10.7	sunny
7 Velenjsko jezero,10h08	18.7.2011	22.1	71.8	289	-12.0	showers
7 Velenjsko jezero, 10h20	15.9.2011	27.3	31.5	249	-12.5	sunny
7 Velenjsko jezero, 10h40	29.9.2011	10.2	54.1	300	-10.7	sunny
7 Velenjsko jezero, 11h00	10.10.2011	10.2	54.1	300	-9.5	sunny, after snow
7 Velenjsko jezero,11h20	11.11.2011	9.5	55.2	260	-18.0	sunny
8 Lepena,10h20	28.1.2011	12.9	44.2	335	-12.4	sunny
8 Lepena,10h30	10.3.2011	16.2	18.0	316	-11.5	sunny
8 Lepena,10h25	30.3.2011	24.8	28.8	309	-13.5	sunny
8 Lepena,10h32	19.4.2011	20.0	21.6	290	-10.7	sunny
8 Lepena,10h33	19.5.2011	25.6	36.8	262	-10.3	sunny
8 Lepena,10h36	16.6.2011	31.4	35.2	244	-12.5	sunny
8 Lepena, 10h28	18.7.2011	21.0	77.2	285	-12.4	showers
8 Lepena, 11h00	26.8.2011	31.1	31.0	271	-12.0	sunny
8 Lepena, 11h20	15.9.2011	27.3	28.7	246	-11.9	sunny
8 Lepena,11h40	29.9.2011	20.6	50.5	282	-11.6	sunny
8 Lepena,12h00	10.10.2011	11.3	50.4	298	-9.0	sunny, after snow
8 Lepena, 12h20	11.11.2011	9.2	52.2	316	-12.2	sunny

9 Škalsko jezero, 10h40	28.1.2011	6.3	66.2	328	-15.0	sunny
9 Škalsko jezero, 10h50	10.3.2011	17.8	23.2	326	-11.7	sunny
9 Škalsko jezero, 10h45	30.3.2011	22.6	27.7	298	-12.7	sunny
9 Škalsko jezero, 11h05	19.4.2011	19.0	29.8	291	-14.5	sunny
9 Škalsko jezero, 11h25	19.5.2011	26.5	37.6	262	-10.1	sunny
9 Škalsko jezero, 11h45	16.6.2011	31.6	35.8	251	-10.5	sunny
9 Škalsko jezero, 12h05	18.7.2011	21.3	74.5	283	-11.9	showers
9 Škalsko jezero, 12h25	26.8.2011	30.2	45.6	270	-11.5	sunny
9 Škalsko jezero, 12h45	15.9.2011	29.7	27.7	272	-12.7	sunny
9 Škalsko jezero, 13h05	29.9.2011	22.0	47.1	285	-11.6	sunny
9 Škalsko jezero, 13h25	10.10.2011	7.4	63.3	293	-8.9	sunny, after snow
9 Škalsko jezero, 13h45	11.11.2011	8.9	53.6	317	-17.9	sunny
10 Paka, at 8h10	28.1.2011	5.6	70.0	330	-12.1	sunny
10 Paka, at 8h20	10.3.2011	11.6	31.0	360	-11.4	sunny
10 Paka, at 8h10	30.3.2011	20.1	29.8	323	-13.8	sunny
10 Paka, at 8h05	19.4.2011	19.7	25.6	305	-9.5	sunny
10 Paka, at 8h02	19.5.2011	24.2	42.3	293	-11.9	sunny
10 Paka, at 8h03	16.6.2011	28.8	40.1	266	-10.5	sunny
10 Paka, at 8h06	18.7.2011	20.0	63.5	333	-13.5	showers
10 Paka, at 8h07	26.8.2011	28.1	53.0	460	-14.9	sunny
10 Paka, at 8h08	15.9.2011	25.7	39.0	267	-13.0	sunny
10 Paka, at 8h15	29.9.2011	17.2	65.9	333	-12.0	sunny
10 Paka, at 8h18	10.10.2011	12.6	37.6	318	-6.4	sunny, after snow
10 Paka, at 8h19	11.11.2011	10.0	53.4	314	-12.3	sunny

Air temperature ranged from 5.6 to 35.0 °C during 2011 (Figure 2A). Relative humidity ranged from 18.0 to 78.0 % with an average value of 43.6 % (Figure 2B).

CO<sub>2</sub> concentration in the atmosphere, expressed in [ppm] as pCO<sub>2</sub> and carbon isotope signatures of carbon dioxide in the atmosphere ( $\delta^{13}\text{C}_{\text{CO}_2}$ ) from the Velenje Basin indicate seasonal variation (Figures 3A and B). Partial pressures (pCO<sub>2</sub>) in the atmosphere from 9 different locations range from

239 to 460 ppm – average 294 ppm. The lowest pCO<sub>2</sub> value was recorded at Velunja location and the maximum value at Paka River (Figure 3A). The values of  $\delta^{13}\text{C}_{\text{CO}_2}$  range from -18 to -6.4 ‰, depending on the source (Figure 3 B). The  $\delta^{13}\text{C}_{\text{CO}_2}$  values that approach -6.4 ‰ (location Paka, South Preloge mine) could reflect bacterial CO<sub>2</sub> and/or endogenic CO<sub>2</sub> from underground coalmine activity (LAZAR et al., 2014), while values approaching -18 ‰ (Škalsko and Velenjsko jezero in November 2011) could be attributed to anthropogenic

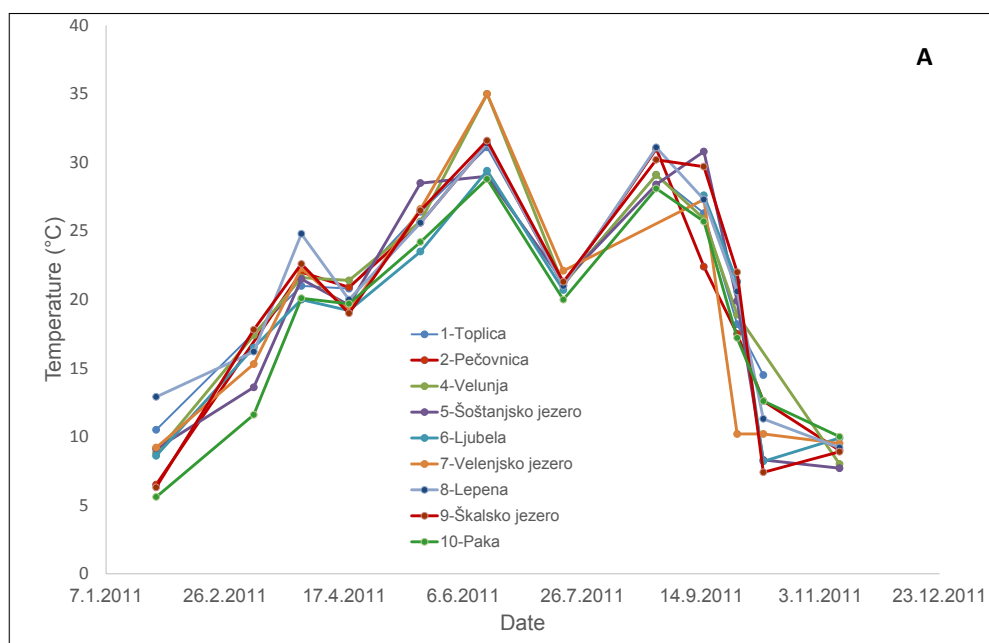


Figure 2A. Air temperature in the calendar year 2011.



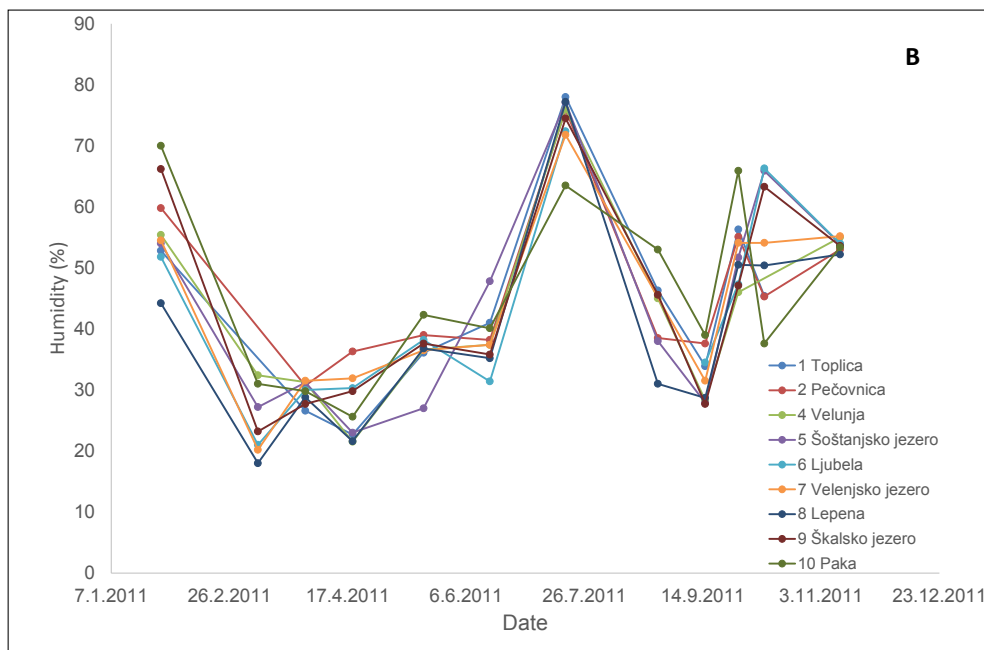


Figure 2B. Humidity in the calendar year 2011. Numbers from 1–10 refer to sampling locations. At location 3 only surface water was sampled.

pollution and natural sources (Figure 3 B). For comparison, the concentration of atmospheric  $\text{CO}_2$  at the pristine river Kamniška Bistrica source was 355 ppm and  $\delta^{13}\text{C}_{\text{CO}_2}$  value  $-9\text{‰}$  in different sampling seasons in 2011 (KANDUČ, unpublished data). The concentrations of  $\text{pCO}_2$  and  $\delta^{13}\text{C}_{\text{CO}_2}$  values reported in this study for Velenje basin are similar to those reported for southern Poland (KUC et al., 2003; ZIMNOCH et al., 2004) (Figure 4). Comparison with Wrocław, Poland was performed since their study was focused on investigation of isotopic composition of carbon in air ( $\delta^{13}\text{C}_{\text{CO}_2}$ ) around anthropogenic sources in relation with other air parameters. The unpolluted  $\delta^{13}\text{C}_{\text{CO}_2}$  value (around  $-8\text{‰}$ ) is taken from Baltic Sea values (WHITE & VAUGHN, 2009) and the  $\delta^{13}\text{C}_{\text{CO}_2}$  values of respiration of C3 plants from PATAKI et al., 2003. In a coal burning chimney,  $\delta^{13}\text{C}_{\text{CO}_2}$  values are  $-24.1\text{‰}$ , exhaust from a gasoline propelled car has values of  $\delta^{13}\text{C}_{\text{CO}_2}$  of  $-31.7\text{‰}$ , from a diesel car  $-31.9\text{‰}$  and from a liquid petroleum gas car  $-33.5\text{‰}$  (GÓRKA et al., 2011). The characteristic value of  $\delta^{13}\text{C}_{\text{CO}_2}$  for a coal-burning chimney is  $-24.1\text{‰}$  and is much lower in comparison to  $\delta^{13}\text{C}_{\text{CO}_2}$  values in our study, where  $\delta^{13}\text{C}_{\text{CO}_2}$  ranges from  $-18.0$  to  $-6.4\text{‰}$  (Table 1).

No correlation was obtained between the following parameters measured in the atmosphere for different locations and in different seasons in Velenje Basin:  $\text{pCO}_2$  vs.  $\delta^{13}\text{C}_{\text{CO}_2}$  ( $R^2=0.0292$ ), H vs.  $\text{pCO}_2$  ( $R^2=0.0324$ ),  $\text{pCO}_2$  vs.  $\delta^{13}\text{C}_{\text{CO}_2}$  ( $R^2=0.0292$ ), T vs.  $\text{pCO}_2$  ( $R^2=0.2644$ ), T vs.  $\delta^{13}\text{C}_{\text{CO}_2}$  ( $R^2=0.0008$ ). Similarly no significant regression was obtained between measured quantities in air (daily temperature vs. humidity, CO concentration,  $\text{CO}_2$  concentration,  $\delta^{13}\text{C}_{\text{CO}_2}$ ) for Wrocław (GÓRKA et al., 2011).

Seasonal variations of total alkalinity,  $\delta^{13}\text{C}_{\text{DIC}}$  and  $\text{pCO}_2$  (ppm) in surface waters, with  $\text{pCO}_2$  (closed system, measurements with cardboard box) measured and  $\text{pCO}_2$  measured just above surface water during year 2011 are presented in

Table 2. Discharge data (Q) were obtained from the Slovenian Environmental Agency gauging stations for the year 2011 for locations Velunja, Lepena and Paka.

Alkalinity in surface waters changes seasonally from 2.2 to 5.7 mM in January 2011, from 2.6 to 5.5 mM in May 2011, from 2.5 to 6.1 mM in August 2011 and from 2.5 to 5.7 mM in October 2011.  $\delta^{13}\text{C}_{\text{DIC}}$  changes seasonally from  $-11.0$  to  $-8.8\text{‰}$  in January 2011, from  $-11.8$  to  $-7.7\text{‰}$  in May 2011, from  $-13.5$  to  $-7.1\text{‰}$  in August 2011 and from  $-12.8$  to  $-9.1\text{‰}$  in October 2011 (Table 2). Higher  $\delta^{13}\text{C}_{\text{DIC}}$  values would be expected in lake water (standing water) since it equilibrates more quickly than surface water (running water), but it is only the case in lake Velenje ( $\delta^{13}\text{C}_{\text{DIC}} = -7.7\text{‰}$  in spring season). The opposite trend is observed between  $\delta^{13}\text{C}_{\text{DIC}}$  and alkalinities (Figure 5A), with the lowest  $\delta^{13}\text{C}_{\text{DIC}}$  value and the highest alkalinity being observed at location Pečovnica (location 2) in January 2011.

Since surface water is an open system, its equilibration with the atmosphere is important. Equilibration lines (Figure 5A) were calculated according to possible biogeochemical processes influencing  $\delta^{13}\text{C}_{\text{DIC}}$  value as follows:

Line 1. Given the isotopic composition of atmospheric  $\text{CO}_2$  of  $-7.8\text{‰}$  (LEVIN et al., 1987) and the equilibration fractionation with DIC of  $+9\text{‰}$ , DIC in equilibrium with the atmosphere should have a  $\delta^{13}\text{C}_{\text{DIC}}$  of about  $+1\text{‰}$ .

Line 2. Considering the average isotopic composition of carbonates ( $\delta^{13}\text{C}_{\text{CaCO}_3}$ ) with a value of  $-2\text{‰}$  (KANDUČ & PEZDIČ, 2005) and isotopic fractionation (and enrichment in  $^{12}\text{C}$ ) due to dissolution of carbonates, which is  $1.0\pm 0.2\text{‰}$  (ROMANEK et al., 1992),  $\delta^{13}\text{C}_{\text{DIC}}$  would be  $-3.0\pm 0.2\text{‰}$ .

Table 2. Carbon species in surface waters (alkalinity,  $\delta^{13}\text{C}_{\text{DIC}}$ ,  $\text{pCO}_2$  air-opened system,  $\text{pCO}_2$  water/air closed system), discharge data ( $\text{m}^3/\text{s}$ ) and surface water temperature ( $^\circ\text{C}$ ) in the year 2011.

Numbers	Locations	Date of sampling	Q ( $\text{m}^3/\text{s}$ )	T ( $^\circ\text{C}$ )	Alkalinity (mM)	$\delta^{13}\text{C}_{\text{DIC}}$ (‰)	$\text{pCO}_2$ air, opened system (ppm)	$\text{pCO}_2$ water/air, closed system (ppm)
1	Toplica	January, 2011		8.6	3.6	-10.4	355	357
2	Pečovnica	January, 2011		2.1	2.2	-10.2	360	356
3	Klančnica	January, 2011						
4	Velunja	January, 2011	0.633	2.0	3.0	-8.8	357	357
5	Šoštanjско jezero	January, 2011		1.2	2.7	-11.0		
6	Ljubela	January, 2011		3.0	5.4	-10.1	361	
7	Velenjsko jezero	January, 2011		2.2	3.2	-9.8	363	
8	Lepena	January, 2011	0.063	3.0	5.7	-10.4	364	355
9	Škalsko jezero	January, 2011		0.7	5.4	-11.0	363	
10	Paka	January, 2011	2.79	2.6	4.4	-10.1	360	363
Numbers	Locations	Date of sampling	Q ( $\text{m}^3/\text{s}$ )	T ( $^\circ\text{C}$ )	Alkalinity (mM)	$\delta^{13}\text{C}_{\text{DIC}}$ (‰)	$\text{pCO}_2$ air, opened system (ppm)	$\text{pCO}_2$ water/air, closed system (ppm)
1	Toplica	May, 2011		16.5	3.6	-9.9	362	365
2	Pečovnica	May, 2011		14.0	3.0	-10.4	404	425
3	Klančnica	May, 2011		16.5	2.9	-11.8	370	388
4	Velunja	May, 2011	0.431	15.8	2.9	-8.9	362	362
5	Šoštanjско jezero	May, 2011		20.2	2.6	-9.1	368	368
6	Ljubela	May, 2011		16.0	5.1	-10.3	358	370
7	Velenjsko jezero	May, 2011		19.6	3.4	-7.7	361	351
8	Lepena	May, 2011	0.052	17.1	5.5	-10.3	387	353
9	Škalsko jezero	May, 2011		20.9	4.9	-8.4	350	356
10	Paka	May, 2011	2.05	14.1	4.1	-9.9	402	389
Numbers	Locations	Date of sampling	Q ( $\text{m}^3/\text{s}$ )	T ( $^\circ\text{C}$ )	Alkalinity (mM)	$\delta^{13}\text{C}_{\text{DIC}}$ (‰)	$\text{pCO}_2$ air opened system (ppm)	$\text{pCO}_2$ water/air, closed system (ppm)
1	Toplica	August, 2011		16.2	4.8	-10.4	360	362
2	Pečovnica	August, 2011		16.7	6.1	-13.1	358	360
3	Klančnica	August, 2011		23.3	2.5	-7.0	355	367
4	Velunja	August, 2011	0.37	16.7	3.4	-7.8	400	408
5	Šoštanjско jezero	August, 2011		16.7	4.6	-12.6	395	396
6	Ljubela	August, 2011		23.3	4.2	-7.7	350	353
7	Velenjsko jezero	August, 2011		16.4	3.1	-11.0	365	370
8	Lepena	August, 2011	0.04	16.4	3.6	-13.5	375	378
9	Škalsko jezero	August, 2011		17.5	3.8	-11.3	360	364
10	Paka	August, 2011	1.86	24.0	2.5	-7.1	350	355
Numbers	Locations	Date of sampling	Q ( $\text{m}^3/\text{s}$ )	T ( $^\circ\text{C}$ )	Alkalinity (mM)	$\delta^{13}\text{C}_{\text{DIC}}$ (‰)	$\text{pCO}_2$ air opened system (ppm)	$\text{pCO}_2$ water/air, closed system (ppm)
1	Toplica	October, 2011		9.3	4.0	-12.5	408	420
2	Pečovnica	October, 2011		6.3	2.5	-12.1	421	450
3	Klančnica	October, 2011			3.2			
4	Velunja	October, 2011	0.37	7.8	3.1	-11.3	388	390
5	Šoštanjско jezero	October, 2011		9.1	3.3	-10.3	386	395
6	Ljubela	October, 2011		7.5	5.1	-12.3	386	400
7	Velenjsko jezero	October, 2011		11.6	2.9	-9.1	386	400
8	Lepena	October, 2011	0.03	7.5	5.7	-12.8	396	402
9	Škalsko jezero	October, 2011		10.4	5.2	-12.1	386	400
10	Paka	October, 2011	1.55	6.7	4.5	-11.0	460	480

Line 3. An average  $\delta^{13}\text{C}$  value of  $-26.6$  ‰ for particulate organic carbon (POC) was assumed to represent the isotopic composition of POC that was transferred to DIC by in-stream respiration. Open system equilibration of DIC with  $\text{CO}_2$  enriches DIC in  $^{13}\text{C}$  by about 9 ‰ (Mook et al., 1974), which corresponds to a value of  $-17.6$  ‰.

Line 4 represents open system equilibration of DIC, with soil  $\text{CO}_2$  originating from degradation of organic matter with  $\delta^{13}\text{C}_{\text{CO}_2}$  of  $-26.6$  ‰.

From Figure 5A it is observed that most of the samples fall between lines 2 and 3: dissolution of carbonates with an average  $\delta^{13}\text{C}_{\text{CaCO}_3} = -2$  ‰ and non-equilibrium carbonate dissolution with carbonic acid produced from soil zone with  $\delta^{13}\text{C}_{\text{CO}_2}$  of  $-26.6$  ‰. The highest  $\text{pCO}_2$  is observed at location Paka (location 10) with a value of 460 ppm (open system),  $\text{pCO}_2$  measured value is 480 ppm (measured as a closed system) in October 2011 probably due to higher degradation of organic matter at the end of the summer season. Elevated  $\text{pCO}_2$  concentrations are also recorded at

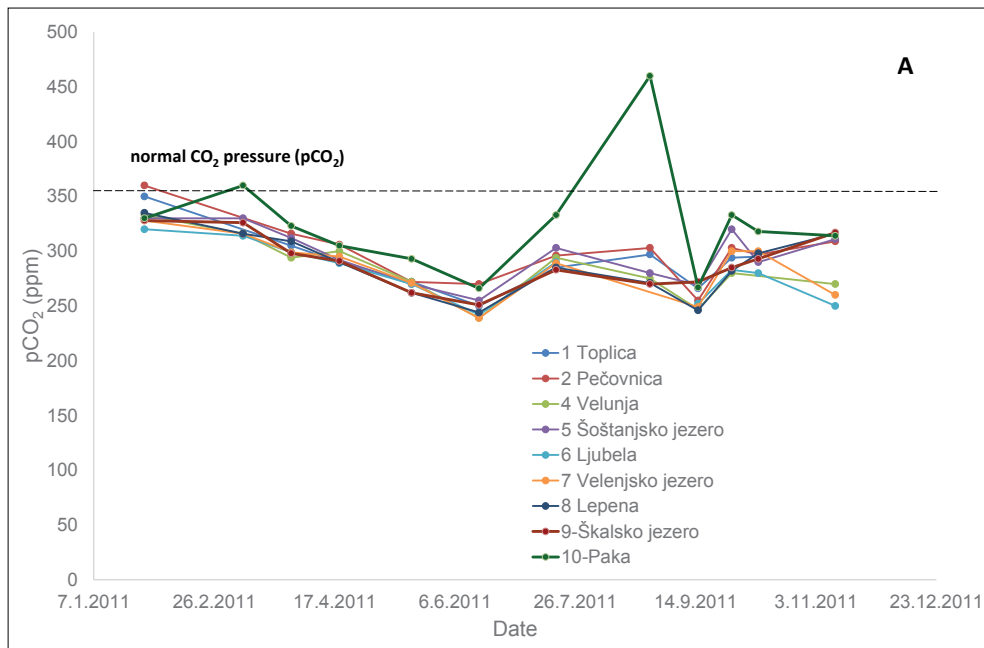


Figure 3A.  $p\text{CO}_2$  (partial pressure in air) in the calendar year 2011.

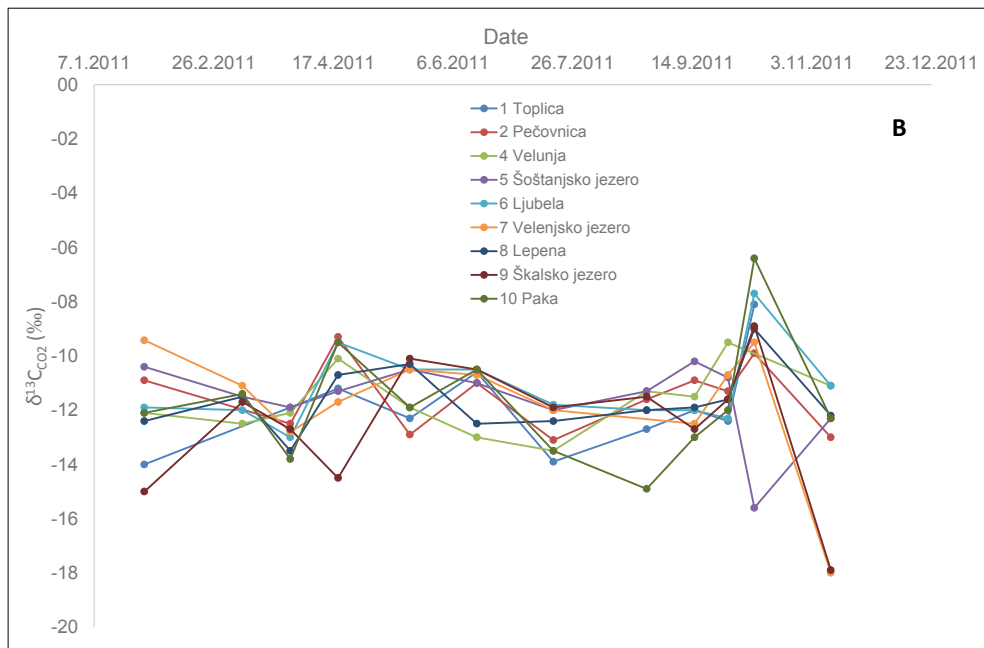


Figure 3B.  $\delta^{13}\text{C}_{\text{CO}_2}$  in the calendar year 2011. Numbers from 1–10 refer to sampling locations. At location 3 only surface water was sampled.

Pečovnica (location 2) with value of 404 ppm in surface water measured in opened system above water and 425 ppm as measured in closed system (in cardboard box) May 2011 (Figure 5B).

### Calculation of fluxes

The  $\text{CO}_2$  flux between surface water and the atmosphere  $[\text{DIC}]_{\text{ex}}$  based on a diffusion model (two layer model in which the molecules are transported through a gas film and a liquid layer adjacent to the surface) can be calculated according to the following equation (BROECKER, 1974):

$$[\text{DIC}]_{\text{ex}} = \frac{D}{z} \cdot ([\text{CO}_2]_{\text{eq}} - [\text{CO}_2]) \quad (1)$$

where  $D$  is the  $\text{CO}_2$  diffusion coefficient in water with value of  $1.26 \times 10^{-5} \text{ cm}^2/\text{s}$  at a temperature of  $10^\circ\text{C}$  and  $1.67 \times 10^{-5} \text{ cm}^2/\text{s}$  at a temperature of  $20^\circ\text{C}$  (JÄHNE et al., 1987),  $z$  is the empirical thickness of the liquid layer [cm],  $[\text{CO}_2]_{\text{eq}}$  and  $[\text{CO}_2]$  are the concentrations of dissolved  $\text{CO}_2$  at equilibrium with the atmosphere and with the studied water  $[\text{mol} \cdot \text{cm}^{-3}]$ , respectively. The thickness of the boundary layer  $z$ , a thin film existing at the air-water interface, depends largely on wind velocity (BROECKER et al., 1978) and water turbulence (HOLLEY, 1977).  $D/z$ , therefore, is the gas exchange rate, which gives the height of the water column that will equilibrate with the atmosphere per unit time. Using a mean wind speed of 4 m/s in all sampling seasons (JÄHNE et al., 1987),  $D/z$  was estimated to be 8 cm/h under low turbulence conditions, 28 cm/h under moderate turbulence conditions and 115 cm/h under high turbulence conditions.



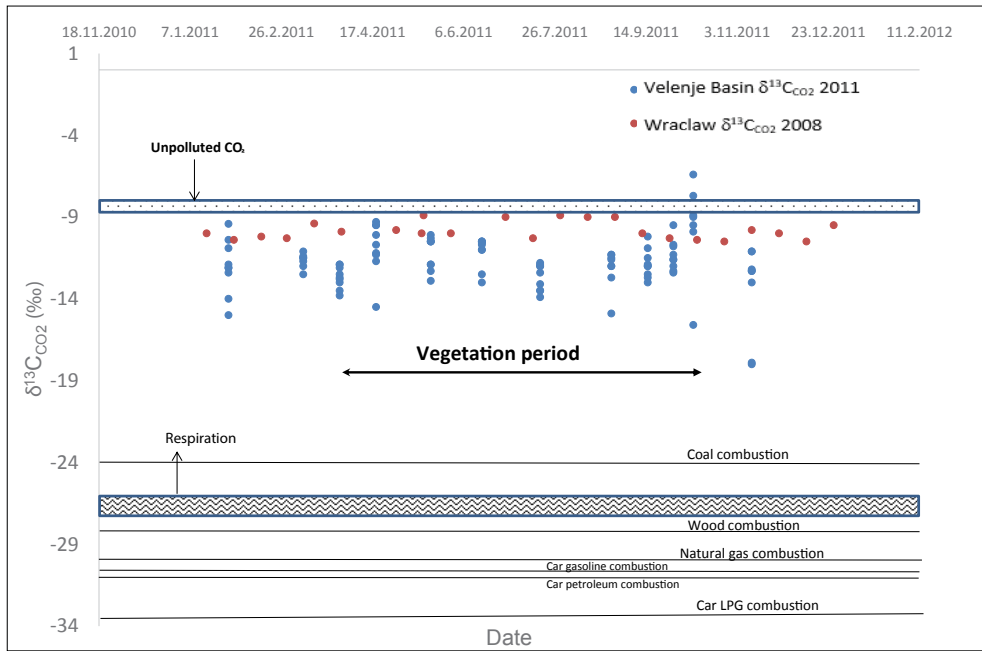


Figure 4.  $\delta^{13}\text{C}_{\text{CO}_2}$  levels in the calendar year 2011 compared with those at Wrocław (GÓRKA et al., 2011). Bold lines indicate the potential anthropogenic sources analyzed in Wrocław (GÓRKA et al., 2011). The  $\delta^{13}\text{C}_{\text{CO}_2}$  value characteristic for the absence of pollution is taken from Baltic Sea values (WHITE & VAUGHN, 2009) and  $\delta^{13}\text{C}_{\text{CO}_2}$  values characteristic for C3 plants respiration from PATAKI et al., 2003.

Calculation of the  $\text{CO}_2$  flux between the river water surface and the atmosphere at the Paka River gauging station, according to equation (1), gives values ranging from  $2.6 \times 10^{-8}$  to  $9.0 \times 10^{-8}$  mol/cm<sup>2</sup>h in spring 2011, from  $6.0 \times 10^{-8}$  to  $20 \times 10^{-8}$  mol/cm<sup>2</sup>h in late summer 2011 and from  $2.7 \times 10^{-8}$  to  $9.4 \times 10^{-8}$  mol/cm<sup>2</sup>h in winter 2011. Taking into consideration the river surface area of 0.40 km<sup>2</sup> (mean width of 10 m and length of 40 km), the total loss of inorganic carbon through its surface in the spring ranges from  $6.0 \times 10^4$  mol/day during periods of low wind speeds to  $2.0 \times 10^5$  mol/day during high turbulence storm events. The predicted total loss of inorganic carbon to the atmosphere in the late summer ranges from  $1.0 \times 10^5$  to  $5.0 \times 10^5$  mol/day and from  $6.0 \times 10^4$  to  $2.1 \times 10^5$  mol/day in winter.

### Concentration diffusion model

In addition, values of the time evolution of stream  $\text{pCO}_2$  and  $\delta^{13}\text{C}_{\text{DIC}}$  were calculated using available diffusion models (e.g. BROECKER 1974; RICHEY et al. 1990; AUCOUR et al., 1999). These calculations yield the amount of time needed for  $\text{CO}_2$  evasion and for stream – atmosphere isotopic exchange relative to the transit time of stream waters. Such calculations were performed only for two main tributaries: Velunja River (location 4) and Paka River (location 10) for all sampling seasons (Figure 1, Table 2). The estimated rate of change of DIC concentration due to  $\text{CO}_2$  evasion are calculated by:

$$\frac{d[\text{DIC}]}{dt} = \frac{D}{zh} \cdot ([\text{CO}_2]_{\text{eq}} - [\text{CO}_2]) \quad (2)$$

and the DIC concentration in water is expressed as a function of time by:

$$[\text{DIC}] = [\text{CO}_2]_{\text{eq}} - ([\text{CO}_2]_{\text{eq}} - [\text{CO}_2]_0) \cdot e^{-\frac{D}{zh}t} \quad (3)$$

where  $h$  is the mean depth of the river [cm] and  $t$  is the time needed for equilibration [min], all other parameters having been determined by equation (1). The calculations assume a value of 8 cm/h for  $D/z$  (low turbulent conditions due to low discharge) for both locations (4 and 10) (MOOK, 1970) and  $h$  values of 10 cm. The computed results, according to equation (3), show that between 0.6 and 2.6 hours (January, 2011), 8.8 and 9.2 hours (May, 2011), 5.7 and 6.4 hours (August, 2011), and from 5.7 to 6.4 hours (October, 2011) would be required for equilibrium between atmospheric  $\text{CO}_2$  and dissolved riverine  $\text{CO}_2$  to be approached.

### Isotopic diffusion model

Additionally, the rate of change of  $\delta^{13}\text{C}_{\text{DIC}}$  resulting from  $\text{CO}_2$  exchange between the river and the atmosphere was also estimated by the equation (AUCOUR et al., 1999):

$$\frac{d\delta^{13}\text{C}_{\text{DIC}}}{dt} = \frac{D[\text{CO}_2]_{\text{eq}}}{zh[\text{DIC}]} \cdot (\delta^{13}\text{C}_a - \delta^{13}\text{C}_{\text{DIC}} + \varepsilon) \quad (4)$$

Again, the DIC concentration ([DIC]) is expressed as a function of time (t) by:

$$\delta^{13}\text{C}_{\text{DIC}} = (\delta^{13}\text{C}_a - \varepsilon) - (\delta^{13}\text{C}_a - \varepsilon - \delta^{13}\text{C}_{\text{DIC},0}) \cdot e^{-\frac{D[\text{CO}_2]_{\text{eq}}}{zh[\text{DIC}]}t} \quad (5)$$

In equations (4) and (5),  $\delta^{13}\text{C}_a$  and  $\delta^{13}\text{C}_{\text{DIC}}$  are the  $\delta^{13}\text{C}$  values of atmospheric  $\text{CO}_2$  (-7.8 ‰; LEVIN et al., 1987) and DIC,  $\delta^{13}\text{C}_0$  is the initial value of DIC and  $\varepsilon$  is the equilibrium fractionation factor between  $\text{CO}_2$  and  $\text{HCO}_3^-$  (ZHANG et al., 1995).

Starting with the  $\delta^{13}\text{C}_{\text{DIC}}$  value of -12.5 ‰ (AUCOUR et al., 1999) and  $h$  value of 10 cm, calculated time of equilibration ranged from 26.2 to 132.6 hours, which would be needed to equilibrate  $\delta^{13}\text{C}_{\text{DIC}}$  and  $\delta^{13}\text{C}_{\text{CO}_2}$  values. This time interval was calculated for Velunja River

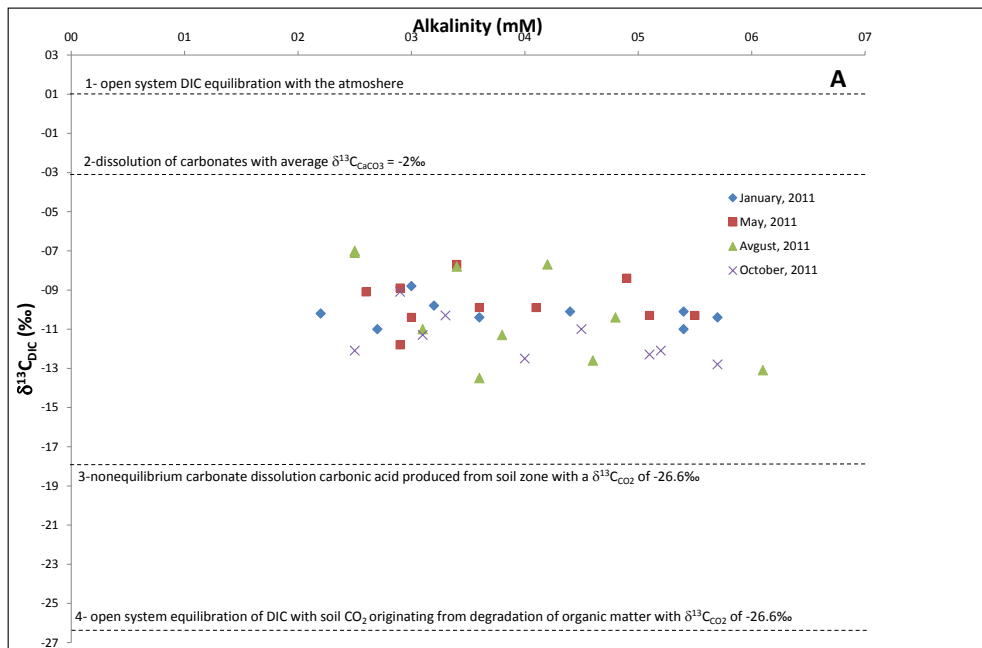


Figure 5A.  $\delta^{13}\text{C}_{\text{DIC}}$  values of surface water samples as a function of alkalinity, with lines indicating processes occurring in surface waters in Velenje Basin. Arrows show expected trends for a variety of biogeochemical processes (COETSIERS & WALRAEVENS, 2009).

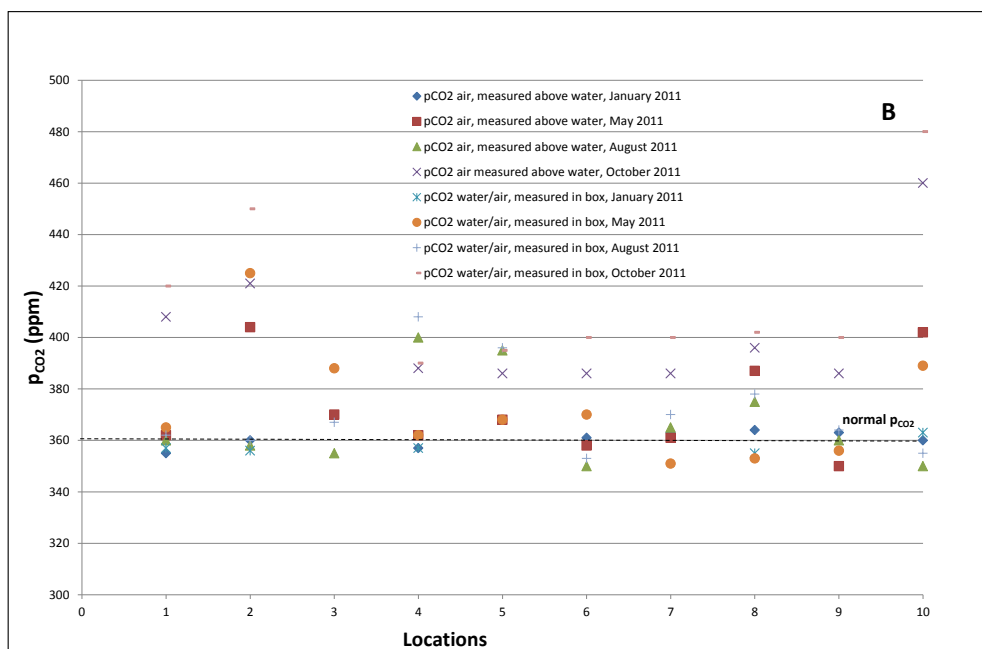


Figure 5B. Seasonal variation of  $\text{pCO}_2$ , comparison between  $\text{pCO}_2$  air (open system) and  $\text{pCO}_2$  water/air (closed system) at 9 locations from Velenje Basin. Normal  $\text{pCO}_2$  in air is considered to be 360 ppm.

(location 4) and Paka River (location 10) and suggests that stream – atmosphere isotopic exchange alone cannot explain the  $^{13}\text{C}$  enrichment of DIC in this carbonate/clastics catchment. Stream – atmosphere isotopic exchange alone cannot explain the  $^{13}\text{C}$  enrichment of DIC since longer time is needed for equilibration than expected. Both models (concentration and isotopic) should provide same values of time of equilibration, but in our case they do not. However, it has been shown that equilibration of  $\text{CO}_2$  between water/air boundaries is more significant in impermeable silicate drainages (KANDUČ et al., 2007). Therefore equilibration of atmospheric  $\text{CO}_2$  does not influence the value of  $\delta^{13}\text{C}_{\text{DIC}}$  in surface waters significantly, which is a consequence of low discharge conditions in the catchment area.

## Conclusions

Values of the carbon isotope composition of atmospheric  $\text{CO}_2$  ( $\delta^{13}\text{C}_{\text{CO}_2}$ ), at locations in the vicinity of the thermal power plant in Velenje Basin, have been measured in the calendar year 2011. Based on measurements of alkalinity and  $\delta^{13}\text{C}_{\text{DIC}}$  for surface water, values of  $\delta^{13}\text{C}_{\text{CO}_2}$  of air samples taken just above water (opened system) and from a closed cardboard box (closed system) it is concluded that combustion of lignite in thermal power plant has little influence on the  $\delta^{13}\text{C}_{\text{CO}_2}$  value in the atmosphere. Measured  $\text{CO}_2$  concentrations (average  $\text{pCO}_2$  value of 294 ppm) and  $\delta^{13}\text{C}_{\text{CO}_2}$  in the atmosphere in the vicinity (few kilometers) of the thermal power plant are in the normal range in the atmosphere (360 ppm) and the influence of lignite combustion is negligible

at the locations investigated in this study. The values of  $\delta^{13}\text{C}_{\text{CO}_2}$  in air range from -18 to -6.4 ‰, with an average value of -11.7 ‰, indicating the absence of influence of coal combustion, since the characteristic value of coal combustion is -24.1 ‰.  $\delta^{13}\text{C}_{\text{CO}_2}$  values in our study (observations during year 2011) are similar as obtained for Wrocław, Poland (observation during year 2008).

The total alkalinity in surface waters ranged from 2.2 to 6.1 mM. Dissolution of carbonates and degradation of organic matter are the most important biogeochemical processes affecting  $\delta^{13}\text{C}_{\text{DIC}}$ . They range seasonally from -13.5 to -7.1 ‰ in the surface waters (lakes, rivers) investigated in this study.  $\text{pCO}_2$  in the air immediately above water (open system) and in the air above the water, measured in the cardboard box (closed system), is similar at all measured locations. The highest  $\text{pCO}_2$  in an open system – immediately above water – and in a closed system (measured in a box) were measured at Paka (location 10) and Pečovnica (location 2) in May 2011 and in October 2011, respectively. Both locations are located in the vicinity of the thermal power plant. Based on thermodynamic modelling and on previous studies reported for Slovenian watersheds (rivers and lakes), surface waters acted like sources of  $\text{CO}_2$  (oversaturated more than 10 times) released to the atmosphere. However, the measurements of  $\text{pCO}_2$  reported here were made just above the surface water, where normal values of  $\text{pCO}_2$  (around 360 ppm) are present.

Two diffusion models (concentration and isotopic) were applied to obtain the time of equilibration at two locations. Between 0.6 and 6.4 hours were required to equilibrate atmospheric  $\text{CO}_2$  and dissolved riverine DIC (concentration diffusion model), and 26.2 to 132.6 hours to equilibrate  $\delta^{13}\text{C}_{\text{DIC}}$  and  $\delta^{13}\text{C}_{\text{CO}_2}$  values (isotopic diffusion model) if equilibration with atmospheric  $\text{CO}_2$  was the only factor influencing DIC values of surface waters.

Even though Velenje Basin is a natural analogue with very large amounts of endogenic and bacterial  $\text{CO}_2$  (with the characteristic value of  $\delta^{13}\text{C}_{\text{CO}_2} \sim 2$  ‰) and with large amounts of  $\text{CO}_2$  emitted (around 4 Mt/year) from lignite combustion from the thermal power plant, we conclude from this study that  $\text{pCO}_2$  concentrations in air around the thermal power plant are not elevated.

#### Acknowledgements

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