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

Tjaša KANDUČ
Jožef Stefan Institute, Jamova cesta 39, SI–1000 Ljubljana, Slovenia; e-mail: tjasa.kanduc@ijs.si

Prejeto / Received 7. 4. 2015; Sprejeto / Accepted 5. 6. 2015

Key words: atmospheric carbon dioxide, carbon isotopes, phase boundary air/water, diffusion model, Velenje Basin, thermal power plant, anthropogenic influence

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

Abstract

CO₂ concentrations (partial pressure of CO₂, pCO₂, and isotope compositions of carbon dioxide in air (δ¹³CCO₂), 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 CO₂ to the atmosphere (around 4M t/year) is located. Values of pCO₂ ranged from 239 to 460 ppm with an average value of 294 ppm, which is below the average atmospheric CO₂ pressure (360 ppm). δ¹³C_CO₂ ranged from -18.0 to -6.4 ‰, with an average value of -11.7 ‰. These values are similar to those measured in Wroclaw, Poland. We performed the comparison of δ¹³CCO₂ values in atmospheric air with Wroclaw since researchers used similar approach to trace δ¹³CCO₂ around anthropogenic sources. The isotopic composition of dissolved inorganic carbon (δ¹³C_DIC) in rivers and lakes from the Velenje basin changes seasonally from -13.5 to -7.1‰. The values of δ¹³C_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 CO₂.

Izvleček

Ta študija opisuje rezultate analize koncentracij CO₂ v zraku (parcialni tlak CO₂, pCO₂) in izotopske sestave ogljika v atmosferskem zraku (δ¹³C_CO₂), 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 največja proizvajalca emisij CO₂ v atmosfero (okoli 4 Mt/leto). Koncentracije pCO₂ v zraku se v času te študije spremenjajo od 239 do 460 ppm. Merjene povprečne koncentracije pCO₂ v naši študiji znašajo 294 ppm in so pod povprečnim atmosferskim tlakom CO₂, ki znaša 360 ppm. Merjena δ¹³C_CO₂ se spremnja od -18,0 do -6,4 ‰ s povprečno vrednostjo δ¹³C_CO₂ -11.7 ‰. Vrednosti atmosferskega CO₂ in δ¹³C_CO₂ so v času te raziskave podobne vrednostim objavljenim za Wroclaw, Poljska. Naredili smo primerjavo z vrednostmi CO₂ v atmosferskem zraku z Wroclawom, ker so raziskovalci uporabili podoben pristop sledenja δ¹³C_CO₂ vrednosti okrog antropogenih virov. Izotopska sestava raztopljenega anorganskega ogljika (δ¹³C_DIC) v rekah in jezerih Velenjskega bazena je v letu 2011 sezonsko spremenjala od -13.5 do -7.1 ‰. Vrednosti δ¹³C_DIC odražajo biogeokemijske procese v površinskih vodah, med katerimi sta najpomembnejša raztapljanje carbonatov in razgradnja organske snovi. Izdelali smo tudi koncentracijski in izotopski difuzijski model za izračun časa uravnoteženja med atmosferskim CO₂ in raztopljenim CO₂ na rečnih tečkah.

Introduction

Investigation of the fate of atmospheric CO₂ 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 CO₂ 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 CO₂ (δ¹³C_CO₂) is determined by the mixing of tropospheric air with locally derived air that is affected by
anthropogenic and/or biogenic CO₂ sources and sinks (ZIMNOCH et al., 2004). Biogenic CO₂ originates from plant respiration and from heterogenic soil microbes which convert soil organic matter to CO₂. Because ¹²C is taken up preferentially by plants during photosynthesis, soils are lower in ¹³C 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 CO₂ respired by vegetation exhibit δ¹³C values between -28 and -20 ‰ (SZARAN, 2002). Values of δ¹³C 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 δ¹³C in air with published data (Wroclaw between 1st January and 31st December 2008) and 3) using the concentration and isotope diffusion model to calculate the time of equilibration of CO₂ needed to equilibrate concentrations of pCO₂ and δ¹³C values between air/water interface.

Materials and methods

Partial pressure of CO₂ (pCO₂) 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 ±3 % of reading or ±50 ppm. Air samples for measurement of the carbon isotope composition in carbon dioxide in air (δ¹³C) 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 (δ¹³C). Air for δ¹³C 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. $\delta^{13}C_{\text{CO}_2}$ 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 CO$_2$ concentrations in air are very low, working standards were diluted to air CO$_2$ concentrations to optimize peak area. At the same locations surface water samples (additionally at location 3, which was not sampled for $\delta^{13}C_{\text{CO}_2}$ air measurements) were collected seasonally for $\delta^{13}C_{\text{DIC}}$ measurements (Table 1, Figure 1).

Surface waters (lakes and rivers) were measured at 10 locations for alkalinity and $\delta^{13}C_{\text{DIC}}$ (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 ($\delta^{13}C_{\text{DIC}}$) 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 µl) to a septum tube and then purged with pure He. A water sample (1 ml) was then injected into the tube and CO$_2$ measured directly from the headspace. Two standard solutions of Na$_2$CO$_3$ (Carlo Erba and Scientific Fisher), with known $\delta^{13}C_{\text{DIC}}$ values of $-10.8 \pm 0.2 \%$ and $-4.8 \pm 0.2 \%$, were used to calibrate $\delta^{13}C_{\text{DIC}}$ measurements (SPÖTL 2005, KANDUC et al., 2007). When sampling surface waters, pCO$_2$ immediately above the surface water was measured in an open system and in a closed system. pCO$_2$ was measured in a closed system above water as follows. A cardboard box with a surface area of 36 cm$^2$ and a probe for 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, pCO$_2$ (partial pressure of CO$_2$) was read.

**Results and discussion**

Atmospheric data: relative humidity (H), temperature (T), $\delta^{13}C_{\text{CO}_2}$ and 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 pCO$_2$, $\delta^{13}C_{\text{CO}_2}$ together with notes on weather conditions.

| No. | Location   | Date       | T (°C) | H (%) | pCO$_2$ (ppm) | $\delta^{13}C_{\text{CO}_2}$ (%) | 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          |
| Place                  | Date          | Time | Temperature | Humidity | Pressure | Wind Speed | Weather Description |
|------------------------|---------------|------|-------------|----------|----------|------------|---------------------|
| 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      |

... (remaining entries)
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).

CO₂ concentration in the atmosphere, expressed in [ppm] as pCO₂ and carbon isotope signatures of carbon dioxide in the atmosphere (δ¹³C_CO₂) from the Velenje Basin indicate seasonal variation (Figures 3A and B). Partial pressures (pCO₂) in the atmosphere from 9 different locations range from 239 to 460 ppm – average 294 ppm. The lowest pCO₂ value was recorded at Velunja location and the maximum value at Paka River (Figure 3A). The values of δ¹³C_CO₂ range from -18 to -6.4 ‰, depending on the source (Figure 3 B). The δ¹³C_CO₂ values that approach -6.4 ‰ (location Paka, South Preloge mine) could reflect bacterial CO₂ and/or endogenic CO₂ from underground coalmine activity (Lazar et al., 2014), while values approaching -18 ‰ (Škalsko and Velenjsko jezero in November 2011) could be attributed to anthropogenic

| Date          | Air temperature (°C) | Humidity (%) | Air pressure (ppm) | Notes          |
|---------------|---------------------|--------------|-------------------|----------------|
| 28.1.2011     | 5.6                 | 70.0         | 330               | sunny          |
| 10.3.2011     | 11.6                | 31.0         | 360               | sunny          |
| 30.3.2011     | 20.1                | 29.8         | 323               | sunny          |
| 19.4.2011     | 19.7                | 25.6         | 305               | sunny          |
| 19.5.2011     | 24.2                | 42.3         | 293               | sunny          |
| 16.6.2011     | 28.8                | 40.1         | 266               | sunny          |
| 18.7.2011     | 20.0                | 63.5         | 333               | showers        |
| 26.8.2011     | 28.1                | 53.0         | 460               | sunny          |
| 15.9.2011     | 25.7                | 39.0         | 267               | sunny          |
| 29.9.2011     | 17.2                | 65.9         | 333               | sunny          |
| 10.10.2011    | 12.6                | 37.6         | 318               | sunny, after snow |
| 11.11.2011    | 10.0                | 53.4         | 314               | sunny          |

Figure 2A. Air temperature in the calendar year 2011.
pollution and natural sources (Figure 3 B). For comparison, the concentration of atmospheric CO₂ at the pristine river Kamniška Bistrica source was 355 ppm and δ¹³C CO₂ value -9 ‰ in different sampling seasons in 2011 (KANDUČ, unpublished data). The concentrations of pCO₂ and δ¹³C CO₂ values reported in this study for Velenje basin are similar to those reported for southern Poland (Kuc et al., 2003; Žemrnoch et al., 2004) (Figure 4). Comparison with Wroclaw, Poland was performed since their study was focused on investigation of isotopic composition of carbon in air (δ¹³C CO₂) around anthropogenic sources in relation with other air parameters. The unpolluted δ¹³C CO₂ value (around -8 ‰) is taken from Baltic Sea values (White & Vaughn, 2009) and the δ¹³C CO₂ values of respiration of C₃ plants from Pataki et al., 2003. In a coal burning chimney, δ¹³C CO₂ values are -24.1 ‰, exhaust from a gasoline propelled car has values of δ¹³C CO₂ of -31.7 ‰, from a diesel car -31.9 ‰ and from a liquid petroleum gas car -33.5 ‰ (Gorška et al., 2011). The characteristic value of δ¹³C CO₂ for a coal-burning chimney is -24.1 ‰ and is much lower in comparison to δ¹³C CO₂ values in our study, where δ¹³C CO₂ ranges from -18.0 to -6.4 ‰ (Table 1).

No correlation was obtained between the following parameters measured in the atmosphere for different locations and in different seasons in Velenje Basin: pCO₂ vs. δ¹³C CO₂ (R²=0.0292), H vs. pCO₂ (R²=0.0324), pCO₂ vs δ¹³C CO₂ (R²=0.0292), T vs. pCO₂ (R²=0.2644), T vs. δ¹³C CO₂ (R²=0.0008). Similarly no significant regression was obtained between measured quantities in air (daily temperature vs. humidity, CO concentration, CO₂ concentration, δ¹³C CO₂) for Wroclaw (Gorška et al., 2011).

Seasonal variations of total alkalinity, δ¹³C DIC and pCO₂ (ppm) in surface waters, with pCO₂ (closed system, measurements with cardboard box) measured and pCO₂ 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. The δ¹³C DIC changes seasonally from -11.0 to -8.8 ‰ in January 2011, from -11.8 to -7.7 ‰ in May 2011, from -13.5 to -7.1 ‰ in August 2011 and from -12.8 to -9.1 ‰ in October 2011 (Table 2). Higher δ¹³C 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 (δ¹³C DIC = -7.7 ‰ in spring season). The opposite trend is observed between δ¹³C DIC and alkalinitities (Figure 5A), with the lowest δ¹³C 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 δ¹³C DIC value as follows:

Line 1. Given the isotopic composition of atmospheric CO₂ of -7.8 ‰ (Levin et al., 1987) and the equilibration fractionation with DIC of +9 ‰, DIC in equilibrium with the atmosphere should have a δ¹³C DIC of about +1 ‰.

Line 2. Considering the average isotopic composition of carbonates (δ¹³C CaCO₃) with a value of -2 ‰ (Kanduč & Pezdič, 2005) and isotopic fractionation (and enrichment in ¹³C) due to dissolution of carbonates, which is 1.0±0.2 ‰ (Romanek et al., 1992), δ¹³C DIC would be -3.0±0.2 ‰.
Table 2. Carbon species in surface waters (alkalinity, $\delta^{13}C_{\text{DIC}}$, $pCO_2$, air-opened system, $pCO_2$, water/air closed system), discharge data (m$^3$/s) and surface water temperature (°C) in the year 2011.

| Numbers | Locations          | Date of sampling | $Q$ (m$^3$/s) | $T$ (°C) | Alkalinity (mM) | $\delta^{13}C_{\text{DIC}}$ (%) | $pCO_2$ air, opened system (ppm) | $pCO_2$ water/air, closed system (ppm) |
|---------|--------------------|------------------|---------------|---------|-----------------|-------------------------------|-----------------------------------|----------------------------------------|
| 1       | Toplica            | January, 2011    | 16.5          | 3.6     | -9.9            | 362                           | 365                               | 365                                    |
| 2       | Pečovnica          | January, 2011    | 14.0          | 3.0     | -10.4           | 404                           | 425                               | 425                                    |
| 3       | Klančnica          | January, 2011    | 16.5          | 2.9     | -11.8           | 370                           | 388                               | 388                                    |
| 4       | Velunja            | January, 2011    | 0.431         | 2.9     | -8.9            | 362                           | 362                               | 362                                    |
| 5       | Šoštanjko jezero    | May, 2011        | 19.6          | 5.1     | -10.3           | 358                           | 370                               | 370                                    |
| 6       | Ljubelica          | May, 2011        | 19.6          | 3.4     | -7.7            | 361                           | 351                               | 351                                    |
| 7       | Velenjsko jezero   | May, 2011        | 5.2           | 4.5     | -9.9            | 402                           | 389                               | 389                                    |
| 8       | Lepena             | May, 2011        | 17.1          | 5.5     | -10.3           | 387                           | 353                               | 353                                    |
| 9       | Škalsko jezero     | May, 2011        | 20.9          | 4.9     | -8.4            | 350                           | 356                               | 356                                    |
| 10      | Paka               | May, 2011        | 2.05          | 14.1    | -9.9            | 402                           | 389                               | 389                                    |

Line 3. An average $\delta^{13}C$ 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 CO$_2$ enriches DIC in $^{13}C$ 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 CO$_2$ originating from degradation of organic matter with $\delta^{13}C_{\text{CO}_2}$ 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 $\delta^{13}C_{\text{CaCO}_3}$ = -2 ‰ and non-equilibrium carbonate dissolution with carbonic acid produced from soil zone with $\delta^{13}C_{\text{CO}_2}$ of -26.6 ‰. The highest $pCO_2$ is observed at location Paka (location 10) with a value of 460 ppm (open system). $pCO_2$ 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 $pCO_2$ concentrations are also recorded at
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 CO₂ flux between surface water and the atmosphere $\Delta$DIC 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):

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

where $D$ is the CO₂ diffusion coefficient in water with value of $1.26 \times 10^{-5}$ cm²/s at a temperature of 10 °C and $1.67 \times 10^{-5}$ cm²/s at a temperature of 20 °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 CO₂ at equilibrium with the atmosphere and with the studied water [mol · 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.
Calculation of the CO₂ 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 x 10⁻⁸ to 9.0 x 10⁻⁸ mol/cm² h in spring 2011, from 6.0 x 10⁻⁸ to 20 x 10⁻⁸ mol/cm² h in late summer 2011 and from 2.7 x 10⁻⁸ to 9.4 x 10⁻⁸ mol/cm² h in winter 2011. Taking into consideration the river surface area of 0.40 km² (mean width of 10 m and length of 40 km), the total loss of inorganic carbon to the atmosphere in the late summer ranges from 1.0 x 10⁻⁵ to 2.0 x 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 x 10⁻⁵ to 5.0 x 10⁻⁵ mol/day and from 6.0 x 10⁻⁴ to 2.1 x 10⁻⁴ mol/day in winter.

**Concentration diffusion model**

In addition, values of the time evolution of stream pCO₂ and δ¹³C_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 CO₂ 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 CO₂ evasion are calculated by:

\[
\frac{d[DIC]}{dt} = \frac{D}{zh} ([CO₂]_{eq} - [CO₂]) \tag{2}
\]

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

\[
[DIC] = [CO₂]_{eq} - ([CO₂]_{eq} - [CO₂]_{in}) \cdot e^{-\frac{D}{zh}} \tag{3}
\]

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 CO₂ and dissolved riverine CO₂ to be approached.

**Isotopic diffusion model**

Additionally, the rate of change of δ¹³C_DIC resulting from CO₂ exchange between the river and the atmosphere was also estimated by the equation (AUCOUR et al., 1999):

\[
\frac{d\delta^{13}C_{DIC}}{dt} = \frac{D[C_{DIC}]_{eq}}{zh[DIC]} \cdot (\delta^{13}C_a - \delta^{13}C_{DIC} + \epsilon) \tag{4}
\]

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

\[
\delta^{13}C_{DIC} - (\delta^{13}C_a - \epsilon) - (\delta^{13}C_a - \epsilon - \delta^{13}C_{DIC,0}) \cdot e^{-\frac{D[C_{DIC}]_{eq}}{zh[DIC]}} \tag{5}
\]

In equations (4) and (5), δ¹³C_a and δ¹³C_DIC are the δ¹³C values of atmospheric CO₂ (-7.8 ‰; LEVIN et al., 1987) and DIC, δ¹³C is the initial value of DIC and \(\epsilon\) is the equilibrium fractionation factor between CO₂ and HCO₃⁻ (ZHANG et al., 1995).

Starting with the δ¹³C_DIC value of -12.5 ‰ (AUCOUR et al., 1999) and \(h\) value of 10 cm, calculated time of equilibration ranged from 26.2 to 32.6 hours, which would be needed to equilibrate δ¹³C_DIC and δ¹³C_CO₂ values. This time interval was calculated for Velunja River.
and Paka River and suggests that stream-atmosphere isotopic exchange alone cannot explain the $^{13}$C enrichment of DIC in this carbonate/clastics catchment. Stream-atmosphere isotopic exchange alone cannot explain the $^{13}$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 CO$_2$ between water/air boundaries is more significant in impermeable silicate drainages (KAndu et al., 2007). Therefore equilibration of atmospheric CO$_2$ does not influence the value of $\delta^{13}$C$_{DIC}$ in surface waters significantly, which is a consequence of low discharge conditions in the catchment area.

Figure 5A. $\delta^{13}$C$_{DIC}$ 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 (Cortesius & Walravens, 2009).

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

Values of the carbon isotope composition of atmospheric CO$_2$ ($\delta^{13}$C$_{CO2}$), 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 $\delta^{13}$C$_{DIC}$ for surface water, values of $\delta^{13}$C$_{CO2}$ 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 $\delta^{13}$C$_{CO2}$ value in the atmosphere. Measured CO$_2$ concentrations (average pCO$_2$ value of 294 ppm) and $\delta^{13}$C$_{CO2}$ 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.

Conclusions

(4) location 4) and Paka River (10) and suggests that stream – atmosphere isotopic exchange alone cannot explain the $^{13}$C enrichment of DIC in this carbonate/clastics catchment. Stream – atmosphere isotopic exchange alone cannot explain the $^{13}$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 CO$_2$ between water/air boundaries is more significant in impermeable silicate drainages (KAndu et al., 2007). Therefore equilibration of atmospheric CO$_2$ does not influence the value of $\delta^{13}$C$_{DIC}$ in surface waters significantly, which is a consequence of low discharge conditions in the catchment area.
at the locations investigated in this study. The values of δ13C\textsubscript{CO\textsubscript{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 %. δ13C\textsubscript{CO\textsubscript{2}} values in our study (observations during year 2011) are similar as obtained for Wroclaw, 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 δ13C\textsubscript{DIC}. They range seasonally from -13.5 to -7.1 % in the surface waters (lakes, rivers) investigated in this study. pCO\textsubscript{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 pCO\textsubscript{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 CO\textsubscript{2} (oversaturated more than 10 times) released to the atmosphere. However, the measurements of pCO\textsubscript{2} reported here were made just above the surface water, where normal values of pCO\textsubscript{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 CO\textsubscript{2} and dissolved riverine DIC (concentration diffusion model), and 26.2 to 132.6 hours to equilibrate δ13C\textsubscript{DIC} and δ13C\textsubscript{CO\textsubscript{2}} values (isotopic diffusion model) if equilibration with atmospheric CO\textsubscript{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 CO\textsubscript{2} (with the characteristic value of δ13C\textsubscript{CO\textsubscript{2}} ~ -2 %) and with large amounts of CO\textsubscript{2} emitted (around 4 Mt/year) from lignite combustion from the thermal power plant, we conclude from this study that pCO\textsubscript{2} concentrations in air around the thermal power plant are not elevated.

Acknowledgements

This study was conducted in the frame of national research projects funded by Slovenian Research Agency (ARRS) Z1-2052, L1-5451 and Programme research group P1-0143. Special thanks are given to Mr. Stojan Žigon for technical support in laboratory. Thanks also to Prof. Roger Pain for linguistic corrections.

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