DE GRUYTER OPEN
DOI: 10.1515/eces-2015-0029 ECOL CHEM ENG S. 2015;22(4):499-511

Stanisław CHMIEL[1*], Stanisław HAŁAS[2], Tomasz PIEŃKOS[2], Sławomir GŁOWACKI[1]
Ewa MACIEJEWSKA[1], Żaneta POLKOWSKA[3], Joanna SPOSÓB[1]
and Andrzej TREMBACZOWSKI[2]

# $CO_2$ EMISSION TO THE ATMOSPHERE FROM CARBONATE WATERS: THE STUDY CASE OF THE LUBLIN UPLAND AND ROZTOCZE REGIONS

## EMISJA $CO_2$ DO ATMOSFERY Z WÓD WĘGLANOWYCH NA PRZYKŁADZIE WYŻYNY LUBELSKIEJ I ROZTOCZA

**Abstract:** The concentration of carbon dioxide dissolved in water ($CO_{2(aq)}$) was measured in consecutive phases of the hydrological cycle. Its potentially possible degassing from groundwaters to the atmosphere was also assessed. The research was conducted in the area of occurrence of carbonate rocks of the Lublin Upland and Roztocze (SE Poland). The results of the measurements of $CO_{2(aq)}$ concentration varied as follows (min-max/mean): precipitation waters < 1-3/2.6 mg · dm$^{-3}$, soil waters 3-50/14.2 mg · dm$^{-3}$, groundwaters 10-70/30.3 mg · dm$^{-3}$, river waters < 1-21/7.6 mg · dm$^{-3}$. The measure of degassing of carbon dioxide from groundwaters to the atmosphere was a decrease in $CO_{2(aq)}$ concentration in fluvial outflow. Based on the value of groundwater outflow from the Lublin Upland and Roztocze, the annual carbon dioxide emission from waters to the atmosphere was calculated at a level of 50 thousand Mg · year$^{-1}$. This value constitutes approximately 1% of anthropogenic emission of carbon dioxide originating from environmentally harmful industrial plants in the Lublin province.

**Keywords:** groundwaters, rivers, carbon dioxide, degassing

# Introduction

Modern climatic changes are frequently considered by researchers as associated with the increasing content of so called greenhouse gases in the atmosphere [1]. The most

[1] Faculty of Earth Sciences and Spatial Management, Maria Curie-Skłodowska University, ul. Kraśnicka 2cd, 20-718 Lublin, Poland, phone +48 81 537 68 62, fax +48 81 537 68 62, email: stanislaw.chmiel@poczta.umcs.lublin.pl, slawek.glowacki@poczta.umcs.lublin.pl, joanna.sposob@poczta.umcs.lublin.pl, ewa.maciejewska@poczta.umcs.lublin.pl
[2] Mass Spectrometry Laboratory, Maria Curie-Skłodowska University, pl. M. Curie-Skłodowskiej 1, 20-031 Lublin, Poland, phone +48 81 537 62 75, fax +48 81 537 61 91, email: stanislaw.halas@poczta.umcs.lublin.pl, andrzej.trembaczowski@poczta.umcs.lublin.pl, tomasz.pienkos@poczta.umcs.lublin.pl
[3] Faculty of Chemistry, Gdańsk University of Technology, ul. G. Narutowicza 11/12, 80-233 Gdańsk, Poland, phone +48 58 347 21 10, fax +48 58 347 21 10, email: zanpolko@pg.gda.pl
[*] Corresponding author: stanislaw.chmiel@poczta.umcs.lublin.pl

important greenhouse gas, apart from water vapour, is carbon dioxide. The contribution of $CO_2$ in the atmosphere increased over the last century from approximately 0.03% to almost 0.04% [2, 3]. This is particularly associated with human industrial activity. It is not clear whether the climate is more affected by anthropogenic or natural factors [4, 5]. It is important, however, to trace such changes, and investigate possibly all of the carbon reservoirs influencing the content of $CO_2$ in the atmosphere.

Research on carbon dioxide emission to the atmosphere in the continental phase particularly concerns industrial, agricultural and forest areas [6-8], as well as areas abundant in $CO_2$ of endogenic origin [9-11]. The stream of carbon dioxide remaining in the continental hydrological circulation is investigated and balanced to a considerably lower degree [12-16]. The circulation of carbon in the inland water cycle is estimated for 3 Gt $\cdot$ year$^{-1}$ [1, 17-21]. Out of this value, fluvial outflow to the ocean is estimated for > 30%, carbon occurring in aquatic sediments amounts to > 20%, and exchange of carbon with the atmosphere in the form of $CO_2$ amounts to 45%. In the global carbon cycle, its circulation in the inland water cycle is estimated at a level of 10% of anthropogenic emission by burning fossil fuels [1, 22]. The postulates to reduce the content of carbon dioxide in the atmosphere with the application of alternative methods of reducing $CO_2$ emission to the atmosphere related *eg* to the intensification of photosynthesis and breathing are therefore of great importance [23].

Migration of $CO_2$ related to water circulation in the environment has a considerable effect on leaching of minerals and incorporating their dissolution products into the hydrological cycle [24, 25]. The largest carbon reservoir in the cycle is constituted by sediment rocks of marine origin rich in carbonates.

The objective of the study was to determine the content of dissolved carbon dioxide in water ($CO_{2(aq)}$) at particular stages of the hydrological cycle in a river catchment, and to assess potential possibilities of degassing from groundwaters to the atmosphere through fluvial outflow. The study was conducted based on selected hydrographic objects in the area of occurrence of carbonate rocks in the Lublin Upland and Roztocze, SE Poland (Fig. 1).

## Study area and methods

In the area of the Lublin Upland and Roztocze, the main reservoir of groundwaters fed to rivers developed in the carbonate rocks of the Upper Cretaceous and Tertiary: limestones, gaizes, opokas, marls, and chalk [26]. Waters of the Cretaceous and Tertiary aquifer in the zones of river valleys are hydraulically interconnected, and constitute one common aquifer drained by springs and rivers. In years with moderate water resources, the mean underground outflow from the area of the Lublin Upland and Roztocze amounted to 3.2 dm$^3$ $\cdot$ s$^{-1}$ $\cdot$ km$^{-2}$, whereas 1/3 of this value was accounted for by spring outflow. The contribution of underground outflow in total outflow exceeds 80%. Numerous springs occurring in the Lublin Upland and Roztocze form natural research polygons for observation of the variability and hydrochemical diversity of waters in the underground cycle.

The research task was implemented based on measurements of the content of $CO_{2(aq)}$ in the hydrological circulation of the Lublin Upland and Roztocze. The measurements encompassed the content of $CO_{2(aq)}$ in: atmospheric precipitation, groundwaters, and river waters. Measurements of the content of $CO_2$ in atmospheric and soil air were also performed. The index of the process of $CO_2$ degassing from waters constituted direct measurements of $CO_{2(aq)}$ in groundwaters (springs) and surface (river) waters.

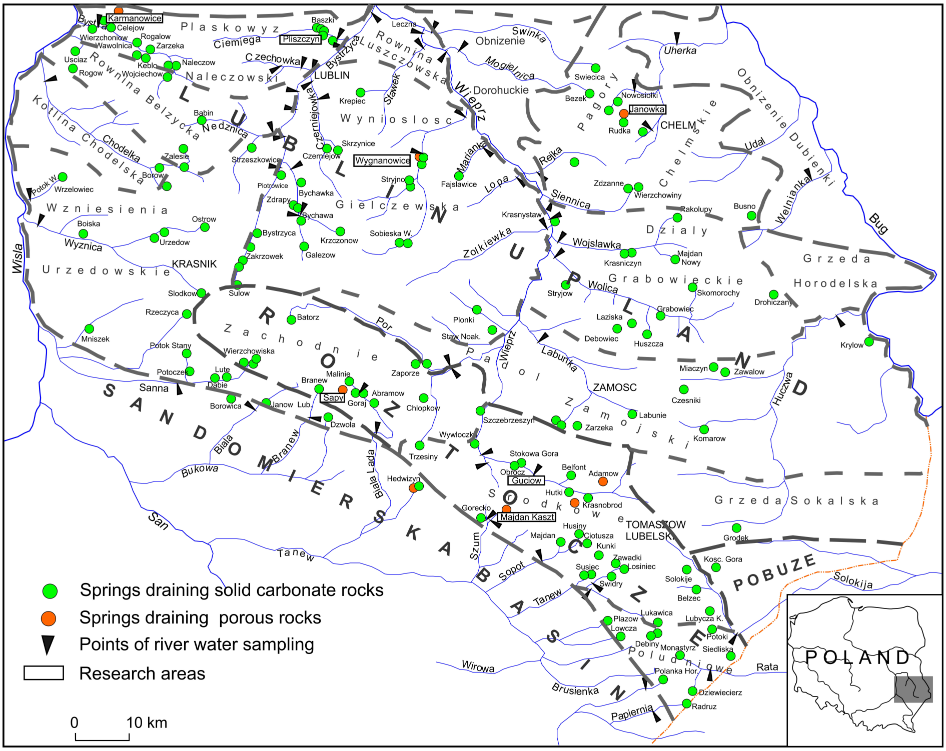


Fig. 1. Location of measurement sites in the study area

Precipitation waters were collected in Lublin as total precipitation, in a daily cycle. The content of $CO_{2(aq)}$ was determined in 84 samples of atmospheric precipitation. $CO_2$ concentration in atmospheric air was measured in one-week intervals. The content of $CO_2$ in soil air and on the six selected study polygons was measured in a monthly cycle. The polygons were representative of soils developed from: loesses (Karmanowice), loess-like formations (Wygnanowice), weak-clayey sands (Guciow), clayey sands (Janowka, Sapy), and sands (Majdan). Probes for collecting soil air were installed permanently. They were plastic tubes with a diameter of 1 cm, immersed into a layer of 0.3-0.6 m b.g.l. On the ground surface, the probes were closed with a stopcock for the purpose of elimination of contact with atmospheric air. In the area of the designated study polygons, the concentration of $CO_2$ in atmospheric air was also measured in a monthly cycle in the space of spring niches as well as the concentration of $CO_{2(aq)}$ in spring (underground) and river waters. One series of analyses was performed for assessing the spatial distribution of $CO_{2(aq)}$ in groundwaters and river waters. For this purpose groundwater samples were collected from 132 springs and from 63 sites located in 32 rivers. The research was conducted in July and August 2010 in conditions of exclusively groundwater feeding.

The content of free dissolved $CO_2$ in water was determined by means of Oxyguard CO2 Analyser. The content of $CO_{2(aq)}$ in soil waters was calculated based on the solubility of carbon dioxide in water, considering measurements of $CO_2$ concentration in soil air and measurements of soil temperature. The measurements of carbon dioxide in atmospheric and soil air were performed by means of a field gauge MultiRAE with an NDIR sensor.

In 2010, the mean air temperature in meteorological station Lublin-Radawiec amounted to 7.4ºC. It was approximate to the mean value for the Lublin region [27]. The annual total precipitation in the Lublin Upland amounted to approximately 750 mm, and in Roztocze to more than 900 mm. It was higher than multiannual means by approximately 30%. Snow cover occurred in the period from December 2009 to February 2010, and again in December 2010. As a result of spring infiltration of meltwaters, the groundwater level increased from March to June [28]. The snow cover accumulated approximately 150 mm of water. An increase in groundwater levels also occurred after heavy rainfalls in May (~160 mm) and September (~170 mm). In the remaining months, the groundwater levels showed a decreasing tendency, or stagnated. The outflow rhythm in the rivers of the study area showed a similar course trend. Feeding to the reservoir of groundwaters and rivers particularly occurred from March to June, and in September.

## Results and discussion

Carbon circulation in the hydrological cycle has a considerable effect on basic physical and chemical water parameters. This particularly concerns areas developed from rocks rich in carbonates, including the Lublin Upland and Roztocze. The carbonate balance commonly occurring in ground- and surface waters involves the interaction of water with carbon dioxide and insoluble carbonates and carbonates dissolved in water, and determines the state of proportion between forms: $HCO_3^-$, $CO_3^{2-}$, $CO_{2(aq)}$, $CO_{2(g)}$, determining water reaction [24]. The basic role in the process of dissolution of carbonate minerals is played by carbon dioxide ($CO_{2(g)}$) of soil origin, and to a considerably lower degree of atmospheric origin. The concentration of $CO_2$ in soil air can periodically even exceed 10% [25, 29]. In atmospheric air, it currently amounts to approximately 0.04% [1].

Table 1

The content of $CO_2$ in atmospheric air in Lublin and in soil air

| **Value [%]** | **I** | **II** | **III** | **IV** | **V** | **VI** | **VII** | **VIII** | **IX** | **X** | **XI** | **XII** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Atmospheric air (*n* = 52) | | | | | | | | | | | | |
| minimum | 0.041 | 0.041 | 0.040 | 0.040 | 0.042 | 0.044 | 0.043 | 0.036 | 0.034 | 0.033 | 0.034 | 0.036 |
| mean | 0.042 | 0.042 | 0.041 | 0.041 | 0.045 | 00046 | 0.045 | 0.039 | 0.036 | 0.037 | 0.036 | 0.039 |
| maximum | 0.043 | 0.044 | 0.043 | 0.043 | 0.049 | 0.047 | 0.048 | 0.042 | 0.038 | 0.039 | 0.039 | 0.040 |
| Spring niches (*n* = 156) | | | | | | | | | | | | |
| minimum | 0.038 | 0.039 | 0.042 | 0.044 | 0.048 | 0.050 | 0.053 | 0.040 | 0.037 | 0.036 | 0.036 | 0.036 |
| mean | 0.042 | 0.045 | 0.047 | 0.053 | 0.052 | 0.058 | 0.064 | 0.053 | 0.048 | 0.040 | 0.041 | 0.040 |
| maximum | 0.045 | 0.059 | 0.050 | 0.090 | 0.062 | 0.065 | 0.075 | 0.062 | 0.059 | 0.052 | 0.053 | 0.049 |
| Soil air (*n* = 72) | | | | | | | | | | | | |
| minimum | 0.13 | 0.12 | 0.14 | 0.19 | 0.50 | 0.56 | 0.51 | 0.49 | 0.43 | 0.31 | 0.26 | 0.18 |
| mean | 0.20 | 0.22 | 0.35 | 0.58 | 0.36 | 0.20 | 0.89 | 0.55 | 0.66 | 0.56 | 0.44 | 0.25 |
| maximum | 0.25 | 0.40 | 0.80 | 0.99 | 0.22 | 0.84 | 0.46 | 0.77 | 0.95 | 0.82 | 0.65 | 0.36 |

*n* - number of samples

Research on the content of carbon dioxide in atmospheric air in Lublin documented its presence ranging from 0.033 to 0.049%, averaging 0.041% (Table 1). In the annual course, considerably higher concentrations were recorded in months from January to July, when the level of $CO_2$ was usually > 0.04%. From August to December, the concentration of $CO_2$ in the atmospheric air usually amounted to < 0.04%. Due to the content of $CO_2$ in atmospheric air, pursuant to the Henry's law, its equivalent content in water should be from ~0.5 to ~1.5 mg · dm$^{-3}$. In the summer period, the concentration of $CO_2$ in atmospheric air shows high daily fluctuations [30-32]. The concentration of $CO_2$ by night is sometimes even 2-3 times higher than by day. Such high $CO_2$ concentration in atmospheric air was also recorded by day in spring niches. The equivalent $CO_{2(aq)}$ concentration in precipitation waters can then reach even more than 3 mg · dm$^{-3}$ $CO_{2(aq)}$. Measured values of $CO_{2(aq)}$ in atmospheric precipitation in 2010 varied from < 1 to 22 mg · dm$^{-3}$, but usually did not exceed 3 mg · dm$^{-3}$ (Table 2).

Table 2

$CO_{2(aq)}$ content in waters

| Object | Number of measurements | Minimum | Quartile 25% | Quartile 50% | Mean | Quartile 75% | Maximum |
|---|---|---|---|---|---|---|---|
| | | [mg · dm$^{-3}$] | | | | | |
| Precipitation | 36 | < 1 | 1 | 2 | 2.6 | 3 | 22 |
| Soil waters | 72* | 2.8 | 6.2 | 11.6 | 14.2 | 18.3 | 51.5 |
| Groundwaters | 132 | 10 | 18 | 28.4 | 30.3 | 38 | 72 |
| River waters | 63 | < 1 | 6 | 7 | 7.6 | 8 | 21 |

*Values calculated based on $CO_2$ concentration in soil air and solubility of carbon dioxide in water for temperature 10ºC

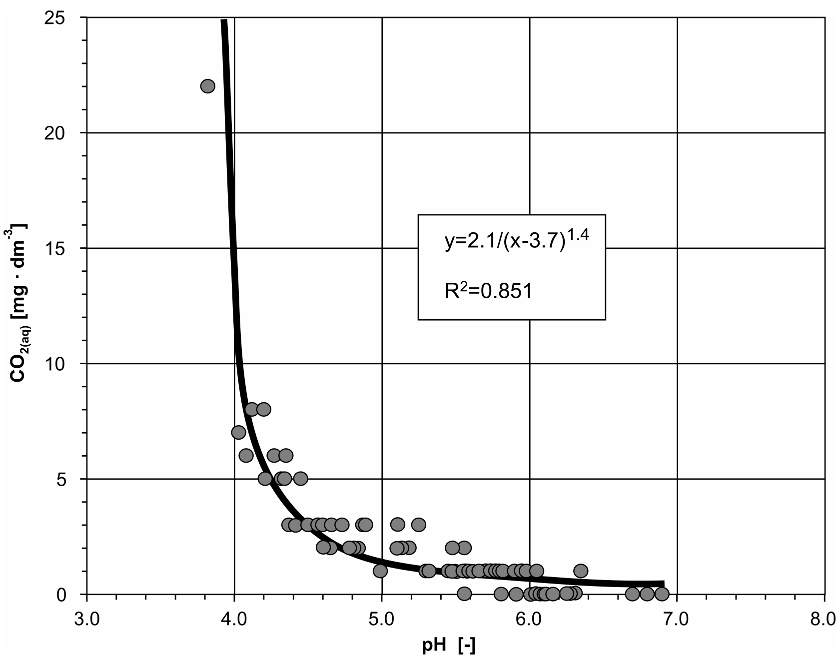


Fig. 2. Correlations between water reaction and $CO_{2(aq)}$ concentration in precipitation waters

High values of $CO_{2(aq)}$ in precipitation waters were identified in samples with low reaction (Fig. 2). This suggests the role of acidic precipitation, and particularly sulphur and nitrogen compounds, in the development of $CO_{2(aq)}$ concentration in precipitation waters. Dissolution of alkaline compounds contained in atmospheric dusts at low water reaction can constitute a considerable source of $CO_{2(aq)}$ in precipitation [2]. Considerably higher $CO_{2(aq)}$ concentrations in precipitation waters were shown by research conducted in the area of Warszawa. The mean values were 2-3 times higher [33].

The concentration of $CO_2$ in soil air was considerably higher than in atmospheric air, amounting to 0.13-2.22%. The highest values were recorded in the winter season, and the lowest during intensified vegetation. Higher values were recorded in soils under agricultural use than in those in forest areas. The correlations are characteristic of the area of the Lublin Upland, as documented in the paper by Dudziak, Halas [6]. Measurements of $CO_2$ concentration in soil air and soil temperature provided the basis for the calculation of the content of $CO_{2(aq)}$ in soil water (Table 2). The calculated $CO_{2(aq)}$ concentration amounted to 3-51 mg · dm$^{-3}$. The highest calculated concentrations occurred in spring months, and the lowest in winter. Washing $CO_{2(aq)}$ from soils to groundwaters in 2010 particularly occurred from March to June and in September. It did not occur or was limited in the remaining months.

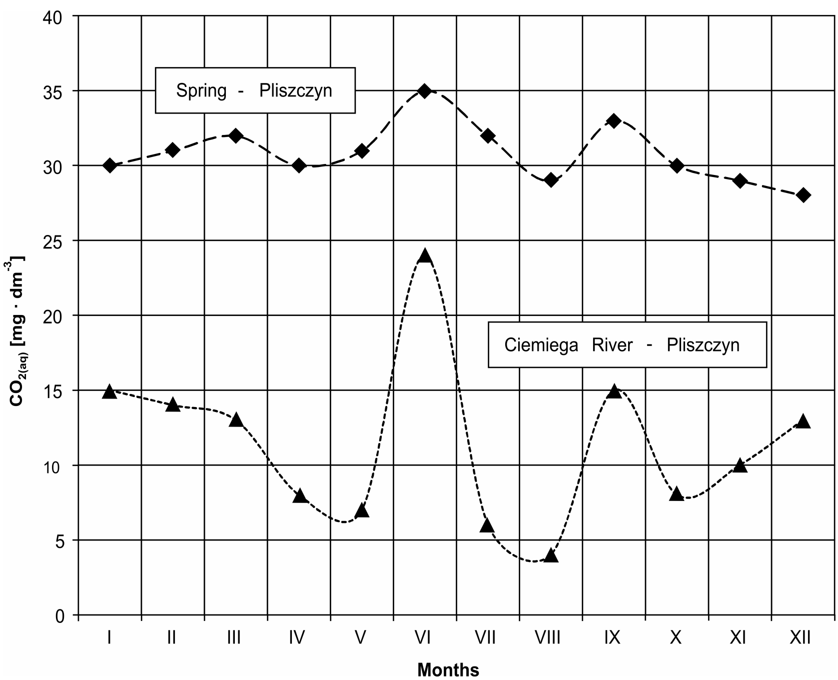


Fig. 3. Monthly changes in $CO_{2(aq)}$ concentration in spring and river waters based on the example of the Ciemiega River catchment in 2010

$CO_{2(aq)}$ content in groundwaters was analysed based on pore springs draining a shallow aquifer of groundwaters and fissure-layer springs, draining the main groundwater reservoir. Groundwaters outflowing to the surface in springs contained $CO_{2(aq)}$ in a range of 10-72 mg · dm$^{-3}$ (Table 2), averaging 30 mg · dm$^{-3}$. The highest values of $CO_{2(aq)}$ in spring waters were recorded in the spring season and after heavy rainfalls which occurred at the end of May and at the beginning of September. In the annual cycle, changes in the concentration of $CO_{2(aq)}$ in the waters of fissure-layer springs usually did not exceed 10 mg · dm$^{-3}$, and in pore springs from 10 to more than 30 mg · dm$^{-3}$. The coefficient of variability of $CO_{2(aq)}$ concentration in spring waters, calculated based on monthly measurements, varied from 30 to 48%, averaging 36%. In the waters of pore springs, it was usually higher than the average values, and in the waters of fissure-layer springs - lower than the average. Example changes in $CO_{2(aq)}$ concentration in a fissure-layer spring in Pliszczyn in the annual cycle amounted to 7 mg · dm$^{-3}$ (Fig. 3), and in the daily cycle they did not exceed 3 mg · dm$^{-3}$ (Fig. 4). Higher daily variability was recorded in measurements performed in summer than in winter.

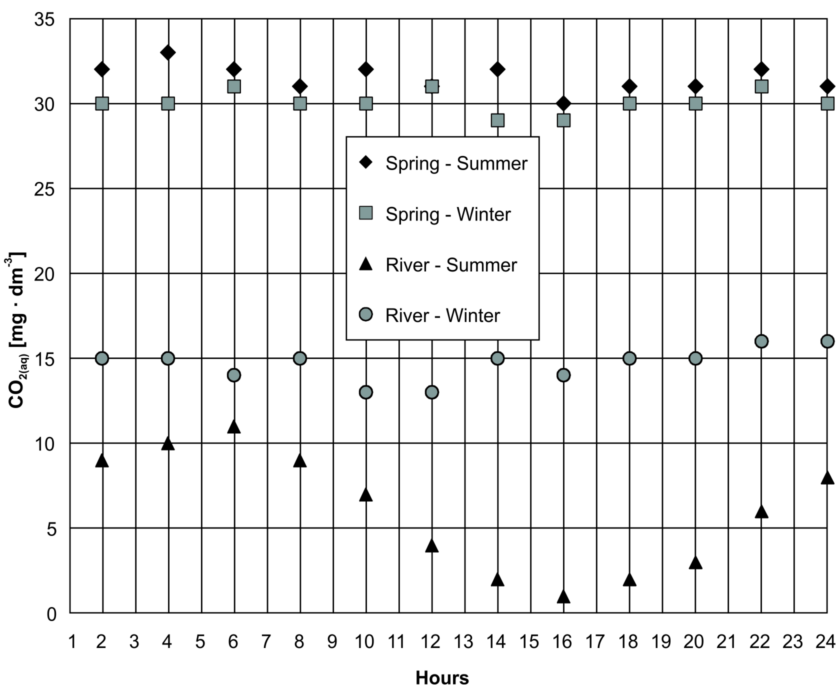


Fig. 4. Daily changes in $CO_{2(aq)}$ concentration in spring and river waters, measurements from January and July 2010

The spatial variability of $CO_{2(aq)}$ concentration in the Lublin Upland and Roztocze (Fig. 5) corresponded with the lithological formation of rocks. High values of $CO_{2(aq)}$ (> 30 mg · dm$^{-3}$) were recorded in areas of occurrence of rocks such as chalk, marls, and loess (regions: Pagory Chelmskie, Plaskowyz Naleczowski, Dzialy Grabowieckie, Roztocze Zachodnie, Padol Zamojski). Lower values (< 30 mg · dm$^{-3}$) were observed in areas with rocks such as opokas, gaizes, and limestone (regions: Wzniesienia Urzedowskie, Wynioslosc Gielczewska, Rownina Belzycka, Roztocze Srodkowe and Roztocze

Poludniowe). High $CO_{2(aq)}$ concentration in the waters of the pore spring in Wygnanowice (the Gielczew River catchment) suggests the effect of fossil soils and/or peats on the content of $CO_{2(aq)}$ in the underground circulation [34]. The effect of peats on the content of $CO_{2(aq)}$ in groundwaters was documented in research conducted on a peatland in the Kampinoski National Park [33].

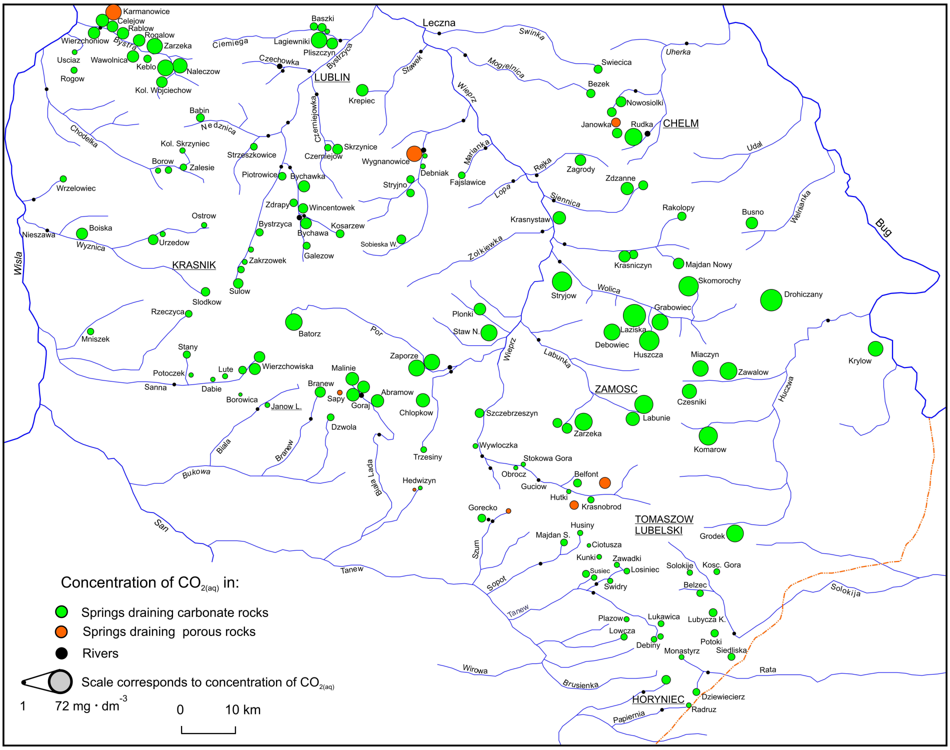


Fig. 5. Spatial variability of $CO_{2(aq)}$ concentration in spring and river waters studied in the summer 2010

Groundwaters are fed to rivers through channel and spring drainage. Degassing of $CO_2$ occurs from rivers to the atmosphere, resulting in a considerable decrease in its content in water [24, 29, 35-37]. Constant exchange of $CO_2$ occurs between the hydrosphere and atmosphere. It results from the maintenance of the balance in the environment in terms of concentration of gases (Henry's law). In rivers, $CO_{2(aq)}$ concentration was usually below 15 mg · dm$^{-3}$ (mean ~8 mg · dm$^{-3}$). Concentration above 10 mg · dm$^{-3}$ was recorded at measurement sites located in profiles of rivers below efficient springs. In the summer season, $CO_{2(aq)}$ concentration usually did not exceed 10 mg · dm$^{-3}$. Particularly low concentrations were recorded below dam reservoirs, where the values decreased below 1 mg · dm$^{-3}$. The comparison of $CO_{2(aq)}$ concentration in ground- and river waters within selected catchments studied in summer 2010 (Fig. 6) suggests a possible level of degassing of carbon dissolved in water to the atmosphere. The degassing of $CO_2$ from groundwaters to the atmosphere is also suggested by measurements of its concentration in the air of spring niches (Table 2). Higher concentration in atmospheric air in spring niches than in hilltops suggests its emission to the atmosphere not only from the soil cover, but also from groundwaters.

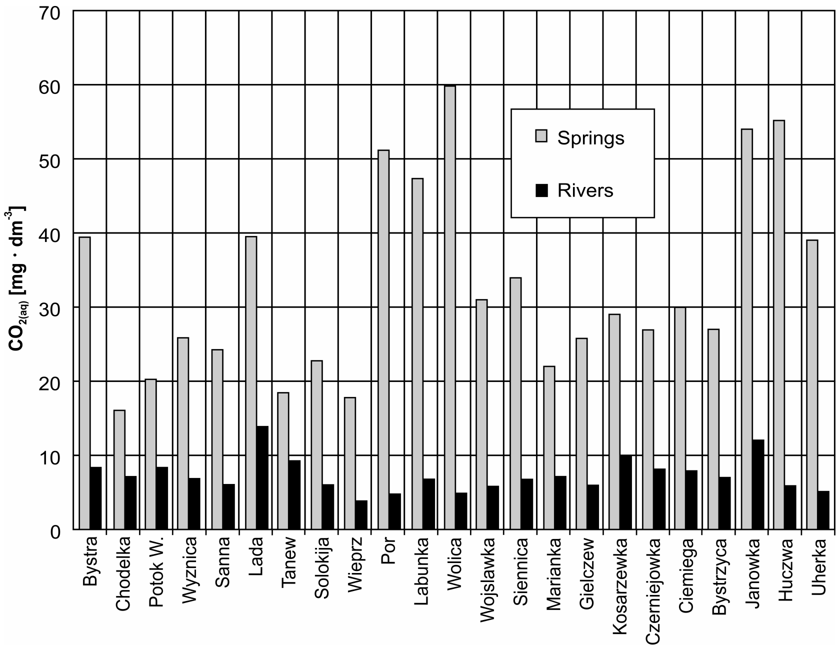


Fig. 6. $CO_{2(aq)}$ concentration in the waters of river catchments studied in the summer 2010



In the process of degassing of carbon dioxide from springs and rivers, daily and seasonal changes in the concentration of $CO_{2(aq)}$ are worth attention. The changes are presented based on the example of measurements performed in the Ciemiega River catchment (Fig. 3). The measurements, taken in a monthly cycle in 2010, showed that seasonal changes in $CO_{2(aq)}$ concentration in the river reached 15 mg · dm$^{-3}$. High contents of $CO_{2(aq)}$ were recorded in the cool half-year (10-15 mg · dm$^{-3}$), and lower values (< 10 mg · dm$^{-3}$) in the summer season. Considerable changes in $CO_{2(aq)}$ concentration occurred during intensive supply of groundwaters to the river after snowmelt in the spring and after heavy rainfalls in May and September. Changes in $CO_{2(aq)}$ concentrations in the Ciemiega River also showed a daily rhythm (Fig. 4), particularly evident in measurements performed in the summer season. Higher concentrations were recorded by night than by day. In the summer season, the daily rhythm of $CO_{2(aq)}$ concentration suggests an effect of biological breathing in the river on its content. The rhythm was also observed in seasonal changes.

The level of carbon dioxide degassing to the atmosphere from the carbonate waters of the Lublin Upland and Roztocze was estimated by means of hydrochem-discharge method (Table 3). The level of degassing constitutes the difference between mean $CO_{2(aq)}$ concentration in ground- and river waters in relation to underground outflow. The level of underground outflow in the Lublin Upland and Roztocze in 2010 year amounts to approximately 92% of total outflow. Total outflow was calculated based on the value of the outflow coefficient, in the Lublin Upland amounting to 20%, and in Roztocze to 27% of atmospheric precipitation.

The value of carbon dioxide degassing from the carbonate waters of the Lublin Upland and Roztocze amounted to 52.5 thousand $Mg \cdot year^{-1}$ ($4.04\ Mg \cdot year^{-1} \cdot km^{-2}$). Research of carbon dioxide degassing from waters from the karst area in China showed the level $19.1\ Mg \cdot year^{-1} \cdot km^{-2}$ [13].

Estimated level of degassing from the carbonate waters of the Lublin Upland and Roztocze was low in relation to anthropogenic emission in that area. For comparison, in the period, the annual $CO_2$ emission from the sugar factory in the town of Krasnystaw amounted to 30 thousand $Mg \cdot year^{-1}$, and the emission from heat and power plant Wrotkow in the Lublin city amounted to 400 thousand $Mg \cdot year^{-1}$. The level of anthropogenic emission of carbon dioxide originating from environmentally harmful industrial plants in the Lublin province was estimated for approximately 5 million $Mg \cdot year^{-1}$.

Table 3

$CO_2$ degassing from the carbonate waters of the Lublin Upland and Roztocze in 2010

| | **Lublin Upland** | **Roztocze** | **Lublin Upland and Roztocze** |
|---|---|---|---|
| Area [$km^2$] | 10,800 | 2,200 | 13,000 |
| Precipitation [mm] | 750 | 925 | 780 |
| Precipitation [$km^3 \cdot year^{-1}$] | 8.1 | 2.0 | 10.1 |
| Total outflow [$km^3 \cdot year^{-1}$] | 1.62 | 0.54 | 2.16 |
| Underground outflow [$km^3 \cdot year^{-1}$] | 1.49 | 0.49 | 1.98 |
| Mean $CO_{2(aq)}$ concentration in groundwaters [$mg \cdot dm^{-3}$] | 38 | 25 | 30 |
| Mean $CO_{2(aq)}$ concentration in rivers [$mg \cdot dm^{-3}$] | 8 | 9 | 8 |
| Degassing of $CO_2$ [$mg \cdot dm^{-3}$] | 30 | 16 | 22 |
| Degassing of $CO_2$ [$Mg \cdot year^{-1}$] | 44,700 | 7,840 | 52,540 |

## Conclusions

In 2010, research was conducted on the concentration of dissolved carbon dioxide ($CO_{2(aq)}$) in consecutive phases of hydrological circulation in the area of occurrence of carbonate rocks of the Lublin Upland and Roztocze, SE Poland. The research showed the following values of $CO_{2(aq)}$ content (min-max/mean): precipitation waters $< 1$-$3/2.6\ mg \cdot dm^{-3}$, soil waters 3-50/14.2 $mg \cdot dm^{-3}$, groundwaters 10-70/30.3 $mg \cdot dm^{-3}$, river waters $< 1$-$21/7.6\ mg \cdot dm^{-3}$.

The obtained results suggest a considerable effect of soils on the content of $CO_{2(aq)}$ in infiltration waters. The concentration of $CO_{2(aq)}$ increased several times in infiltration waters in comparison to precipitation waters. The content of $CO_{2(aq)}$ in groundwaters was strongly affected by the lithological type of rocks washed by flowing water. The highest $CO_{2(aq)}$ concentrations were recorded in waters circulating in soft solid carbonate rocks such as chalk, marls, and porous formations such as loess. Lower values were recorded in solid hard rocks such as opoka, limestone, or gaize.

In river waters, $CO_{2(aq)}$ concentration was usually lower by approximately 60% than in groundwaters. This correlation suggested exchange of $CO_2$ between the hydrosphere and atmosphere, occurring in the surface phase of water outflow. The process resulted from lower partial pressure of carbon dioxide in the atmosphere than in the rock mass, as determined by the Henry's law. Carbon dioxide emission from the carbonate rocks of the

Lublin Upland and Roztocze related to the process was estimated for 50 thousand Mg · year$^{-1}$. The value constituted approximately 1% of the anthropogenic emission of carbon dioxide from environmentally harmful industrial plants in the Lublin province.

Considering the forecasted climate warming, the level of carbon dioxide emission to the atmosphere from carbonate rocks will increase. The obtained results can be used for calculating the natural stream of $CO_2$ from waters to the atmosphere from land in the moderate climate zone.

## Acknowledgments

This study was supported from the funds of the Ministry of Sciences and High Education in the framework of grant No. N N306181237.

## References

[1] IPCC. Carbon and Other Biogeochemical Cycles - Final Draft Underlying Scientific-Technical Assessment. 2013. www.ipcc.ch/pdf/press/ipcc_leaflets_2010/ipcc_ar5_leaflet.pdf.

[2] Berner EK, Berner RA. Global Environmental. Water, Air and Geochemical Cycles. Upper Saddle River, New Jersey: Prentice Hall; 1996.

[3] Prentice IC, Farquhar GD, Fasham MJR, Goulden ML, Heimann M, Jaramillo VJ, et al. The carbon cycle and atmospheric carbon dioxide. In: Houghton JT, Ding Y, Griggs DJ, Noguer M, van der Linden PJ, Dai X, et al, editors. Climate Change 2001: The Scientific Basis, Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge: Cambridge University Press; 2001;185-237.

[4] Robinson AB, Robinson ZW, Sonn W. Environmental effects of increased atmospheric carbon dioxide. J Am Phys Surg. 2007;3:79-90. http://www.oism.org/pproject/s33p36.htm.

[5] Chilingar GV, Sorokhtin OG, Khilyuk LF, Liu M. do increasing contents of methane and carbon dioxide in the atmosphere cause global warming? Atmosph Climate Sci. 2014;4:819-827. DOI: 10.4236/acs.2014.45072.

[6] Dudziak A, Hałas S. Diurnal cycle of carbon isotope ratio in soil $CO_2$ in various ecosystems. Plant Soil. 1996;183:291-299. DOI: 10.1007/BF00011444.

[7] Anthoni PM, Knohl A, Rebmann C, Freibauer A, Mund M, Ziegler W, et al. Forest and agricultural land-use-dependent $CO_2$ exchange in Thuringia, Germany. Glob Change Biol. 2004;10(12):2005-2019. DOI: 10.1111/j.1365-2486.2004.00863.x.

[8] Janssens IA, Freibauer A, Schlamadinger B, Ceulemans R, Ciais P, Dolman AJ, et al. The carbon budget of terrestrial ecosystems at country-scale - A European case study. Biogeosciences. 2005;2:15-26. DOI: 10.5194/bg-2-15-2005.

[9] Kerrick D.M. Present and past nonanthropogenic $CO_2$ degassing from the solid Earth. Rev Geophys. 2001;39(4):565-586. DOI: 10.1029/2001RG000105.

[10] Mörner N-A., Etiope G. Carbon degassing from the lithosphere. Global Planet Change. 2002;33:185-203. DOI: 10.1016/S0921-8181(02)00070-X.

[11] Werner C, Brantley S. $CO_2$ emissions from the Yellowstone volcanic system. Geochem Geophys Geosyst. 2003;4(7):1-27. DOI: 10.1029/2002GC000473.

[12] Jing ZC, Yuan DX. $CO_2$ source-sink in karst processes in karst areas of China. Episodes. 1999;22:1:33-35.

[13] Liu Z, Zhao J. Contribution of carbonate rock weathering to the atmospheric $CO_2$ sink. Environ Geology. 1999;39(9):1053-1058. DOI: 10.1007/s002549900072.

[14] Kindler R, Siemens J, Kaiser K, Walmsley DC, Bernhofer C, Buchmann N, et al. Dissolved carbon leaching from soil is a crucial component of the net ecosystem carbon balance. Glob Change Biol. 2011;17:1167-1185. DOI: 10.1111/j.1365-2486.2010.02282.x.

[15] Butman D, Raymond PA. Significant efflux of carbon dioxide from streams and rivers in the United States. Nat Geosci. 2011;4:839-842. DOI: 10.1038/ngeo1294.

[16] Wang ZA, Bienvenu DJ, Mann PJ, Hoering KA, Poulsen JR, Spencer RGM, et al. Inorganic carbon speciation and fluxes in the Congo River. Geophys Res Lett. 2013;40:511-516. DOI: 10.1002/grl.50160.

[17] Kessler TJ, Harvey CF. The global flux of carbon dioxide into groundwater. Geophys Res Lett. 2001;28(2):279-282.
[18] Cole JJ, Prairie YT, Caraco NF, McDowell WH, Tranvik LJ, Striegl RG, et al. Plumbing the global carbon cycle: Integrating inland waters into the terrestrial carbon budget. Ecosystems. 2007;10:171-184. DOI: 10.1007/s10021-006-9013-8.
[19] Houghton RA. Balancing the global carbon budget. Ann Rev Earth Planet Sci. 2007;35:313-347. DOI: 10.1146/annurev.earth.35.031306.140057.
[20] Battin TJ, Luyssaert S, Kaplan LA, Aufdenkampe AK, Richter A, Tranvik LJ. The boundless carbon cycle. Nat Geosci. 2009;2:598-600. DOI: 10.1038/ngeo618.
[21] Aufdenkampe AK, Mayorga E, Raymond PA, Melack JM, Doney SC, Alin SR, et al. Riverine coupling of biogeochemical cycles between land, oceans, and atmosphere. Front Ecol Environ. 2011;9:53-60. DOI: 10.1890/100014.
[22] Liu Z, Dreybrodt W, Wang H. A new direction in effective accounting for the atmospheric $CO_2$ budget: Considering the combined action of carbonate dissolution, the global water cycle and photosynthetic uptake of DIC by aquatic organisms. Earth-Sci Rev. 2010;99:162-172. DOI: 10.1016/j.earscirev.2010.03.001.
[23] Xiaoping Z, Baran S, Cel W, Cao Y. Sustainable approach to mitigation of $CO_2$ emission. Ecol Chem Eng S. 2014;21(4):617-622. DOI: 10.1515/eces-2014-0044.
[24] Stumm W, Morgan JJ. Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters. New York: John Wiley&Sons; 1996.
[25] Appelo CA, Postma D. Geochemistry, groundwater and pollution. Rotterdam, Brookfield: Balkema; 1999.
[26] Michalczyk Z, Chmiel S, Głowacki S, Zielińska B. Changes of springs' yield of Lublin Upland and Roztocze Region in 1998-2008. J Water Land Dev. 2008;12:113-125.
[27] Kaszewski BM, Pidek IA, Piotrowska-Weryszko K, Weryszko-Chmielewska A. Annual pollen sums of Alnus in Lublin and Roztocze in the years 2001-2007 against selected meteorological parameters. Acta Agrob. 2008;61(2):57-64. DOI: 10.5586/AA.2008.033.
[28] QBG. Quarterly bulletin of groundwaters. Polish Hydrogeol Survey. 2010:9(30),8(29),8(28),8(27),8(26). http://www.psh.gov.pl.
[29] Langmuir D. Aqueous Environmental Geochemistry. Upper Saddle River, New Jersey: Prentice Hall, Inc, Simon & Schuster/A Viacom Company; 1997.
[30] Szaran J, Niezgoda H, Trembaczowski A. Respiration and assimilation processes reflected in the carbon isotopic composition of atmospheric carbon dioxide. Nukleonika. 2002;47(Supplement 1):59-61. http://www.ichtj.waw.pl/ichtj/nukleon/back/full/vol47_2002/v47s1p059f.pdf.
[31] Zimnoch M, Florkowski T, Necki JM, Neubert REM. Diurnal variability of d13C and d18O of atmospheric $CO_2$ in the urban atmosphere of Krakow, Poland. Isot Environ Health Stud. 2004;40:129-143. DOI: 10.1080/10256010410001670989.
[32] Szaran J, Dudziak A, Trembaczowski A, Niezgoda H, Hałas S. Diurnal variations and vertical distribution of d13C, and concentration of atmospheric and soil $CO_2$ in a meadow site, SE Poland. Geol Quart. 2005;49(2):135-144. http://www.pgi.gov.pl/images/stories/przeglad/pdf/gq_49_2_p135.pdf.
[33] Pawlicka D. Content of dissolved oxygen and carbon dioxide in rainwaters and groundwaters within the forest reserve of the Kampinos National Park and the urban area of Warsaw. Poland. Geol Quart. 2003:47(2):187-194. http://www.pgi.gov.pl/images/stories/przeglad/pdf/gq_47_2_p187.pdf.
[34] Chmiel S, Hałas S, Janusz J, Głowacki S, Trembaczowski A. Studies on quantitative and qualitative changes in dissolved inorganic carbon content in a river drainage area. Przem Chem. 2015;94(6):994-998. DOI: 10.15199/62.2015.6.27.
[35] Polsenaere P, Abril G. Modelling $CO_2$ degassing from small acidic rivers using water $pCO_2$, DIC and δ13C-DIC data. Geochim Cosmochim Acta. 2012;91:220-239. DOI: 10.1016/j.gca.2012.05.030.
[36] Li S, Lu XX, He M, Zhou Y, Li L, Ziegler AD. Daily $CO_2$ partial pressure and $CO_2$ outgassing in the upper Yangtze River basin: a case study of the Longchaun River, China. J Hydrol. 2012;466-467, 141-150.
[37] Khadka MB, Jonathan B, Martin JB, Jin J. Transport of dissolved carbon and $CO_2$ degassing from a river system in a mixed silicate and carbonate catchment. J Hydrol. 2014;513:391-402. DOI: 10.1016/j.jhydrol.2014.03.070.

# EMISJA $CO_2$ DO ATMOSFERY Z WÓD WĘGLANOWYCH NA PRZYKŁADZIE WYŻYNY LUBELSKIEJ I ROZTOCZA

[1] Wydział Nauk o Ziemi i Gospodarki Przestrzennej, Uniwersytet Marii Curie-Skłodowskiej, Lublin
[2] Zakład Spektrometrii Mas, Uniwersytet Marii Curie-Skłodowskiej, Lublin
[3] Wydział Chemiczny, Politechnika Gdańska

**Abstrakt:** W pracy przedstawiono wyniki badań zawartości rozpuszczonego ditlenku węgla w wodzie ($CO_{2(aq)}$) na poszczególnych etapach obiegu hydrologicznego zlewni rzecznej oraz oceniono jego potencjalne możliwości degazacji z wód podziemnych do atmosfery. Badania prowadzono na przykładzie wybranych obiektów hydrograficznych w obszarze skał węglanowych Wyżyny Lubelskiej i Roztocza, SE Polska. Zawartość $CO_{2(aq)}$ w wodach opadowych kształtowała się na poziomie < 1-3 mg · dm$^{-3}$, w wodach glebowych od 3-50 mg · dm$^{-3}$, wodach podziemnych 10-70 mg · dm$^{-3}$, a w wodach rzecznych od < 1 do 21 mg · dm$^{-3}$. Zebrany materiał wskazuje, że emisja ditlenku węgla z wód węglanowych Wyżyny Lubelskiej i Roztocza kształtuje się na poziomie 50 tys. Mg · rok$^{-1}$. Wartość ta stanowi około 1% emisji antropogenicznej ditlenku węgla pochodzącego ze spalania paliw stałych na badanym obszarze.

**Słowa kluczowe:** wody podziemne, rzeki, ditlenek węgla, degazacja