

Original Research

# Atmospheric Concentrations of Carbon Dioxide in Southern Poland: Comparison of Mountain and Urban Environments

L. Chmura, K. Rozanski\*, J. M. Necki, M. Zimnoch, A. Korus, M. Pycia

Faculty of Physics and Applied Computer Science, AGH University of Science and Technology,  
Al. Mickiewicza 30, 30-059 Kraków, Poland

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## Abstract

The results of regular observations of atmospheric CO<sub>2</sub> mixing ratios, carried out during the period 1996-2006 at two continental sites located in southern Poland, approximately 100 km apart, are presented and discussed. These sites (Kasprowy Wierch, 49°14'N, 19°59'E, 1989 m a.s.l. and Kraków, 50°04'N, 19°55'E, 220 m a.s.l.) are located in two contrasting environments: (i) high-altitude mountainous area, relatively free of anthropogenic influences, and (ii) typical urban environment with numerous local sources of carbon dioxide of anthropogenic origin. The mean annual CO<sub>2</sub> concentration recorded at Kasprowy Wierch increased from 361.8 ppm in 1997 to 382.7 ppm in 2006. The resulting mean annual growth rate ( $2.14 \pm 0.57$  ppm year<sup>-1</sup>) is slightly higher than that derived for the marine CO<sub>2</sub> reference curve ( $2.02 \pm 0.26$  ppm year<sup>-1</sup>), calculated for the latitude band within which Kasprowy Wierch station is located (48.6°N–53.1°N). The CO<sub>2</sub> mixing ratios measured in the urban atmosphere revealed quasi-permanent excess concentration of this gas when compared with the regional reference. The mean concentration of CO<sub>2</sub> in Kraków for the period 2003-06 was ca. 8.5% higher than that recorded at the high-altitude mountain site (Kasprowy Wierch).

**Keywords:** carbon dioxide, mixing ratios, Kasprowy Wierch, Kraków, urban environment

## Introduction

The gradual increase of atmospheric CO<sub>2</sub> concentration over the last 100 years, by far exceeding natural variations, has been unequivocally attributed to human activities [1, 2]. The anthropogenic impact on the global carbon cycle is mainly related to fossil fuel and biomass burning, land-use changes, as well as various industrial activities [3]. Although the level of atmospheric CO<sub>2</sub> is increasing, its growth rate is varying with time, responding to changes in

the magnitude of the CO<sub>2</sub> fluxes entering and leaving the atmospheric carbon reservoir to or from the land biosphere and the world oceans. These short-term changes have both anthropogenic and natural origins [4-6]. Identification and quantification of sources and sinks of carbon and their temporal and spatial variability on both global and regional scales is a prerequisite for a better understanding of the dynamics of the carbon cycle and its response to ever increasing human impact [2, 7].

The development of reliable carbon cycle models requires adequate observational data. They are delivered mostly by the existing global and regional monitoring networks such as Global Atmospheric Watch [8], Global

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\*e-mail: rozanski@novell.ftj.agh.edu.pl

Cooperative Air Sampling Network [9], or European Sampling Network [10]. Apart from the mixing ratios, isotopic composition of carbon dioxide is also measured at a number of locations. Isotope characteristics of carbon dioxide constitute a powerful tool for identification of sources and sinks of carbon and partitioning of carbon derived from burning fossil fuels [11-14].

The transition to a market economy in the Eastern European countries has been associated with major changes of industrial technologies and resulting shifts in the structure of total energy consumption (gradual shift from coal to oil and natural gas). These changes have also had a significant impact on the strength and distribution of major sources of greenhouse gas emissions, in particular CO<sub>2</sub>, in this part of Europe.

This work summarizes the data on atmospheric CO<sub>2</sub> mixing ratios gathered in southern Poland during the past decade (1996-2006). The data originate from two ground-level continental sites located in contrasting environments: (i) high-altitude mountainous area, relatively free of local anthropogenic influences, and (ii) typical urban environment with numerous local sources of carbon dioxide of anthropogenic origin. Although the distance between both

sites is relatively small (ca. 100 km), they differ in elevation by as much as 1770 m. Apart from the CO<sub>2</sub> mixing ratios, the carbon isotope composition of atmospheric CO<sub>2</sub> also has been regularly measured at both sites. These data are discussed in detail elsewhere [15].

The presented study was undertaken with the main aim to characterize spatial and temporal variability of CO<sub>2</sub> mixing ratios at regional scale in the lower troposphere of Central Europe and to quantify the differences in this variability caused by specific characteristics of the observation sites.

## Site Description

### Kasprowy Wierch

The Kasprowy Wierch station is located in the south of Poland, within the High Tatra Mountains (Fig. 1). The meteorological observatory which hosts the monitoring station is located on top of a mountain peak called Kasprowy Wierch (49°14'N, 19°59'E, 1989 m a.s.l., 300 m above timber line). Kasprowy Wierch is situated at the intersection of three main valleys, at the border between Poland and Slovak Republic. The nearest town, Zakopane, is located approximately 900 meters below, 6 km north of Kasprowy Wierch. This is a small tourist town. During winter, from November to March, relatively large amounts of wood and fossil fuels are combusted in the Zakopane area. The Kasprowy Wierch observatory is equipped with an electrical heating system and does not use any fossil fuel. During wintertime, diesel-operated snow cars are used in nearby valleys to maintain proper conditions for skiing.

The climate of the Kasprowy Wierch area is typical for a continental mountainous location, with relatively large diurnal and seasonal variations of temperature, high precipitation rate, frequent changes of atmospheric pressure and strong winds. Fig. 2 shows the distribution of wind direction and wind speed at Kasprowy Wierch. Surface winds are blowing predominantly along S-N and SW-NE axis. Periods without wind constitute only 1.2% of the total observation time. Although westerly transport of air masses in the lower troposphere prevails in the region, the direction of surface winds in the vicinity of Kasprowy Wierch is strongly influenced by the local topography of surrounding valleys. Snow cover in the vicinity of the station lasts for 6-8 months and ends rapidly due to strong foehn circulation.

Regular observations of atmospheric CO<sub>2</sub> mixing ratios at Kasprowy Wierch began in 1994, as a joint project of the AGH University of Science and Technology, Kraków, Poland, and the University of Heidelberg, Germany. Continuous measurements using GC technique were initiated in 1996. The intake of outside air is located ca. 1 meter above the roof of the observatory and ca. 6 meters above the ground (Fig. 1).

The Kasprowy Wierch station is situated within the transition zone between the free troposphere and the planetary boundary layer and is relatively free of local influences. Therefore, it can be considered as a regional reference station for trace gas measurements in this part of Europe.

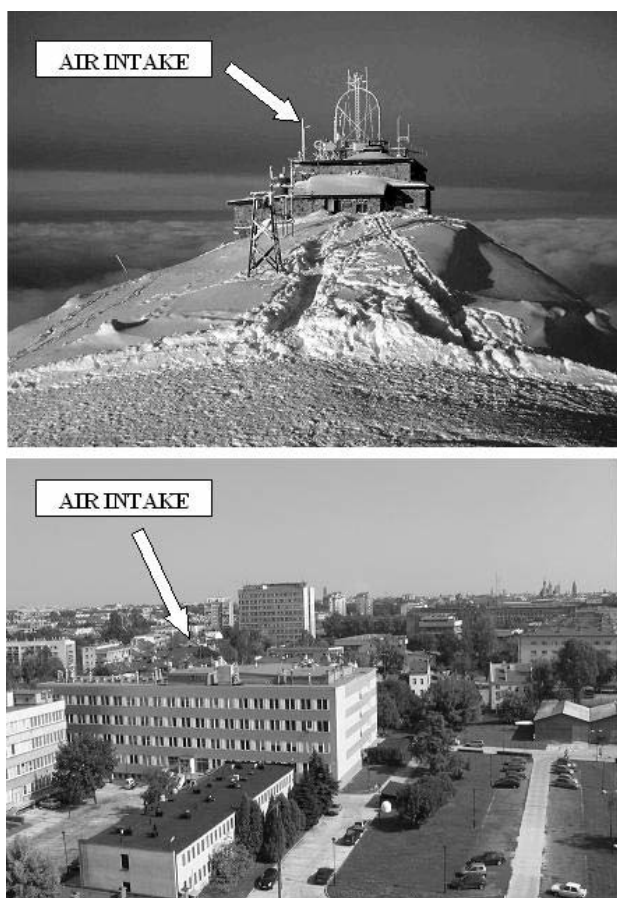


Fig. 1. Aerial view of the CO<sub>2</sub> monitoring sites discussed in the paper. Upper photo: high-altitude mountain station Kasprowy Wierch, Tatra Mountains, southern Poland. Lower photo: surroundings of the monitoring site in the city of Kraków.

The CO<sub>2</sub> data gathered for Kasprowy Wierch station until 2000 have been summarized by Necki et al., [17]. This work summarizes the quasi-continuous data on CO<sub>2</sub> mixing ratios obtained at the station using GC technique in the course of the last decade (1996-2006).

### Kraków

Kraków (50°04'N, 19°55'E, 220 m a.s.l.), the second largest city of Poland, is located approximately 100 km north of Kasprowy Wierch. With more than 800,000 inhabitants, rapidly growing car traffic and significant industrial activities, it represents a typical urban environment. Moreover, due to prevailing westerly circulation, the Kraków region is under substantial influence of a large coal mining and industrial centre (Upper Silesia) located approximately 60 km west of the city. The characteristic features of the local climate are generally weak winds (Fig. 2) and frequent inversions, sometimes extending over several days, particularly during winter. Periods without wind constitute around 18.5% of the total observation time. These factors favour the accumulation of gases originating from surface sources within the lower atmosphere above the city.

The sampling site is situated on the university campus (Fig. 1) located in the western part of the city, bordering recreation and sports grounds. The intake of air is located on the roof of the faculty building, approximately 20 meters above the ground.

### Analytical Methods

Gas chromatography technique was employed at both sites to measure the mixing ratios of atmospheric CO<sub>2</sub>. Automated gas chromatographs (Hewlett Packard, Series 5890, with FID detector and Ni catalyst for conversion of CO<sub>2</sub> to CH<sub>4</sub> and Porapak Q column) were used. Reference working standard was injected after each sample. Four determinations of CO<sub>2</sub> mixing ratios per hour were performed in an automatic mode of operation. The air was cryogenically dried at -70°C prior to analysis. Typical reproducibility of the CO<sub>2</sub> mixing ratio measurements was around ±0.1 ppm. Further technical details of the analytical set-up are reported in Necki et al, [17]. The data are reported on WMO CO<sub>2</sub> mole fraction scale maintained via secondary standards periodically calibrated against primary reference gases.

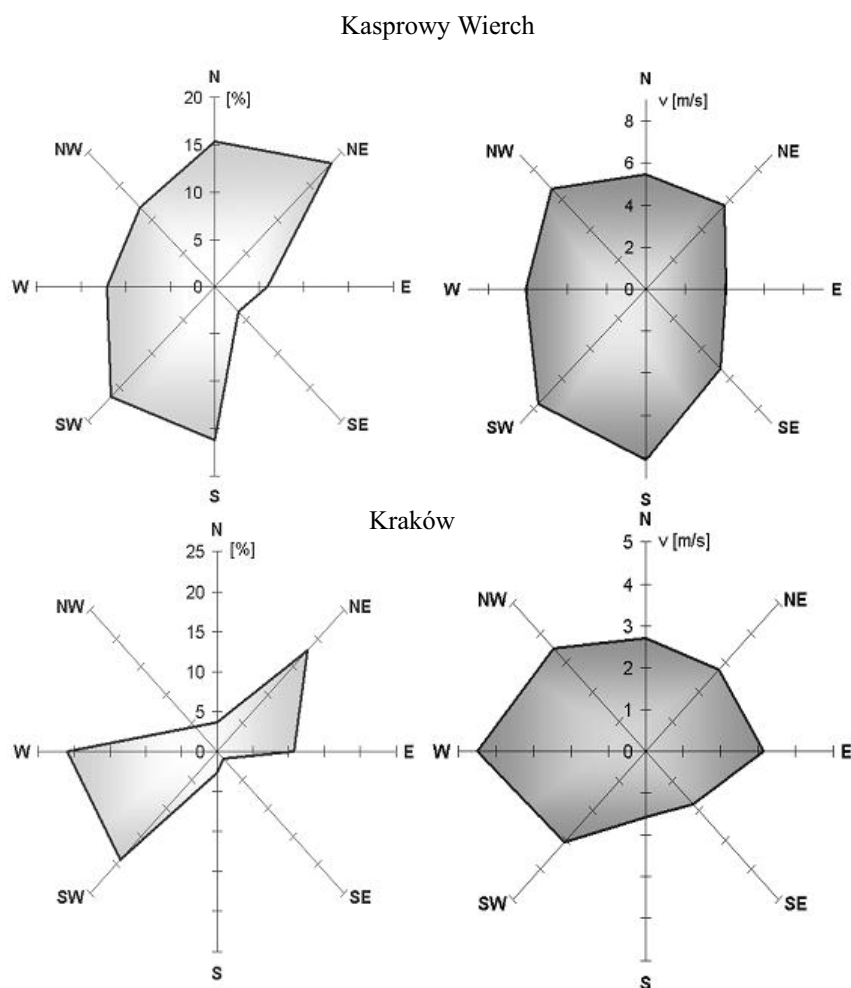


Fig. 2. Distribution of wind direction and wind speed (left- and right-hand panels, respectively) at Kasprowy Wierch and Kraków-Balice meteorological stations for the period 1996-2006 [16]. Period without wind constitutes 1.2% of the total observation time for Kasprowy Wierch and 18.5% for Kraków.

## Results and Discussion

The CO<sub>2</sub> mixing ratios recorded at Kasprowy Wierch during the period 1996–2006 are presented in Fig. 3. In order to extract long-term characteristics from quasi-continuous record of CO<sub>2</sub> mixing ratios, the raw data representing individual measurements were “cleaned” of local influences. The data selection procedure consisted of three steps: (i) only night-time values (22 p.m.–6 a.m.) were considered, (ii) the mean value for the given night was accepted only if it did not deviate from the average of the accepted mean values calculated for seven preceding nights by more than 3 standard deviations. However, (iii) the mean value for the given night was rejected if the calculated standard deviation for the set of data available for that night was larger than 2 times standard deviation calculated for the entire population of the respective standard deviations derived on the basis of the values accepted in steps (i) and (ii).

Whereas step (ii) should remove events of anomalously high (low) CO<sub>2</sub> levels lasting at least several hours, the role of step (iii) is to filter-out periods of high-frequency variations [17].

The selected data were used to calculate daily mean CO<sub>2</sub> mixing ratios which are shown as open circles in Fig. 3 (upper panel). The selected data were further smoothed using FFT algorithm [18], resulting in the smoothed CO<sub>2</sub> record (heavy line) and the trend line (broken line) shown in the upper panel of Fig. 3. This panel also contains a marine reference curve for the latitude band 48.6°N–53.1°N (thin grey line) within which Kasprowy Wierch station is located [19]. The lower panel of Fig. 3 shows smoothed, de-trended CO<sub>2</sub> records for Kasprowy Wierch and for the marine reference curve. The smoothed CO<sub>2</sub> records presented in Fig. 3 were used to derive mean annual CO<sub>2</sub> concentrations as well as peak-to-peak amplitudes of the seasonal CO<sub>2</sub> cycles at Kasprowy Wierch station (Table 1).

The record of CO<sub>2</sub> mixing ratios presented in Fig. 3 reveals typical behaviour of CO<sub>2</sub> concentration as observed at mid-latitude continental sites of the Northern Hemisphere. Winter maximum of CO<sub>2</sub> mixing ratio ends up in March, when the photosynthetic activity of the biosphere starts to remove CO<sub>2</sub> from the local atmosphere. Afterwards, the atmospheric CO<sub>2</sub> concentration gradually decreases, reaching a minimum in August/September and increases again towards winter maximum. Spikes of anomalously high CO<sub>2</sub> concentrations occurring predominantly during winter months can be attributed to combustion of relatively large amounts fossil fuels and wood in nearby Zakopane and its surroundings.

Fig. 3, as well as the data presented in Table 1, reveal significant year-to-year variability of the measured CO<sub>2</sub> mixing ratios, both with respect to the observed annual growth rate as well as the amplitude of seasonal changes. The seasonal peak-to-peak amplitudes at Kasprowy Wierch vary between 14.7 ppm (2003) and 20.4 ppm (1997), with the corresponding values for the marine reference curve being 13.2 ppm (2002) and 14.6 ppm (2004 and 2005).

The average peak-to-peak amplitudes for the period 1997–2006 equal 18.3 ppm and 14.0 ppm, for the Kasprowy Wierch and the marine reference curve, respectively. The significantly higher amplitudes of seasonal CO<sub>2</sub> changes observed at Kasprowy Wierch are due to both generally higher winter maxima and occasionally lower summer minima, when compared to the reference curve (Fig. 2, lower panel). This most probably reflects cumulative effects of net photosynthetic sink for CO<sub>2</sub> over the European continent during summer months, and of continental emissions of CO<sub>2</sub> due to fossil-fuel burning during winter months. As a result, the air masses reaching Kasprowy Wierch, which is under prevailing influence of westerly circulation, are depleted in CO<sub>2</sub> during summer and enriched during winter, relative to the marine reference curve.

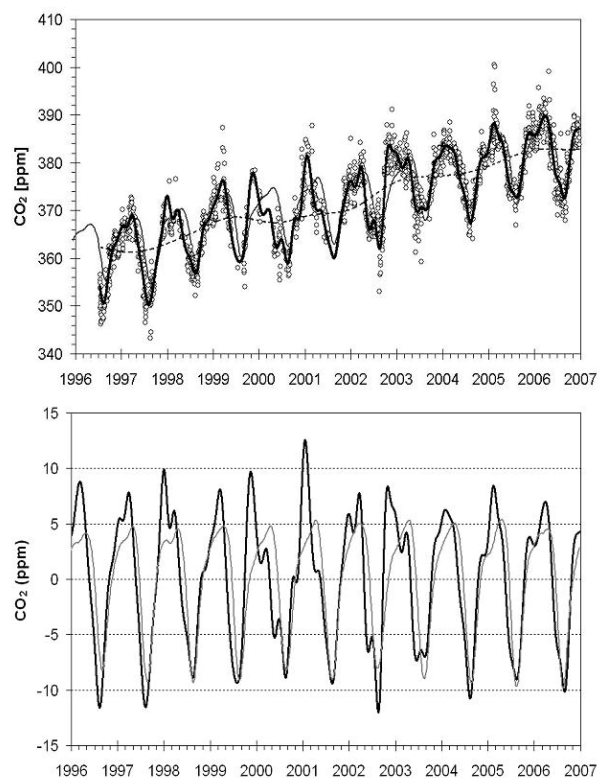


Fig. 3. Record of CO<sub>2</sub> mixing ratios available for Kasprowy Wierch station for the period 1996–2006. Upper panel - Daily mean CO<sub>2</sub> mixing ratios (open circles) calculated on the basis of individual GC measurements (four readings per hour) which were submitted to the selection procedure described in the text. The daily means which passes the selection procedure were smoothed, resulting in the continuous CO<sub>2</sub> record (heavy line) and the trend line (broken line). The marine reference CO<sub>2</sub> curve is also shown for comparison (thin line). Lower panel - Seasonal variations of CO<sub>2</sub> mixing ratios recorded at Kasprowy Wierch (heavy line) compared with the seasonal variations of the marine reference CO<sub>2</sub> curve (thin line). Seasonal variations are shown as departures from the corresponding trend curves representing selected and smoothed Kasprowy Wierch data and the marine reference curve.

Table 1. Mean annual CO<sub>2</sub> mixing ratios and seasonal amplitudes recorded at Kasprowy Wierch station (49°14'N, 19°59'E) during the period 1997-2006, compared with analogous values for the marine reference curve derived for the latitude band 48.6°N–53.1°N.

Year	Kasprowy Wierch – selected data (49°14'N, 19°59'E, 1989 m a.s.l.)		Marine reference curve [19]	
	Average CO <sub>2</sub> concentration (ppm)	Peak-to-peak amplitude <sup>1)</sup> (ppm)	Average CO <sub>2</sub> concentration (ppm)	Peak-to-peak amplitude <sup>1)</sup> (ppm)
1997	361.8	20.4	363.9	13.9
1998	365.1	17.9	366.4	14.0
1999	369.4	18.3	368.9	14.0
2000	366.5	20.0	370.4	13.3
2001	369.7	19.6	371.8	14.2
2002	373.7	20.1	373.8	13.2
2003	376.3	14.7	376.3	14.2
2004	377.7	18.1	378.2	14.6
2005	381.3	16.8	380.4	14.6
2006	382.6	17.1	383.0	14.4 <sup>2)</sup>

<sup>1)</sup> Calculated for the given year by averaging the differences between two adjacent maxima and the summer minimum values of the detrended CO<sub>2</sub> record (Fig. 2)

<sup>2)</sup> Since the marine reference curve was available only till the end of 2006, the amplitude for that year was calculated as a difference between maximum and minimum CO<sub>2</sub> mixing ratio.

It is worth to note that the 2003 summer draw-down of CO<sub>2</sub> concentration at Kasprowy Wierch was anomalously low (peak-to-peak amplitude of 14.7 ppm, when compared to 20.1 ppm in 2002 and 18.1 ppm in 2004). This effect was most probably linked to an extreme heat wave in summer 2003 which affected mostly western Europe and reduced photosynthetic activity in large areas of the European continent [20].

The annual growth-rate of CO<sub>2</sub> mixing ratios at Kasprowy Wierch, averaged over the period 1997–2006, is equal to  $2.14 \pm 0.57$  ppm year<sup>-1</sup>. This is to be compared with  $2.02 \pm 0.26$  ppm year<sup>-1</sup>, calculated for the same period for the marine reference curve. The quoted uncertainties of the mean values clearly indicate much larger year-to-year variability of the CO<sub>2</sub> growth rate in the interior of the continent, when compared to the marine reference. This most probably reflects interannual changes in the intensity of carbon cycling over the European continent.

In order to obtain better insight into daily variations of CO<sub>2</sub> mixing ratios measured at Kasprowy Wierch station, the raw data available for 2003 were averaged into mean diurnal cycles, for four selected months (February, April, July, October) representing different seasons of a year. The results are shown in Fig. 4. It is apparent that the shape of daily changes of CO<sub>2</sub> concentration varies substantially with the season. During winter months, when photosynthetic activity in the surroundings of Kasprowy Wierch is absent, daily CO<sub>2</sub> changes are generally very small, with a slight maximum during mid-day and early afternoon hours. After sunrise, the mixing ratio rises gradually as CO<sub>2</sub>-laden air from local sources in the valley reaches the station.

During the night, CO<sub>2</sub> decreases gradually towards background levels, recorded typically during early morning hours (from ca. 4 a.m. to 6 a.m.). The observed mean peak-to-peak amplitude of the diurnal CO<sub>2</sub> cycle in winter is in the order of 1.5–2.0 ppm.

During summer and early autumn, the opposite behaviour is apparent - the amplitude of daily CO<sub>2</sub> variations increases to several ppm, with a distinct minimum occurring during daytime. During summer, photosynthetic activity of

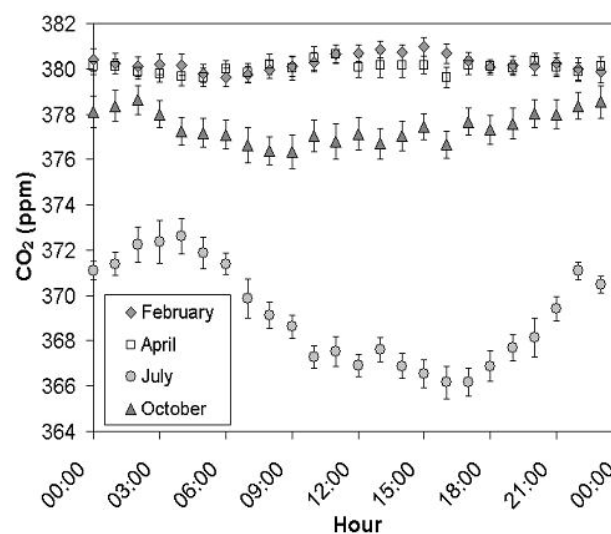


Fig. 4. Mean diurnal variations of CO<sub>2</sub> mixing ratios at Kasprowy Wierch calculated for February, April, July and October 2003. Error bars indicate one standard uncertainty ( $\pm\sigma$ ) of all available values for the given hour.

the plant cover in the valleys below the station gradually reduces the CO<sub>2</sub> content in the surrounding air. When the inversion layer is broken and breeze winds start to transport CO<sub>2</sub>-depleted air upslope towards the station, the recorded mixing ratios gradually decrease, reaching the minimum around 4–6 p.m. After sunset, when plant assimilation stops and the inversion layer starts to develop again, the CO<sub>2</sub> mixing ratio rises, reaching the maximum between 2 a.m. and 4 a.m. The mean peak-to-peak amplitude of the diurnal CO<sub>2</sub> cycle in July 2003 was around 6.5 ppm.

Regular measurements of the CO<sub>2</sub> mixing ratios in the urban atmosphere of Kraków were initiated in 2003. In contrast to Kasprowy Wierch station, where continuous measurements were interrupted only occasionally due to technical reasons, the measurements in Kraków had a form of sampling campaigns lasting from several days to two weeks, whenever the GC system was available for continuous measurement. Fig. 5 summarizes the data gathered for the period 2003–06. Shown are daily mean values of the CO<sub>2</sub> mixing ratios recorded in Kraków, without any selection procedure. For comparison, daily mean values for Kasprowy Wierch (not selected) as well as the marine reference curve are also shown in Fig. 5. It is apparent that the local atmosphere in Kraków is loaded with significant excess of CO<sub>2</sub>, when compared to the regional reference level. Daily mean values of CO<sub>2</sub> mixing ratios occasionally exceed 500 ppm level. When the available data are averaged over the entire observation period (April 2003 – October 2006), the mean CO<sub>2</sub> concentration recorded in Kraków (411.8 ppm) turns out to be approximately 32 ppm (8.5%) higher than the average CO<sub>2</sub> concentration derived for Kasprowy Wierch for the same period (no data selection, averaging only for periods for which the data are available also for Kraków). This can be compared with ca. 1 ppm

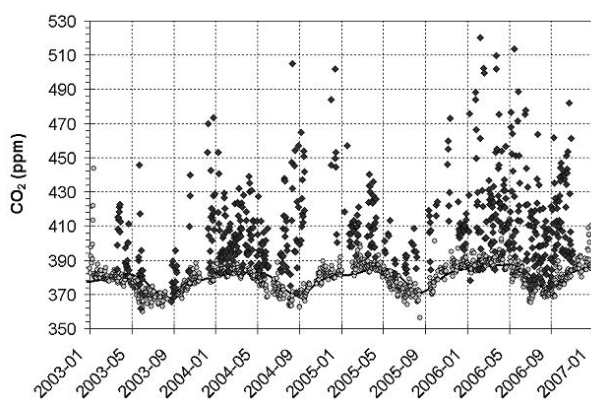


Fig. 5. The daily mean values of CO<sub>2</sub> mixing ratios observed in polluted urban environment (Kraków) during the period 2003–05 (black diamonds – 607 data points), compared with the daily mean values of CO<sub>2</sub> mixing ratios at Kasprowy Wierch (grey circles – 1058 data points). The daily mean values for both stations were calculated using available individual measurements, without any selection procedure. The marine reference curve calculated for the latitude band: 48.6°N–53.1°N (thin line) is shown for comparison.

difference seen in the average Northern Hemisphere vertical profile of CO<sub>2</sub> mixing ratios at non-polluted sites [6], taking into account the elevation difference between Kasprowy Wierch and Kraków. Thus, large surplus of CO<sub>2</sub> in near-ground atmosphere apparent in Kraków data is undoubtedly linked with substantial anthropogenic emissions of this gas. Occasionally, daily means of CO<sub>2</sub> mixing ratios recorded in Kraków fall below the regional reference curve. This occurs during summer and early autumn and reflects the activity of biospheric sink in the vicinity of the sampling site.

Better insight into short-term variations of CO<sub>2</sub> mixing ratios in the urban atmosphere can be gained from Fig. 6, where diurnal variations of CO<sub>2</sub> mixing ratios, as observed during winter (December, January, February) and summer

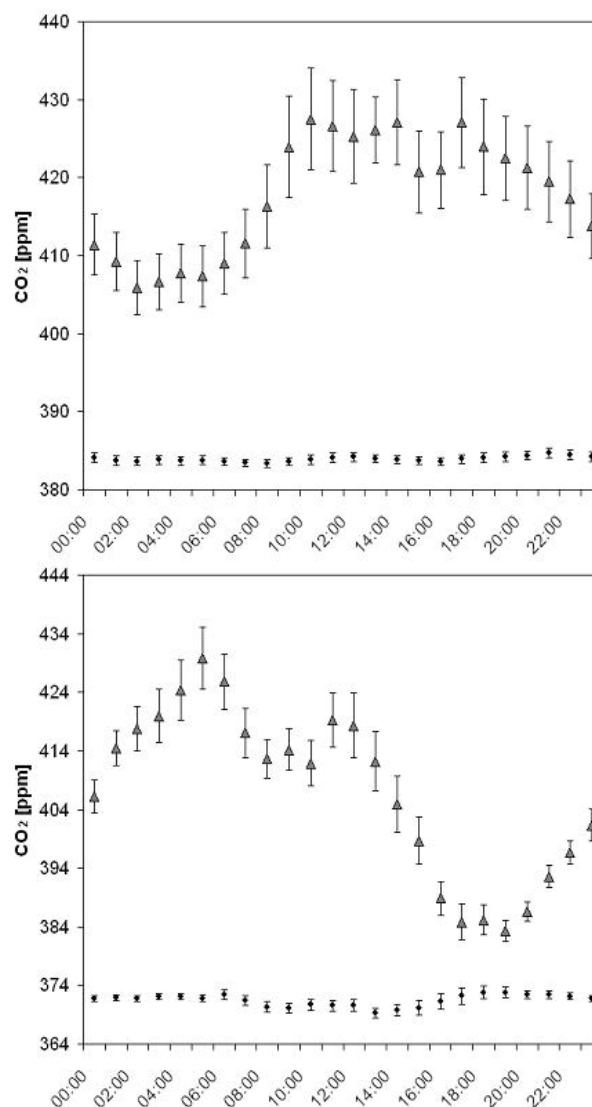


Fig. 6. Comparison of diurnal changes of CO<sub>2</sub> mixing ratios, as observed at Kasprowy Wierch and Kraków stations. Shown are mean diurnal changes of CO<sub>2</sub> mixing ratio occurring at both monitoring sites in the course of 2004, during winter (December, January, February – upper panel) and summer months (June, July, August – lower panel).

months (June, July, August) in Kraków, are shown on the background of diurnal changes observed during the same periods of time at Kasprowy Wierch. It is apparent that both the amplitude and the shape of diurnal CO<sub>2</sub> changes differ considerably. During winter time, a broad maximum of CO<sub>2</sub> concentration during day time is observed in Kraków. This can be linked to intense anthropogenic emissions, mostly car traffic, active during day time. This leads to a build-up of CO<sub>2</sub> in the local atmosphere, despite enhanced vertical mixing during the day. As discussed earlier (Fig. 4), daily changes of CO<sub>2</sub> concentration in Kasprowy Wierch during winter months also reveal small, broad maximum during day time, although with much lower amplitude (approximately 1 ppm, to be compared with ca. 20 ppm in Kraków).

During summer months, the photosynthetic sink operates at both sites, leading to a decrease of CO<sub>2</sub> concentrations during day time. Interestingly, the minimum of CO<sub>2</sub>

concentration in Kraków is shifted to afternoon hours (ca. 16:00–20:00), while at Kasprowy Wierch it occurs during mid day. The small plateau seen in the Kraków data between ca. 7 a.m. and 1 p.m. may result from two processes: (i) growing photosynthetic sink, removing CO<sub>2</sub> from the atmosphere at increasing rates, and (ii) rising anthropogenic emissions (mainly car traffic) adding CO<sub>2</sub> to the local atmosphere.

After ca. 1 p.m. this dynamic equilibrium is apparently destroyed by enhanced vertical mixing of the lower atmosphere, reducing the CO<sub>2</sub> levels near the ground.

Apart from daily and seasonal changes, also synoptic-scale variations of CO<sub>2</sub> mixing ratios are occasionally recorded at Kasprowy Wierch station. They are associated with variable CO<sub>2</sub> loads of different air masses transported across the European continent. Depending on the history of the given air mass, these differences can be large enough to be recorded as distinct “events” in the concentration record.

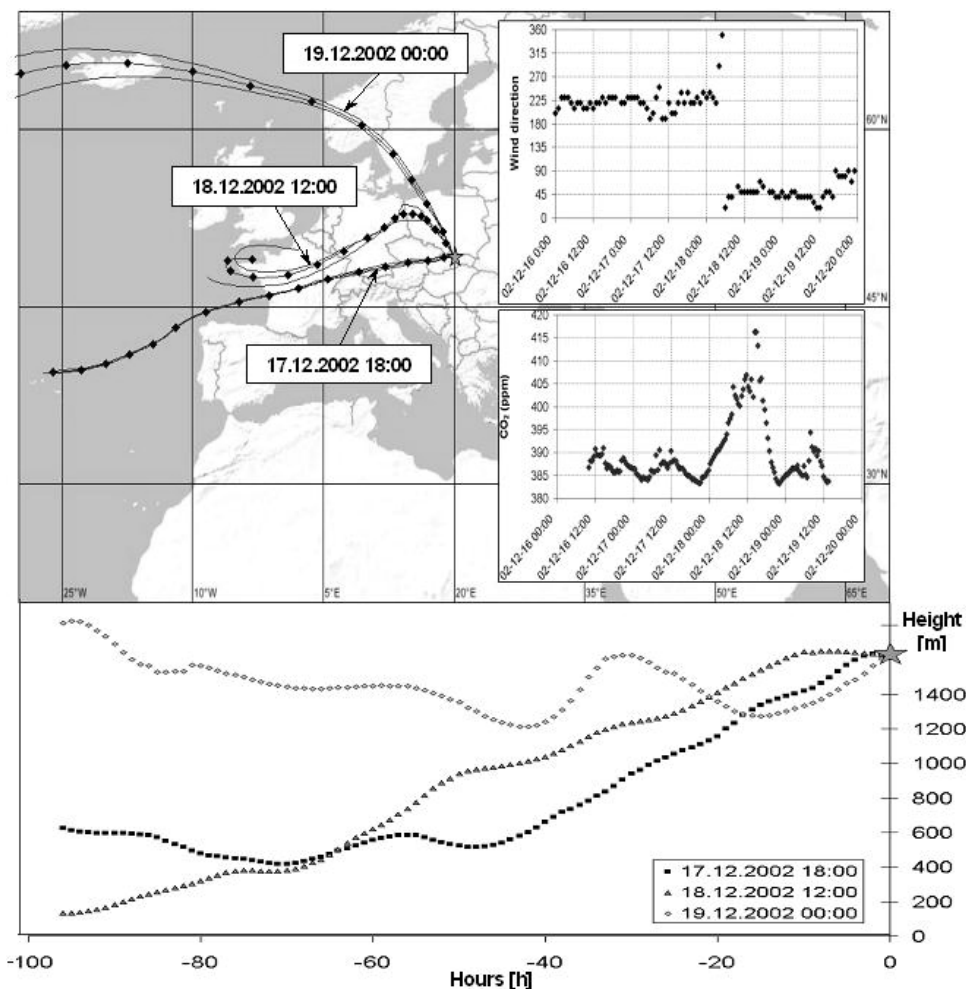


Fig. 7. Example of anomalously high CO<sub>2</sub> concentration events recorded at Kasprowy Wierch station during the period 17-19 December 2002. Three backward trajectories of air masses arriving at Kasprowy Wierch at specific time intervals are shown on the left-hand side of the figure. Black diamonds on three selected trajectories mark 6-hour intervals. Two accompanying trajectories were calculated for the arrival time one hour before and one hour after the indicated date and hour. The inserted panels on the right-hand side show the CO<sub>2</sub> mixing ratios and the wind direction, as observed during the discussed period at Kasprowy Wierch. The lower panel shows elevation changes of the centre of gravity of air masses represented by three trajectories shown in the upper panel of the figure.

They have nothing in common with similar events due to local contamination. Distinction of these two classes of events is possible by retrospective analyses of regional atmospheric circulation with the aid of back trajectory modelling or full-fledged 3D transport models.

Fig. 7 shows example of such events which were recorded at Kasprowy Wierch in December 2002. Left-hand side of Fig. 7 shows backward trajectories (96 hours) of air masses crossing Kasprowy Wierch on 17, 18 and 19 December 2002. The backward trajectories shown in Fig. 7 were calculated with the aid of HYSPLIT code [21]. The CO<sub>2</sub> concentration and wind direction measured during this period at Kasprowy Wierch are shown on the inserted panels in Fig. 7. During the whole day of December 17, 2002, Kasprowy Wierch was under the influence of air mass of Atlantic origin, crossing European continent from SW to NE. Residence time of this air mass above the continent was around two days. During the night from 17 to 18 December the circulation patterns have changed and Kasprowy Wierch falls under the influence of the air mass sitting over Western Europe on relatively low elevation for four preceding days. During that time this air mass picked up CO<sub>2</sub> from surface emissions, most probably associated with the burning of fossil fuels. The recorded CO<sub>2</sub> mixing ratios at Kasprowy Wierch increased from ca. 385 ppm late in the evening on December 17, to ca. 415 ppm six hours later. The CO<sub>2</sub> concentration stayed high till the afternoon of December 18 and then returned to the levels observed before the event around midnight of the same day. This can be linked to the fact that Kasprowy Wierch began to sample still another air mass which originated in the North Atlantic, southwest of Greenland. This air mass crossed the North Sea and Baltic at a relatively high elevation (ca. 1500 m a.s.l.) and arrived relatively quickly in southern Poland, late in the evening on December 18. The residence time of this air mass over the continent was short, probably less than one day.

It should be noted that such concentration events occur from time to time at different stations across the European continent [10]. If they are synchronized and attributed to specific meteorological situations, they may serve as valuable calibration/validation tools for regional CO<sub>2</sub> transport models.

### Conclusions

The presented work was focused on characterization of spatial and temporal variability of atmospheric concentrations of carbon dioxide, as recorded at two ground-level continental stations situated in southern Poland. These sites, operating in contrasting environments, revealed substantial differences in the recorded CO<sub>2</sub> levels both on short and long time scales. The peak-to-peak amplitude of daily CO<sub>2</sub> changes reaches 20 ppm in Kraków during winter and ca. 45 ppm during summer, to be compared with ca. 1 ppm and 3 ppm, respectively, observed at Kasprowy Wierch. This reduced short-term variability of CO<sub>2</sub> mixing

ratios recorded at Kasprowy Wierch station stems from its location higher in the troposphere, far from strong anthropogenic sources of CO<sub>2</sub>. Both stations differ also in the average CO<sub>2</sub> level: urban atmosphere of Kraków reveals quasi-permanent surplus of CO<sub>2</sub> content in the order of 8.5% when compared to Kasprowy Wierch, undoubtedly linked to numerous local emissions of this gas related to anthropogenic activities.

Such quasi-permanent excess concentration of CO<sub>2</sub> gas, when compared with the regional reference level, is probably characteristic for all urban centres. For large cities with several million inhabitants this surplus of CO<sub>2</sub> may be significantly higher than that observed in this study. The elevated concentrations of CO<sub>2</sub> are expected near the ground where people live and the biosphere is present. One may argue that the local climate in urban centres will be further modified by the presence of these elevated CO<sub>2</sub> concentrations, enhancing the effect of urban heat islands.

The Kasprowy Wierch CO<sub>2</sub> record, when compared to the marine reference record, reveals similarities but also remarkable differences. Although the mean annual growth rates of CO<sub>2</sub> characterizing both records are similar, the apparent year-to-year variability of this parameter in the considered period of time is substantially higher for Kasprowy Wierch. The peak-to-peak amplitudes of seasonal changes observed at Kasprowy Wierch are consistently higher than those characterizing the marine reference curve. The mean difference for the discussed period of observation (1996-2006) is equal to 4.3 ppm. The seasonality of CO<sub>2</sub> mixing ratios should be more pronounced for sites located eastward of Kasprowy Wierch station. Amplification and modification of the seasonal CO<sub>2</sub> cycles over the continent can be attributed to the cumulative effect of net biospheric CO<sub>2</sub> sink during summer and net anthropogenic CO<sub>2</sub> source during winter, operating across the continent, from the coast towards the interior of the continent. These seasonal differences may serve as useful diagnostic tools for regional transport models. The "events" of anomalously high CO<sub>2</sub> concentration, which occur from time to time at different stations across the European continent, can play a similar role in model development.

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